THE XVTH INTERNATIONAL CONGRESS ON RHEOLOGY

The Society of Rheology 80th Annual Meeting

Monterey, California *3–8 August 2008*

Program and Abstracts

SPONSORING ORGANIZATION
The Society of Rheology

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Monterey Conference Center
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Rheology 2008
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Papers of presentations marked with 💿 are available in the Congress Proceedings.

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Printed in the United States of America

Contents

Session Schedule

Plenary Lectures

PL1.	From molecules to mechanics: Nuclear magnetic resonance and rheological insight *Paul T. Callaghan* (MacDiarmid Inst. for Advanced Materials and Nanotechnology, New Zealand)	Monday	8:20	Serra I
PL2.	Non-equilibrium mechanics of active gels and living cells *Fred MacKintosh* (Vrije Universiteit, The Netherlands)	Friday	12:00	Serra I

Keynote Lectures

KL1.	Dynamics of entangled polymers *Michael Rubinstein* (University of North Carolina, USA)	Monday	1:15	Steinbeck
KL2.	Multiphase flows in microfluidic devices: Drops, vesicles, and cells *Howard A. Stone* (Harvard University, USA)	Monday	1:15	Serra I
KL3.	Nonlinear elasticity of elastomers and gels as revealed by multiaxial deformations *Kenji Urayama* (Kyoto University, Japan)	Tuesday	8:30	Serra I
KL4.	Biopolymer, protein and protein-biopolymer interfaces and gels: Structure-property-function relationships and relevance to tissue generation *Justin J. Cooper-White* (The University of Queensland, Australia)	Tuesday	8:30	Steinbeck
KL5.	Independent control over the mechanical and electrical properties of solid polymer electrolytes for lithium batteries *Nitash P. Balsara* (University of California – Berkeley, USA)	Tuesday	1:15	De Anza I-II
KL6.	Modeling liquid crystal materials and processes in biological systems *Alejandro D. Rey* (McGill University, Canada)	Tuesday	1:15	Steinbeck
KL7.	Tailoring the rheology of soft particle dispersions *Michel Cloitre* (ESPCI, France)	Wednesday	8:30	Steinbeck
KL8.	Could we raise glasses? – *Bingham Lecture* *Hans Christian Öttinger* (ETH Zurich, Switzerland)	Wednesday	8:30	Serra I
KL9.	Elastic turbulence: A random flow without inertia *Victor Steinberg* (Weizmann Institute of Science, Israel)	Thursday	8:30	Serra I
KL10.	Residual stresses and viscoelastic deformation of injection molded parts *Jae R. Youn* (Seoul National University, Korea)	Thursday	8:30	Steinbeck
KL11.	Recent progress in shear banding in complex fluids *Peter D. Olmsted* (University of Leeds, UK)	Thursday	1:15	Steinbeck
KL12.	Anomalous rheology of polymer-nanoparticle suspensions *Michael E. Mackay* (Michigan State University, USA)	Thursday	1:15	Serra I
KL13.	A new look at stress relaxation in melts of unlinked rings *Scott T. Milner* (Penn State University, USA)	Friday	8:30	Serra I
KL14.	A geophysical perspective of grain-fluid flows *Richard M. Iverson* (U.S. Geological Survey, USA)	Friday	8:30	Steinbeck

Materials Processing

MP-1.	Extension Dominated Flows	Monday	9:45 – 11:45	Ferrante I-III
MP-2.	Coating and IT Applications	Monday	2:30 – 5:30	Ferrante I-III
MP-3.	Injection Molding	Tuesday	9:45 – 11:45	Ferrante I-III
MP-4.	Extrusion	Tuesday	2:30 – 5:30	Ferrante I-III
MP-5.	Nanocomposites	Tuesday	2:30 – 5:30	Colton I-III
MP-6.	Other Processes	Wednesday	9:45 – 11:45	Ferrante I-III
MP-7.	Particulates	Thursday	9:45 – 11:45	Colton I-III
MP-8.	Nanocomposites and Blends	Thursday	2:30 – 5:30	Colton I-III
MP-9.	Stability and Crystallization	Friday	9:45 – 11:45	Colton I-III

Complex Flows

CF-1.	Flow Instabilities I	Monday	9:45 – 11:45	Steinbeck
CF-2.	Computational and Multiscale Modeling I	Monday	9:45 – 11:45	Colton I-III
CF-3.	Flow Instabilities II	Monday	2:30 – 5:30	Steinbeck
CF-4.	Shear Banding I	Tuesday	9:45 – 11:45	Steinbeck

CF-5.	Shear Banding II	Tuesday	2:30 – 5:30	Steinbeck
CF-6.	Viscoelastic Turbulence	Tuesday	2:30 – 5:30	San Carlos I
CF-7.	Computational and Multiscale Modeling 2	Wednesday	9:45 – 11:45	Steinbeck
CF-8.	Computational and Multiscale Modeling 3	Thursday	9:45 – 11:45	Steinbeck
CF-9.	Hydrodynamics in Confining Media	Thursday	2:30 – 5:30	Steinbeck
CF-10.	Computational and Multiscale Modeling 4	Friday	9:45 – 11:45	Steinbeck

Homogeneous Polymeric Systems

HP-1.	Unentangled Polymers	Monday	9:45 – 11:45	San Carlos III
HP-2.	Polyelectrolytes and Ionomers	Monday	9:45 – 11:45	San Carlos I
HP-3.	Entangled Polymers I	Monday	2:30 – 5:30	San Carlos III
HP-4.	Applied and Industrial Rheology	Monday	2:30 – 5:30	San Carlos I
HP-5.	Entangled Polymers I	Tuesday	9:45 – 11:45	San Carlos III
HP-6.	Cross-linked Polymers and Gels	Tuesday	9:45 – 11:45	San Carlos I
HP-7.	Entangled Polymers I	Tuesday	2:30 – 5:30	San Carlos III
HP-8.	Polymer Solutions	Wednesday	9:45 – 11:45	San Carlos III
HP-9.	Entangled Polymers II	Thursday	9:45 – 11:45	San Carlos III
HP-10.	Entangled Polymers II	Thursday	2:30 – 5:30	San Carlos III
HP-11.	Entangled Polymers I	Friday	9:45 – 11:45	San Carlos III

Heterogeneous and Self-Assembling Polymeric Systems

HS-1.	Liquid Crystalline Polymers & FIC	Monday	9:45 – 11:45	San Carlos IV
HS-2.	FIC/Composites/Imm. Polymer Blends	Monday	2:30 – 5:30	San Carlos IV
HS-3.	Immiscible Polymer Blends	Tuesday	9:45 – 11:45	San Carlos IV
HS-4.	Immiscible & Miscible Polymer Blends	Tuesday	2:30 – 5:30	San Carlos IV
HS-5.	Block Copolymers	Thursday	9:45 – 11:45	San Carlos IV
HS-6.	Telechelic/Associative Polymers	Thursday	2:30 – 5:30	San Carlos IV
HS-7.	Telechelic/Associative Polymers	Friday	9:45 – 11:45	San Carlos IV

Bio-Rheology

BR-1.	Rheology of the Cytoskeleton	Tuesday	9:45 – 11:45	Redwood
BR-2.	Rheology of Biomacromolecules	Tuesday	2:30 – 5:30	Redwood
BR-3.	Physiological Fluids I	Wednesday	9:45 – 11:45	Redwood
BR-4.	Physiological Fluids II	Thursday	9:45 – 11:45	Redwood
BR-5.	Rheology of Tissues and Scaffolds	Thursday	2:30 – 5:30	Redwood
BR-6.	Cell Mechanics	Friday	9:45 – 11:45	Redwood

Suspensions and Colloids

SC-1.	Particle Level Simulation and Theory I	Monday	9:45 – 11:45	De Anza III
SC-2.	Particle Level Simulation and Theory II	Monday	2:30 – 5:30	De Anza III
SC-3.	Yielding and Thixotropy I	Tuesday	9:45 – 11:45	De Anza III
SC-4.	Jamming and Shear Thickening	Tuesday	2:30 – 5:30	De Anza III
SC-5.	Yielding and Thixotropy II	Wednesday	9:45 – 11:45	De Anza III
SC-6.	Suspension Hydrodynamics I	Wednesday	9:45 – 11:45	Portola
SC-7.	Yielding and Thixotropy III	Thursday	9:45 – 11:45	De Anza III
SC-8.	Suspension Hydrodynamics II	Thursday	9:45 – 11:45	Portola
SC-9.	Dynamics and Scattering in Colloids	Thursday	2:30 – 5:30	De Anza III
SC-10.	Multiphase Flows	Thursday	2:30 – 5:30	Portola
SC-11.	Field Effects: ER and MR Fluids	Friday	9:45 – 11:45	De Anza III
SC-12.	Colloids, Nanotubes and Nanocomposites	Friday	9:45 – 11:45	Portola

Surfactants, Emulsions and Foams

SE-1.	Rheology of Foams	Monday	2:30 – 5:30	De Anza II
SE-2.	Foam Stability	Tuesday	9:45 – 11:45	De Anza II
SE-3.	Complex Flows in Surface Active Systems	Tuesday	2:30 – 5:30	De Anza II
SE-4.	Surfactant Solutions	Wednesday	9:45 – 11:45	De Anza II
SE-5.	Emulsions	Thursday	9:45 – 11:45	De Anza II

SE-6.	Liquid-Liquid Systems and Blends	Thursday	2:30 – 5:30	De Anza II
Granular Materials and Ageing				
GA-1.	Collisional Flows and Inelastic Gases	Wednesday	9:45 – 11:45	Bonsai III
GA-2.	Modeling and Expt. in Quasi-Static Limit	Thursday	2:30 – 5:30	Bonsai III
GA-3.	Advances in Simulation Techniques	Friday	9:45 – 11:45	Bonsai III
Microfluidics				
MF-1.	Microfluidics with Polymers	Monday	9:45 – 11:45	Portola
MF-2.	Microfluidics: Non-Newtonian Flows	Monday	2:30 – 5:30	Portola
MF-3.	Microfluidics: Surface Wettability	Tuesday	9:45 – 11:45	Portola
MF-4.	Microfluidics: Droplets	Tuesday	2:30 – 5:30	Portola
Colloidal Gels and Glasses				
CG-1.	Slow Dynamics, Aging and Transitions	Wednesday	9:45 – 11:45	San Carlos I
CG-2.	Induced Gels and Attractive Glasses	Thursday	9:45 – 11:45	San Carlos I
CG-3.	Gels and Glasses	Thursday	2:30 – 5:30	San Carlos I
CG-4.	Yielding	Friday	9:45 – 11:45	San Carlos I
Interfacial Rheology				
IR-1.	Interfacial Rheology and Thin Film Flow	Monday	9:45 – 11:45	Bonsai I
IR-2.	Interfacial Rheology and Thin Film Flow	Monday	2:30 – 5:30	Bonsai I
IR-3.	Interfacial Rheology and Thin Film Flow	Tuesday	9:45 – 11:45	Bonsai I
Micro-Rheology				
MR-1.	Cells and Non-Equilibrium Systems	Monday	9:45 – 11:45	Redwood
MR-2.	Passive and Active Microrheology	Monday	2:30 – 5:30	Redwood
New Experimental Methods				
EM-1.	Free Surface Rheometry	Monday	9:45 – 11:45	De Anza I
EM-2.	Extensional Rheometry	Monday	2:30 – 5:30	De Anza I
EM-3.	Amplitude Oscillation Shear Rheometry	Tuesday	9:45 – 11:45	De Anza I
EM-4.	RheoOptics/NMR	Wednesday	9:45 – 11:45	De Anza I
EM-5.	Microscopic and Microfluidic Rheometry	Thursday	9:45 – 11:45	De Anza I
EM-6.	Extreme Rheology	Thursday	2:30 – 5:30	De Anza I
EM-7.	Squeeze Flow Rheometry	Friday	9:45 – 11:45	De Anza I
Food Rheology				
FR-1.	Food Gels and Perception	Tuesday	2:30 – 5:30	Bonsai I
FR-2.	Food Dispersions	Wednesday	9:45 – 11:45	Bonsai I
Rheology of Solids and Glasses				
SG-1.	Polymer Dynamics	Monday	9:45 – 11:45	San Carlos II
SG-2.	Glass Transition Dynamics	Monday	2:30 – 5:30	San Carlos II
SG-3.	Effect of Nanoconfinement on Dynamics	Tuesday	9:45 – 11:45	San Carlos II
SG-4.	Effect of Nanoconfinement on Dynamics	Tuesday	2:30 – 5:30	San Carlos II
SG-5.	Mechanics of Nanocomposites	Wednesday	9:45 – 11:45	San Carlos II
SG-6.	Numerical Simulations	Thursday	9:45 – 11:45	San Carlos II
SG-7.	Modeling	Thursday	2:30 – 5:30	San Carlos II
SG-8.	Polymer Viscoelasticity	Friday	9:45 – 11:45	San Carlos II
General Rheology				
GR-1.	General Rheology	Monday	9:45 – 11:45	Bonzai III
GR-2.	General Rheology	Monday	2:30 – 5:30	Bonzai III
GR-3.	General Rheology	Tuesday	9:45 – 11:45	Bonzai III
GR-4.	General Rheology	Tuesday	2:30 – 5:30	Bonzai III
Poster Session		Tuesday	6:00 – 9:00	Serra I

Presentation and Event Schedule

Sunday – August 3, 2008

2:00	Registration 2:00 – 8:00 (*De Anza Foyer*)
6:00	Opening Reception 6:00 – 8:00 (*Serra I*)

Monday – August 4, 2008

8:00	Opening Ceremonies (*Serra I*)												
8:20	P. Callaghan (PL1, *Serra I*)												
9:15	Coffee Break (*Serra II*)												
9:45	HS1	SG1	HP1	HP7	MR1	MP1	IR1	SC1	GR1	CF1	MF1	EM1	CF7
10:05	HS2	SG2	HP2	HP8	MR2	MP2	IR2	SC2	GR2	CF2	MF2	EM2	CF8
10:25	HS3	SG3	HP3	HP9	MR3	MP3	IR3	SC3	GR3	CF3	MF3	EM3	CF9
10:45	HS4	SG4	HP4	HP10	MR4	MP4	IR4	SC4	GR4	CF4	MF4	EM4	CF10
11:05	HS5	SG5	HP5	HP11	MR5	MP5	IR5	SC5	GR5	CF5	MF5	EM5	CF11
11:25	HS6			HP12			IR6	SC6	GR6	CF6	MF6	EM6	CF12
11:45	Lunch Break												
1:15	M. Rubinstein (KL1, *Steinbeck*) / H. Stone (KL2, *Serra I*)												
2:00	Coffee Break (*Serra II*)												
2:30	HS7	SG7	HP13	HP22	MR7	MP7	IR7	SC7	GR7	CF13	MF7	EM7	SE1
2:50	HS8	SG8	HP14	HP23	MR8	MP8	IR8	SC8	GR8	CF14	MF8	EM8	SE2
3:10	HS9	SG9	HP15	HP24	MR9	MP9	IR9	SC9	GR9	CF15	MF9	EM9	SE3
3:30	HS10	SG10	HP16	HP25	MR10	MP10	IR10	SC10	GR10	CF16	MF10	EM10	SE4
3:50	HS11	SG11	HP17	HP26	MR11	MP11	IR11	SC11	GR11	CF17	MF11	EM11	SE5
4:10	HS12	SG12	HP18	HP27	MR12	MP12	IR12	SC12	GR12	CF18	MF12	EM12	SE6
4:30	HS13	SG13	HP19	HP28	MR13	MP13	IR13	SC13	GR13	CF19	MF13		SE7
4:50	HS14		HP20	HP29	MR14	MP14	IR14	SC14		CF20	MF14		SE8
5:10	HS15		HP21	HP30	MR15	MP15				CF21	MF15		
5:30	End												
7:30	Strolling Dinner Reception 7:30–10:30 (*Monterey Bay Aquarium*, bus transportation begins at 7:00)												

Tuesday – August 5, 2008

8:30	K. Urayama (KL3, *Serra I*) / J. Cooper-White (KL4, *Steinbeck*)												
9:15	Coffee Break (*Serra II*)												
9:45	HS16	SG16	HP31	HP37	BR1	MP16	IR16	SC16	GR16	CF22	MF16	EM16	SE10
10:05	HS17	SG17	HP32	HP38	BR2	MP17	IR17	SC17	GR17	CF23	MF17	EM17	SE11
10:25	HS18	SG18	HP33	HP39	BR3	MP18	IR18	SC18	GR18	CF24	MF18	EM18	SE12
10:45	HS19	SG19	HP34	HP40	BR4	MP19	IR19	SC19	GR19	CF25	MF19	EM19	SE13
11:05	HS20	SG20	HP35	HP41	BR5	MP20	IR20	SC20	GR20	CF26	MF20	EM20	SE14
11:25		SG21	HP36	HP42					GR21	CF27	MF21	EM21	
11:45	Lunch Break												
1:15	N. Balsara (KL5, *De Anza I-II*) / A. Rey (KL6, *Steinbeck*)												
2:00	Coffee Break (*Serra II*)												
2:30	HS22	SG22	HP43	FR1	BR7	MP22	MP31	SC22	GR22	CF28	MF22	CF37	SE16
2:50	HS23	SG23	HP44	FR2	BR8	MP23	MP32	SC23	GR23	CF29	MF23	CF38	SE17
3:10	HS24	SG24	HP45	FR3	BR9	MP24	MP33	SC24	GR24	CF30	MF24	CF39	SE18
3:30	HS25	SG25	HP46	FR4	BR10	MP25	MP34	SC25	GR25	CF31	MF25	CF40	SE19
3:50	HS26	SG26	HP47	FR5	BR11	MP26	MP35	SC26	GR26	CF32	MF26	CF41	SE20
4:10	HS27	SG27	HP48	FR6	BR12	MP27	MP36	SC27	GR27	CF33	MF27	CF42	SE21
4:30	HS28	SG28	HP49	FR7	BR13	MP28	MP37	SC28	GR28	CF34	MF28	CF43	SE22
4:50	HS29		HP50	FR8	BR14	MP29		SC29		CF35	MF29	CF44	SE23
5:10				FR9				SC30		CF36	MF30		SE24
5:30	End												
6:00	Poster Session 6:00–9:00 (*Serra I*)												
7:00	Poster Session Reception 7:00 – 9:30 (*De Anza I*)												

Wednesday – August 6, 2008

8:30	M. Cloitre (KL7, *Steinbeck*) / H. C. Öttinger (KL8, *Serra I*)											
9:15	Coffee Break (*Serra II*)											
9:45	SG31	HP52	FR10	BR16	MP40	CG1	SC31	SC37	CF46	GA1	EM22	SE25
10:05	SG32	HP53	FR11	BR17	MP41	CG2	SC32	SC38	CF47	GA2	EM23	SE26
10:25	SG33	HP54	FR12	BR18	MP42	CG3	SC33	SC39	CF48	GA3	EM24	SE27
10:45	SG34	HP55	FR13	BR19	MP43	CG4	SC34	SC40	CF49	GA4	EM25	SE28
11:05	SG35	HP56	FR14	BR20	MP44	CG5	SC35	SC41	CF50	GA5	EM26	SE29
11:25		HP57	FR15	BR21	MP45	CG6		SC42	CF51	GA6	EM27	SE30
11:45	End											
12:00	Wednesday Afternoon Excursion (Times and venues vary, box lunch provided)											
6:30	Wednesday Night Beach Party 6:30–11:00 (*Pirate's Cove*)											

Thursday – August 7, 2008

8:30	V. Steinberg (KL9, *Serra I*) / J. Youn (KL10, *Steinbeck*)											
9:15	Coffee Break (*Serra II*)											
9:45	HS31	SG37	HP58	BR22	MP46	CG7	SC43	SC49	CF52		EM28	SE31
10:05	HS32	SG38	HP59	BR23	MP47	CG8	SC44	SC50	CF53		EM29	SE32
10:25	HS33	SG39	HP60	BR24	MP48	CG9	SC45	SC51	CF54		EM30	SE33
10:45	HS34	SG40	HP61	BR25	MP49	CG10	SC46	SC52	CF55		EM31	SE34
11:05	HS35	SG41	HP62	BR26	MP50	CG11		SC53			EM32	SE35
11:25		SG42	HP63			CG12		SC54			EM33	SE36
11:45	Lunch Break											
1:15	P. Olmsted (KL11, *Steinbeck*) / M. Mackay (KL12, *Serra I*)											
2:00	Coffee Break (*Serra II*)											
2:30	HS37	SG43	HP64	BR28	MP52	CG13	SC55	SC64	CF58	GA7	EM34	SE37
2:50	HS38	SG44	HP65	BR29	MP53	CG14	SC56	SC65	CF59	GA8	EM35	SE38
3:10	HS39	SG45	HP66	BR30	MP54	CG15	SC57	SC66	CF60	GA9	EM36	SE39
3:30	HS40	SG46	HP67	BR31	MP55	CG16	SC58	SC67	CF61	GA10	EM37	SE40
3:50	HS41	SG47	HP68	BR32	MP56	CG17	SC59	SC68	CF62	GA11	EM38	SE41
4:10	HS42	SG48	HP69	BR33	MP57	CG18	SC60	SC69	CF63	GA12	EM39	SE42
4:30	HS43	SG49	HP70	BR34	MP58	CG19	SC61	SC70	CF64	GA13	EM40	SE43
4:50	HS44	SG50	HP71	BR35	MP59	CG20	SC62	SC71	CF65	GA14	EM41	
5:10		SG51	HP72		MP60	CG21		SC72		GA15		
5:30	End											
5:45	SoR Business Meeting (*De Anza I*)											
7:00	Thursday Reception 7:00–8:00 (*Serra II*)											
8:00	Thursday Banquet 8:00–10:00 (*Serra I*)											

Friday – August 8, 2008

8:30	S. Milner (KL13, *Serra I*) / R. Iverson (KL14, *Steinbeck*)										
9:15	Coffee Break										
9:45	HS46	SG52	HP73	BR37	MP61	CG22	SC73	SC79	CF67	GA16	EM43
10:05	HS47	SG53	HP74	BR38	MP62	CG23	SC74	SC80	CF68	GA17	EM44
10:25	HS48	SG54	HP75	BR39	MP63	CG24	SC75	SC81	CF69	GA18	EM45
10:45	HS49	SG55	HP76	BR40	MP64	CG25	SC76	SC82	CF70	GA19	EM46
11:05	HS50	SG56	HP77	BR41		CG26	SC77	SC83	CF71		EM47
11:25	HS51		HP78			CG27	SC78				EM48
11:45	Break										
12:00	F. MacKintosh (PL2, *Serra I*)										
1:00	Friday Closing Reception/Lunch 1:00–3:00 (*Serra II*)										

Social Program and Events

Sunday, August 3	**Registration**	2:00 pm – 8:00 pm	*De Anza Foyer*
	Opening Reception	6:00 pm – 8:00 pm	*Serra Grand Ballroom I*
Monday, August 4	**Opening Ceremonies**	8:00 am – 8:20 am	*Serra Grand Ballroom I*
	Exhibits	8:00 am – 5:30 pm	*Serra II* (also location of coffee breaks)
	Strolling Dinner Reception	7:30 pm – 10:30pm	*Monterey Bay Aquarium*
	Bus service from the Portola and Marriott begins at 7:00 pm. The last bus departs from the Aquarium at approximately 10:45 pm. *Hosted by The Society of Rheology.*		
Tuesday, August 5	**Exhibits**	8:00 am – 5:30 pm	*Serra II* (also location of coffee breaks)
	Poster Session	6:00 pm – 9:00 pm	*Serra Grand Ballroom I*
	Poster Session Reception *Hosted by TA Instruments.*	7:00 pm – 9:30 pm	*De Anza Ballroom I*
Wednesday, August 6	**Exhibits**	8:00 am – noon	*Serra II* (also location of coffee breaks)
	Wed Afternoon Excursion	Times and venues vary, box lunch provided	
	Wed Night Beach Party *Supported by TA Instruments.*	6:30 pm – 11:00 pm	*Pirate's Cove*
Thursday, August 7	**Exhibits**	8:00 am – 2:30 pm	*Serra II* (also location of coffee breaks)
	SoR Business Meeting	5:45 pm – 7:00 pm	*De Anza Ballroom I*
	Thursday Reception *Wine supported by Anton Paar.*	7:00 pm – 8:00 pm	*Serra Grand Ballroom II*
	Thursday Banquet *Wine supported by Anton Paar.*	8:00 pm – 10:00 pm	*Serra Grand Ballroom I*
Friday, August 8	**Closing Reception/Lunch**	1:00 pm – 3:00 pm	*Serra Grand Ballroom II*

Wednesday Afternoon Excursion

- Carmel Valley Wine Tour
- Steinbeck Country Wine Tour
- Big Sur Coastline Tour
- Monterey Marine Sanctuary Whale Watching Tour
- Kayak Tour
- Bike Tour
- Goft at Poppy Hills

Accompanying Person Additonal Excursions

- Scenic Highlights of Monterey Bay (*Monday 9 am – 1 pm*)
- Bike Tour (*Monday 2 pm – 5 pm*)
- Santa Cruz Beach Boardwalk (*Tuesday 9 am – 5 pm*)
- Carmel Walking Tour and Shopping (*Tuesday 10 am – 4 pm*)
- Kayak Tour (*Tuesday 2 pm – 5 pm*)
- Point Lobos Nature Walk (*Thursday 12 pm – 5 pm*)
- Bike and Kayak All Day Freestyle (*day and time your choice*)

Exhibitors

- Anton Paar USA
- ATS RheoSystems
- Brookfield Engineering Laboratories
- Goettfert Inc.
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Monday Morning – 4 August 2008

PL-1. Opening Plenary Lecture

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: L. Gary Leal

Monday 8:20 Serra I PL1

From molecules to mechanics: Nuclear magnetic resonance and rheological insight

Paul T. Callaghan
School of Chemical and Physical Sciences, MacDiarmid Inst. for Advanced Materials and Nanotechnology, Wellington, New Zealand

Nuclear Magnetic Resonance (NMR) has been able to address, in part, two challenges for modern rheology. The first concerns the need to obtain detailed information about the flow field generated by the device used to induce deformational flow, and in particular to be able to visualize, in real time, strain-rate heterogeneity and discontinuity, examples being shear banding, fracture and wall slip. The second concerns the enhancement of mechanical measurements with insight regarding molecular or colloidal organisation and dynamics, under conditions of flow, and ideally with spatial resolution.

In this latter sense Rheo-NMR belongs to a wider class of methods in which rheological measurements are enhanced by spectroscopic or scattering techniques capable of revealing information about molecular, or molecular organisational length-scale structure and dynamics. Amongst these techniques are light or X-ray scattering, neutron scattering and birefringence/ellipsometry measurement. NMR offers the possibility of measuring nuclear spin relaxation times and molecular self-diffusion coefficients, sensitive respectively to molecular brownian motions and their restrictions due to local structure. Furthermore, through the use of orientation-dependent terms in the spin interactions, such as the nuclear quadrupole or dipolar interactions, NMR permits the measurement of molecular orientational order parameters. When combined with imaging methods, NMR in principle allows such measurements to be spatially localized, often with resolution down to a few 10s of microns

Our "Rheo-NMR" approach utilises microscopic resolution in small volume (<1 ml) flow cells, allowing examination of speciality materials. Recent work has included the measurement of the full deformation tensor for sheared polymer melts, director re-alignment in liquid crystalline polymers, T2 relaxation enhancement in sheared polymer solutions, hydrogen bond disruption under shear and extension, and the correlation of stress, shear and surfactant chain ordering fluctuations in wormlike micelles. These studies of shear banding and band instabilities in wormlike micelles solutions have recently been extended to soft glassy materials, including semidilute star polymers and dense hard sphere packings. One factor to emerge has been the significance of time-dependency in the mechanics of complex fluids. A variety of measurements, including our own NMR studies, have revealed the importance of transients and fluctuations and quasi-chaotic behaviour, while in soft glassy materials, aging/rejuvenation effects play a role. This talk will review some recent work, emphasizing studies of fluctuations and ordering, and with a special emphasis on the phenomena associated with shear-banded flow.

HS-1. Liquid Crystalline Polymers & FIC

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chair: Hiroshi Watanabe

Monday 9:45 San Carlos IV HS1

The modification of time-dependent mechanical properties of polyamides due to sterilization

Urska Florjancic[1], Barbara Zupancic[1], Elizabeth Sutton[2], Ksenija Rener Sitar[3], Ljubo Marion[3], Urska Batista[4], Dusan Groselj[5], and Igor Emri[1]
[1]Center for Experimental Mechanics, University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana 1000, Slovenia; [2]College of Dental Medicine, Medical University of South Carolina, Charleston, SC, USA; [3]Chair of Dental Prosthetics, University of Ljubljana, Faculty of Medicine, Ljubljana, Slovenia; [4]Institute of Biophysics, University of Ljubljana, Faculty of Medicine, Ljubljana, Slovenia; [5]Chair of Mouth Diseases and Parodontology, University of Ljubljana, Faculty of Medicine, Ljubljana, Slovenia

The macroscopic properties of materials depend on their inherent structures. Structure of polymers may be modified by changing boundary conditions to which the material has been exposed to during solidification (i.e., technology) and/or by modifying its initial kinetics (i.e., topology of individual molecules, their masses, and mass distribution). The molecular mass distribution of polymers determines the time-scale of the material structure formation and its time-dependent properties. Thus, by modifying the distribution of length of macromolecules (thus, the molecular mass distribution), the properties of the material can be tailored. Polyamide 6 is currently used in medical practice, namely in sutures. There are new possibilities in modifying functionality of products via adjustment of physical properties of materials as required by the application. One possible medical and dental application for PA 6 is in the production of implants. During mastication, dental implants are dynamically loaded; thus, understanding their time-dependent behavior is critical in predicting the durability of implants. We investigated the effect of sterilization on the morphology, thermal properties, and time-dependent mechanical behavior of two types of Polyamide 6 (PA 6) having different molecular mass distribution. Investigated specimens were exposed to three different sterilization methods, i.e., autoclave, ethylene oxide, and hydrogen peroxide plasma. We performed optical microscopy to view the bulk structure, DSC to determine thermal properties, and torsional creep experiments to test time-dependent mechanical properties of analyzed materials. When three different sterilization methods were applied to mono-modal and bi-modal PA 6 materials, no effect was observed by optical microscopy. The difference in structure was only observed between mono- and bi-modal PA 6, indicating the formation of spherical crystals with mono-modal PA 6 and small grains with bi-modal PA 6. Thermal analysis showed no effect of sterilization on the thermal properties of the two PA 6 materials. Significant difference was observed in crystallization temperatures of mono- and bi-modal PA 6. The sterilization methods used in the present study significantly affected the time-dependent mechanical properties of mono-modal PA 6 while no effect was observed for bi-modal PA 6. We may conclude that two materials having different initial kinetics and processed with the same technology, when exposed to sterilization, change their time-dependent mechanical properties in significantly different ways.

Monday 10:05 San Carlos IV HS2

Simulations of shearing rheology of thermotropic liquid crystalline polymers

Hongyan Chen and Arkady I. Leonov

Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301, USA

The simulations present a first attempt to describe the rheological properties of the LCP's, using recently developed thermodynamic theory of weakly viscoelastic nematodynamics. In this theory the complicated rheological properties of nematic LCP's are modeled by a set of quasi-linear anisotropic viscoelastic constitutive equations (CE) with anisotropy described by director, whose viscoelastic evolution is coupled with the CE. Although this theory is valid for relatively small Deborah numbers, it is still possible to compare the simulations with experimental data. A new mathematical tool, algebra of nematic operators, is helpful in operations with this multi-parametric theory. . Eight parameters in the theory which include 3 viscosities, 3 elastic moduli, and 2 tumbling (elastic and viscous) parameters, could be decreased in so called soft cases. These parameters established for steady shearing are used for the calculations of evolution of shear stress and first normal stress difference with corresponding evolution of director, during relaxation and start up flow. The problem with initial conditions for director in start up flow is resolved in the following way. We preliminary fitted the experimental data for stresses in steady shearing with following adjustment of parameters to describe also the relaxation of stresses. In this case the parameters of evolution equation for director, along with its orientation in steady shearing were also established. The orientation of director during stress relaxation was then easily calculated, and its final orientation at the rest state was taken as initial one for the start up flow. We demonstrate that our simulations are at least in a semi-quantitative agreement with experimental data obtained for two industrial and two "academic" LCP's. Dependencies of fitted theoretical parameters on temperature and structure of LCP's are also discussed.

[1] A.I. Leonov, Z. angew. Math. Phys.DOI 10.1007/s00033-006-0072-7; [2] A.I. Leonov, http://arxiv.org/e-print/cond-mat/0409274; [3] K.M. Lee and C.D. Han, Macromolecules, 35, 6263-6273 (2002); [4] M.J. Belatreche, "A theoretical and Experimental Study of Liquid Crystalline Polymers, MS. Thesis, The University of Akron, 2002.

Monday 10:25 San Carlos IV HS3

Effects of director angle anchoring conditions on the dynamic moduli of heterogeneous nematic polymers

Eric P. Choate[1], M. Gregory Forest[2], Zhenlu Cui[3], and Lili Ju[1]

[1]Department of Mathematics, University of South Carolina, Columbia, SC 29210, USA; [2]Mathematics, Biomedical Engineering, University of North Carolina, Chapel Hill, NC 27599-3250, USA; [3]Mathematics and Computer Science, Fayetteville State University, Fayetteville, NC 28301, USA

We examine the linear viscoelastic response of heterogeneous nematic polymers to small amplitude oscillatory shear flow, paying special attention to the macroscopic influence of strong plate anchoring conditions. To predict the dynamic moduli, we model the system with Stokes hydrodynamic equations with viscous and nematic stresses coupled with orientational dynamics driven by the flow, an excluded volume potential, and a two-constant distortional elasticity potential. First, we show that for special cases of normal and tangential anchoring, we recover explicitly solvable Leslie-Ericksen-Frank behavior. In this case we observe significant differences between the moduli for normal and tangential anchoring, including a two-to-three order of magnitude enhancement of the storage modulus for normal over tangential anchoring. Then, we turn to a numerical study of oblique anchoring conditions, which are more complicated due to the appearance of order parameter gradients at leading order. When the anchoring angle is near 45 degrees, we observe significantly different scaling behavior in the storage modulus for high frequencies compared to the behavior for normal or tangential anchoring. Furthermore, we find that for low frequencies, normal anchoring gives the largest storage modulus and tangential the lowest; however, we see a brief window of higher frequencies where the maximum storage modulus occurs at an oblique anchoring angle.

Monday 10:45 San Carlos IV HS4

Solid-like properties of liquid crystal in smectic phase controlled with electric field applied

Takatsune Narumi[1], Hitoshi Uematsu[2], and Tomiichi Hasegawa[1]

[1]Faculty of Engineering, Niigata University, Niigata City 950-2181, Japan; [2]Graduate School, Niigata University, Niigata City 950-2181, Japan

Electro-rheological characteristics of a liquid crystal (8CB) in smectic-A phase were investigated utilizing a parallel-plate rheometer under the stress control mode. Solid like behavior of the liquid crystal under DC or AC electric fields were examined. Bingham-like properties were observed and the yield stress obtained was affected with the electric field conditions. When the electric field strength was low, the yield stress was almost the same as that obtained under no electric field. Above a threshold of DC electric field, the yield stress increased and then became constant. An opposite tendency was observed under AC electric fields. It appeared that the smectic poly-domain structure was maintained under low electric field conditions and the structure became more orderly and stronger when the higher DC electric field was applied. By contrast, the AC electric field would loosen the poly-domain structure because of the alternating electrical current on the molecules. In order to clarify the yield process in detail, the structure of the liquid crystal between two parallel plates was directly observed with an optical system. Under the DC electric fields, we found there were partially collapsed structures at the first stage of yield process and then large-scale deformation was generated. We had also conducted a strain-recovery test under small strain conditions where the partially collapsed structures were observed. It was found that the structure in this region had partially elastic recoverable strain.

Monday 11:05 San Carlos IV HS5

Kinetic Monte Carlo simulations of anisotropic nucleation in polymer melts under strong flow

Richard S. Graham[1] and Peter D. Olmsted[2]

[1]School of Mathematical Sciences, University of Nottingham, Nottingham NG7 2RD, UK; [2]School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK

The tube model is the most established framework to describe the dynamics of entangled polymers under flow. Recent refinements of tube model have been verified against both bulk stress and neutron scattering measurements and these comparisons show that the model can accurately predict the configurations of polymer chains under strong flow[1,2]. This effect of flow on chain configuration is believed to play a key role in the effect of flow on crystallisation in semi-crystalline polymer melts. However, these models have not yet been used to provide insight into flow induced crystallisation.

In this work, we present a scheme for computing the effect of molecular configuration under flow on anisotropic nucleation and growth of polymer crystals. We use a kinetic Monte Carlo algorithm to model the growth of polymer crystals, resulting in a computationally inexpensive model for polymer crystal nucleation. Changes in crystallisation kinetics due to molecular stretching and orientation are accounted for using the instantaneous molecular configuration under flow, which is computed using a tube model. The effect of flow on the orientation of polymer crystallites is also accounted for during the simulation, with the crystallites' orientational relaxation time depending on the crystallite size and aspect ratio. The simulation algorithm predicts the effect of bulk flow conditions and melt molecular weight distribution on both the nucleation rate and resulting crystal orientation.

[1] Graham R.S., Likhtman A.E., McLeish T.C.B., Milner S.T., Microscopic theory of linear, entangled polymers under rapid deformation including chain stretch and convective constraint release, Journal of Rheology 47(5) 1171-1200 (2003); [2] Bent J., Hutchings L.R, Richards R.W., Gough T., Spares R., Coates P.D., Grillo I., Harlen O.G., Read D.J., Graham R.S., Likhtman A.E., Groves D.J., Nicholson T.M., McLeish T.C.B. Neutron Mapping Polymer Flow: Scattering, Flow-Visualisation and Molecular Theory, Science 301 1691-1695 (2003).

Monday 11:25 San Carlos IV HS6

Density fluctuations in crystallizing polymers: Fact or fiction?

Jimmy Baert and Peter Van Puyvelde

Department of Chemical Engineering, K.U. Leuven, Leuven, Belgium

Recently, the initial stages of (semicrystalline) polymer crystallization have gained particular importance. However, a clear picture of the nucleation phenomena in polymer crystallization is still lacking. Conflicting results favouring various proposed models (e.g. nucleation and growth, spinodal decomposition, stepwise crystallization via mesomorphic domains, ...) have been reported, but no convincing conclusions have been reached. The ongoing discussion on the mechanisms that govern these early stages confirms the need for further investigations into this domain. In the present work, the fact that nucleation might be accompanied by large scale density fluctuations has been investigated for the flow-induced crystallization of iPB. To understand what controls the structure formation in semicrystalline polymers and to exploit the effects of flow on the early stages in more detail, a method to measure and separate density and orientation fluctuations from the spatial arrangement of anisotropic crystals is needed. Small Angle Light Scattering (SALS) has been used to provide this information, whereas complementary results were obtained from polarizing optical microscopy (POM). In a first part, an overview of polymer crystallization studies using SALS is given: experimental methods, analysis techniques, observations and their relation with respect to other techniques (DSC, WAXS and SAXS, dilatometry, microscopy, rheometry, ...) are compared and discussed. In a second part, the results on iPB are presented and discussed. The evolution of the scattering patterns is described in terms of the invariants and that are an expression of the growing fluctuations of density and orientation respectively. Measurements compare the effect of processing conditions (temperature, shear flow) on the kinetics and the intensity of these fluctuations. The combination with POM enables to link the results with the developing semi-crystalline structures and confirms that density fluctuations, at least at the instant they are detected with SALS, do not necessarily develop before the crystalline units. SALS experiments were carried out not only during isothermal crystallization, but also during melting of the crystallized structure. The goal of the melting experiments in this study was to verify if, on heating the samples from the crystalline state, density fluctuations still exist after orientation fluctuations have disappeared. For both crystallization and melting experiments, the observations seem to suggest that the detected density fluctuations result from the presence of low anisotropic domains, rather than being an indication of densification before the onset of crystallization.

SG-1. Polymer Dynamics

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Juan Colmenero

Monday 9:45 San Carlos II SG1

The bulk modulus of polystyrene and comparison to the shear modulus

Sindee L. Simon and Yan Meng

Dept. of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, USA

Isothermal pressure relaxation as a function of temperature in two pressure ranges has been measured for polystyrene using a self-built pressurizable dilatometer. A master curve for pressure relaxation in each pressure regime is obtained based on the time-temperature superposition principle, and time-pressure superposition of the two master curves is found to be applicable when the master curves are referenced to their pressure-dependent Tg. The pressure relaxation master curves, the shift factors, and retardation spectra obtained from these curves are compared with those obtained from shear creep compliance measurements for the same material. The shift factors for the bulk and shear responses have the same temperature dependence, and the retardation spectra overlap at short times. Our results suggest that the bulk and shear response have similar molecular origin, but that long-time chain mechanisms available to shear are lost in the bulk response. In addition, using mercury to calibrate the PVT response of the dilatometer, the viscoelastic bulk modulus is obtained from the pressure relaxation experiments and is compared with other measurements in the literature. In addition, the effect of jump size and jump direction on the bulk modulus will be discussed.

Monday 10:05 San Carlos II SG2

Crystals in polymers may afford better mechanical performance than solid mesophases

Finizia Auriemma and Claudio De Rosa

Dipartimento di Chimica P. Corradini, Università di Napoli Federico II, Napoli 80126, Italy

The deformation behavior of semi-crystalline polymers associated with polymorphic transformations under tensile deformation is discussed in the case of some polyolefin-based materials with tailored architectures, produced using metallorganic catalysts. The mechanical properties of semi-crystalline polymers, and of polyolefins in particular, are largely related to the crystal structure and morphology, which in turn depend on the chain microstructure, (i.e. concentration and distribution of stereodefects and regiodefects, constitutional defects as typically the presence of comonomeric units) generated by the specific used catalyst [1,2]. We show that the occurrence of polymorphic transformations during plastic deformation induced by application of uniaxial stretching, plays a fundamental role in these systems. In particular, it is demonstrated that the possible formation of the disordered mesomorphic form during solid-state drawing of metallocene-made isotactic polypropylene samples gives rise to a different mechanical behavior, because the mesophase facilitates the subsequent deformation of the sample, so that the material behaves as a highly flexible plastomer [1]. We also show, in the case of metallocene-made syndiotactic polypropylene samples, that when the crystalline form that develops by stretching is metastable, it may transform into a more stable form, by removing the tensile stress. This transformation is reversible and is associated with a non-trivial elastic recovery. The entity of plastic versus elastic deformation experienced by the material upon releasing the stress, may critically depend on the relative stabilities of the two crystalline forms that develop during successive cycles of stretching and relaxation [2]. In all cases, polymorphic transitions occurring during tensile deformations in unoriented films involve breaking of preexisting lamellae of the original crystalline form and formation of fibrils of the new crystalline form. These transitions, appear strain controlled rather than stress controlled. The values of the critical strain linked to the polymorphic transitions are namely affected by the chain microstructure, whereas the corresponding values of the stress depend also on other factors as temperature, degree of crystallinity, etc. Direct crystal-crystal phase transitions may instead occur upon stretching and relaxing oriented fibers, that is, specimens that have already undergone plastic deformation. In these cases the structural transition may play a key role in the elastic recovery of the sample, when the crystalline form obtained by stretching is less stable than the crystalline form that develops upon releasing the tension [1,2].

[1] De Rosa, C.; Auriemma F. J. Am. Chem. Soc. 2006, 128, 11024; De Rosa, C.; Auriemma, F. Lect. Notes Phys. 2007, 714, 345; [2] De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O. Phys. Rev. Lett. 2006, 96, 167801; Auriemma, F.; De Rosa, C.; Esposito, S.; Mitchell, G. R. Angew. Chem. Int. Ed. 2007, 46, 4325.

Monday 10:25 San Carlos II SG3

Component terminal dynamics in miscible, interacting blends

Sahban N. Ozair[1] and Timothy P. Lodge[2]
[1]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA; [2]Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

Great attention continues to be paid to the study of dynamics of miscible polymer blends. However, most of the blends studied have been athermal; component dynamics in interacting blends have not been extensively investigated. The component terminal dynamics have been studied in a model interacting system, poly(ethylene oxide)/poly(vinyl phenol) (PEO/PVPh) using a commercial rheometer. The strong hydrogen bonding between the two components provides additional complexity to the temperature and composition dependent dynamic behavior of each component. The rheological methods employed for this investigation examined relaxation of a small percentage of long chains of one component dispersed in low molecular weight blend matrices. Using appropriate polymer dynamics models, the monomeric friction factor of each component was extracted for a wide range of temperatures at different compositions. The molecular weight effect on component dynamics was also studied. These results and also the implications of hydrogen bonding on dynamic heterogeneity of these blends will be discussed.

Monday 10:45 San Carlos II SG4

Multivariate feature of dielectric relaxation processes in liquid sugar alcohol system with the glass transition

Ryusuke Nozaki
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We have studied dielectric relaxation processes in liquid sugar alcohol system in the frequency range from 10microHz up to 10GHz. Liquid samples examined in this work are pure materials of glycerol, threitol, xylitol and sorbitol, the binary mixtures of them, and ones with small amount of water. All the samples show two dielectric relaxation processes those are, respectively, the structural alpha relaxation process and the Johari-Goldstein (JG) beta process, as is usually seen in typical glass forming liquids [1-5]. The glass transition temperatures Tg of the samples depend on the number of carbons Nc including the cases of the average values for the mixtures. Adding water into the pure materials decreases the glass transition temperature. Thus, we have constructed the unique relaxation map, in which logarithms of the relaxation frequencies (log fm) are plotted against not only the inverse of temperature (1/T) but also (Nc) and the sugar fraction in water-in-sugar liquids (X). Surprising finding is that the locus of log fm for the alpha process follows not only the VFT function with respect to 1/T but also the function with respect to Nc or X. All the plots also indicate the alpha-beta bifurcation with decreasing T, increasing Nc or X. This multivariate feature for the alpha and beta process is recognized for the first time. Since the elementally process of dipolar relaxation in the present system is considered to be a part of the hydrogen bonding networks associated with the component molecules, the local viscosity related to the dipolar orientation would be also multivariate. Such concept must be very important to understand the universality of complex systems including life process.

[1] Nozaki et. al., J. Non Cryst. Solids, 235-237, 393-398 (1998); [2] Nozaki et. al., J. Non-Crysl. Solids, 307-310, 349-355 (2002); [3] Minoguchi et. al., Phys. Rev. E., 68 (3), 031501 1-7 (2003); [4] T. Psurek et. al., Phys. Rev. E, 70, 011503 1-6 (2004); [5] Minoguchi et. al., J. Non-Cryst. Solids, 352, 4742 (2006).

Monday 11:05 San Carlos II SG5

Dynamics and morphology of grafted copolymers

Serge Etienne[1], Magali Billy[2], Anne Jonquières[2], Robert Clement[2], and Laurent David[3]
[1]LPM, Ecole Des Mines, Nancy-Université, Nancy, France; [2]LCPM, ENSIC, Nancy-Université, Nancy, France; [3]LMPB, Université Lyon 1, Villeurbanne, France

The interactions between the main chain and lateral chains in grafted polymers play an important role on their dynamics. This is a complex issue, since several length scales are to be taken into account, from the local intramacromolecular interactions between linked moieties up to intermolecular interactions in phase separated systems. For example, a slowing down of the dynamics of the grafted chains is expected when the main chains have a much slower dynamic. Specific dynamic effects occur after phase separation of the grafted lateral chains, according to their density, length and compatibility with the main chain. The aim of the work is to investigate such phenomena on the basis of new copolymers obtained by controlled radical polymerization. The effect of two parameters are studied separately, namely i) the number of grafted chains on the main chain and ii) the length of grafted moieties. This is achieved in the case of cellulose acetate (purchased from Fluka, Mn=52000g/mol, 40 wt% acetyl) grafted with poly(methyl(diethylene glycol)methacrylate) (poly(MDEGEMA) synthesized by Atom Transfer Radical Polymerization (ATRP). The grafted moieties were either long (24 wt%, Mn=7680 g/mol) (44 wt %, Mn=18500 g/mol), or short (24 wt%, Mn=1390 g/mol) (47 wt%, Mn =3960 g/mol). The dynamics was assessed by Low Frequency Mechanical Spectroscopy. The complex elastic modulus was measured on thin films (0.06 mm thickness) as a function of frequency and temperature. The sensitivity of this spectroscopy, as compared to calorimetry measurements, allowed to underline the effects of (i) the chemical structure of the copolymers and (ii) the microstructure at the nanoscale, as investigated by Small Angle X Ray Scattering.

HP-1. Unentangled Polymers

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Doug E. Smith and Patrick S. Doyle

Monday 9:45 San Carlos III HP1

Dynamics of single tethered DNA in shear flow

Christopher A. Lueth[1] and Eric Shaqfeh[2]
[1]Chemical Engineering, Stanford University, Stanford, CA, USA; [2]Departments of Chemical and Mechanical Engineering, Stanford University, Stanford, CA 94305, USA

Organic molecules as charge carriers play a key role in the developing field of "plastic electronics". To test the electrical properties of organic single molecules, it is necessary to create a closed circuit containing the molecule. We wish to develop a simple, repeatable process to create such circuits using DNA as a scaffold. By using dip-pen nanolithography (DPN) we can control the tethering location of a 3 &μυm DNA-conducting organic molecule-DNA (DOD) sandwich. The single-tethered DOD is then exposed to shear flow stretching the chain and creating contact between the free end and a second electrode. The free end is subsequently tethered via an additional chemical functionalization and the DNA segments in the bridge are metallized, creating conducting wires separated by an organic single molecule. To make this process repeatable, we must understand the dynamics of a single tethered DNA molecule in shear flow.

In this talk, we will examine the dynamics of a single tethered DNA molecule under the influence of shear flow. With the ability to perform Brownian dynamic simulations and single molecule fluorescence experiments in the flow-gradient plane we will study the effect of high shear rates on fractional extension and end-wall contact [2] as well as show that there is a characteristic frequency of cyclic motion for low shear rates as predicted by Schroeder et. al. [3]. Ultimately, our results will afford precise control over the creation of the DOD bridges.

[1] E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, Nature. 391, 775 (1998); [2] C. Lueth and E.S.G. Shaqfeh, Kor. Aust. J. Rheol. (to be published); [3] C.M. Schroeder, R.E. Teixeira, E.S.G. Shaqfeh, S. Chu, Phys. Rev. Lett. 95, 018301 (2005).

Monday 10:05 San Carlos III HP2

Modelling the dynamic scaling of dilute polymer solutions and its application to rheology

P Sunthar[1] and J R. Prakash[2]
[1]Chemical Engineering, IIT Bombay, Mumbai, Maharashtra 400076, India; [2]Chemical Engineering, Monash University, Melbourne, VIC 3800, Australia

One of the intriguing observations of polymer solution behaviour is the existence of an apparent molecular weight scaling in the good-solvent regime which is different for dynamic properties, such as the viscosity and diffusivity, from that of static properties, such as the radius of gyration. With a bead-spring chain formulation that incorporates the solvent quality explicitly, we show, using Brownian dynamics simulations, that the apparent difference is due to the presence of fluctuating hydrodynamic interactions. The experimentally observed cross-over from theta-solvent to good-solvent behaviour for dynamic properties is quantitatively accurately captured in our model. The implication of this for the prediction of rheological properties with molecular theories is that the equilibrium description of a polymer, which have so far been a curve fitting exercise using several experimentally observed quantities, can be carried out with the knowledge of just two parameters: the radius of gyration under theta conditions and the solvent quality. Further, in order to predict rheological properties far from equilibrium, where the finite extensibility of the polymer is a dominant feature, the only additional parameter required for quantitative prediction is the fully stretched length of the polymer. We show how this information can be obtained with minimal additional measurements, such as the molecular weight and temperature, for polymer-solvent systems with known radius of gyration at the theta temperature.

Monday 10:25 San Carlos III HP3

Evaluation of the Gaussian Blob model for coarse-graining hydrodynamic interactions in isolated polymer molecules

Ranganathan Prabhakar
Department of Mechanical and Aerospace Engineering, Monash University, Clayton, Victoria 3800, Australia

Hydrodynamic interactions (HI) are important in a variety of systems such as colloidal suspensions and polymer solutions, both near and well beyond equilibrium. Detailed particulate simulations are increasingly an important tool in exploring the behaviour of such systems. An accurate method for coarse-graining long-range HI is desirable for designing efficient simulations, particularly when no obvious spatial symmetries can be exploited, as in the case of isolated flexible polymer molecules in solution. A recent model [Prabhakar et al, Phys. Rev. E, 76:011809 (2007)] proposed coarse-graining HI in a dilute polymer solution by representing a macromolecule as a chain of axisymmetric ellipsoidal Gaussian density fields, whose instantaneous dimensions are derived from their end-to-end stretch and orientation by invoking the assumption of local equilibrium. In this "Gaussian Blob" (GB) model, an expression was derived for the tensor describing HI between any pair of blobs. By combining the resulting mobility matrix with entropic spring force laws also based on the local equilibrium assumption, the GB model provides an alternative to the conventional bead-spring chain model with Rotne-Prager-Yamakawa HI. The advantage of the new model is that it has no free parameters, and all model parameters are uniquely related back to the polymer contour length, the Kuhn step length and the hydrodynamic diameter of the polymer contour. Preliminary simulations indicated that, in comparison with the conventional bead spring model, the GB model achieves a considerable reduction in the variation of predictions with respect to the number of blobs N chosen to represent the chain, irrespective of whether chains are stretched, or coiled near equilibrium. In this talk, I present more detailed results to confirm the practical viability of the coarse-grained HI used in the GB model. Firstly, the universal viscoelastic features predicted by both the GB and conventional models are identical, in the linear response regime, in strong extensional flows, and during relaxation after being initially expanded. In addition, the much smaller variation with N observed with the GB model means that a single low choice of N ~ 5 can be used to perform reliable and computationally efficient simulations under a variety of conditions without adjusting parameters. I also discuss applications of this model to model more complex structures and illustrate its use with simulations for linear and nonlinear rheological properties of rod-coil block co-polymers.

Monday 10:45 San Carlos III HP4

A Brownian dynamics study of the effect of solvent quality on the coil-stretch transition

Shikha Somani[1], Eric Shaqfeh[2], and J R. Prakash[3]

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It is now well known that when long chain, linear polymers in dilute solution are subjected to purely elongation flows (or elongation-dominated mixed flows), the solution properties show a sharp variation near a critical flow rate where the conformation of the polymer changes from a coiled to a stretched state or vice versa. Because the solution properties change dramatically at this so-called coil-stretch transition, it is important in many applications. The transition is primarily characterized by the critical flow rate for a given polymer molecular weight and solvent quality. While the effect of solvent quality on equilibrium properties of polymer solutions has been widely studied, there have been relatively few attempts at examining its influence on properties far from equilibrium. Cifre and Torre have recently examined, via Brownian dynamics, the effect of solvent quality on the critical elongation rate for coil-stretch transition and suggested that there was no effect on the transition properties. However, critical elements of the newly developed method of successive fine graining (SFG) were not considered in their work nor were the new theories surrounding coil-stretch hysteresis. We therefore revisit the specific problem of steady, homogeneous elongational flow, and attempt to determine precisely the dependence of the critical elongational rate on solvent quality and chain length, including rigorously effects such as fluctuating hydrodynamic interactions (HI) and excluded volume (EV). The solvent effect is captured systematically using the EV parameter 'z' which is the appropriate parameter in perturbation expansions determining the effect of solvent quality about the 'theta' state. A noteworthy aspect of this approach is the use of a narrow Gaussian repulsive potential, which acts pair-wise between the beads of the polymer chain. Exact results are obtained numerically using Brownian dynamics simulations, and the Successive Fine Graining (SFG) technique has been used to extrapolate the results of the bead-spring chain simulations to the limit where the number of springs approaches the number of rods in a bead rod model. The SFG technique eliminates the arbitrariness in the choice of the number of beads in the bead spring chain model. The approach is then further extended to study the effect of solvent quality on the phenomena associated with polymer conformational hysteresis, including the nature of transition states and the activation energy for the transition.

Monday 11:05 San Carlos III HP5

On the influence of excluded volume in polymer melts

Hendrik Meyer, Joachim P. Wittmer, and Jorg Baschnagel

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Flory's ideality hypothesis states that polymer chains in the melt have random walk like conformations as if there would be no excluded volume. However, it was shown recently that the excluded volume interaction induces corrections to scaling which are long range and which give rise to a power law decay of bond-bond correlation function [1] as well as to corrections to the Kratky plateau of the form factor [2]. In this presentation, we extend the study to dynamic quantities: The excluded volume potential is switched on gradually to study the crossover from phantom chains (representing perfect random walks described by the Rouse model) to real polymer melts [3]. This gives evidence that subdiffusive behaviour found in contradiction to the Rouse model [4] is also caused by the excluded volume interaction. The influence on the shear relaxation modulus will also be briefly addressed.

[1] J. Wittmer, H. Meyer, J. Baschnagel et. al. Phys. Rev. Lett. 93 (2004) 147801. Phys. Rev. E 76 (2007) 011803; [2] J. Wittmer et. al. EPL 77 (2007) 56003; [3] H. Meyer et. al. submitted to Eur. Phys. J (2007); [4] W. Paul, Chem. Phys. 284 (2002) 59.

HP-2. Polyelectrolytes and Ionomers

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Julia A. Kornfield and Claude Cohen

Monday 9:45 San Carlos I HP7

Polyelectrolyte solution rheology

Ralph H. Colby

Materials Science and Engineering, Penn State University, University Park, PA 16802, USA

The viscosity and relaxation time of polyelectrolyte solutions in high dielectric constant solvents are reported. The effects of polyelectrolyte concentration, polyelectrolyte charge density, solvent dielectric constant, solvent quality and salt concentration are well described by scaling theory. The overlap and entanglement concentrations are apparent from the concentration dependence of viscosity. While the overlap concentration has the expected chain length dependence, the entanglement concentration does not. Semidilute unentangled solutions are described by the Rouse model and a new path to understanding shear thinning in the Rouse model is presented. New data are presented for partially quaternized poly(2-vinylpyridine) in ethylene glycol (EG) and N-methyl formamide (NMF). EG and NMF are good solvents for the neutral polymer before quaternization, enabling the effects of polyelectrolyte charge density to be studied over an unusually wide range. EG also can be purified to have essentially zero salt ion contaminants, allowing dilute solutions of high molecular weight polyelectrolytes to be studied in the low salt limit (whereas this is impossible for all aqueous solutions and solutions in NMF). Hence, the scaling model can be fully tested in EG solutions. After multiple distillations, NMF has even larger quantities of residual salt than distilled water. However, the rheology of polyelectrolyte solutions in NMF can be understood by identifying the concentration at which the number density of free counterions equals the number density of salt ions. At higher concentrations, the solution viscosity obeys the low salt scaling predictions and at lower concentrations the viscosity obeys the high salt predictions.

Monday 10:05 San Carlos I HP8

Ionic effects on the dynamics of DNA confined in nanoslits

Chih-Chen Hsieh and Patrick S. Doyle
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The conformational and dynamical properties of polyelectrolytes depend strongly on their ionic environment. Such effects are even more significant when a polyelectrolyte is confined. In this study we have used lambda-DNA confined in a nanoslit as a model polyelectrolyte. We experimentally study the diffusivity and longest relaxation time as a function of ionic strength and confinement. We find that the change in DNA diffusivity and relaxation time can be quantitatively explained by Blob theory with an electrostatically mediated DNA persistence length and effective width. Surprisingly, it is found that instead of the persistence length, the effective width of DNA (which characterizes the electrostatic repulsion between segments) is the main driving force for significant change in DNA dynamics. Our results provide important insight into DNA and other polyelectrolytes behavior under confinement.

Monday 10:25 San Carlos I HP9

Ion Solvation Energetics

Wenjuan Liu[1], Michael J. Janik[2], and Ralph H. Colby[1]
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We used ab initio quantum chemistry calculations to estimate dipole moments and interaction energetics in ion-containing polymers. Interactions are reported for various small cations with common functional groups found on polymers and also carboxylate, sulfonate and phosphonate groups that can be present in anionic ionomers. The results provide parameters for a simple four-state model for counterions in ion-containing polymers: free ions, separated ion pairs, contact pairs and quadrupoles. Our calculations are used to interpret the importance of electrostatic interactions and solvation energetics for ions interacting with various functional groups. The utility of this simple model is demonstrated for explaining observations from dielectric spectroscopy, such as free ion content, conductivity and dielectric constant. We also suggest how these interaction energies might be utilized to design polymer membranes with facile ion transport.

Monday 10:45 San Carlos I 💿 HP10

Viscoelasticity, conformational transition and ultrastructure of kappa-carrageenan in the presence of potassium ion around the critical total ion concentration

María C. Núñez-Santiago[1], Alberto Tecante[2], Sylvie Durand[3], Catherine Garnier[3], and Jean L. Doublier[3]
[1]Departamento de Desarrollo Tecnológico, Centro de Desarrollo de Productos Bioticos-IPN, Yautepec, Morelos 62731, Mexico; [2]Departamento de Alimentos y Biotecnología, Universidad Nacional Autónoma de México, Mexico, Mexico; [3]URBIA, INRA, Nantes 44316, France

The gelation mechanism of kappa carrageenan (kC) in the presence of K+ ions consists of two stages. First, a disorder-order transition from random coil to double helix takes place. Then, aggregation of helical structures into a three-dimensional network occurs. According to the sol-gel transition diagram, which is the relationship between log C and 1/T, with C being the total ion concentration and T the absolute temperature, there is a critical total ion concentration (C*), that represents the minimum ion concentration necessary for kC to form gels. In this work, the effect of K+ ion on the viscoelastic behavior, the disorder-order transition and the ultrastructure of kC in aqueous solution in the vicinity of a C* value of 0.007 eq/L were studied by means of rheological, microDSC and Confocal Laser Scanning Microscopy (CLSM) techniques, respectively. Concentrations were 0.5% for kC and 0 to 5 mM for KCl. kC was dispersed in deionized water at 25 °C, heated to 80 °C and held at this temperature for 15 min before being examined in a strain rheometer (RFS II, Rheometrics, France). The hot solutions were placed in a cone-plate fixture (diam. 50 mm, angle 0.04°) previously equilibrated at 9 °C. The evolution with time of G' and G" was monitored for 7 hours at constant frequency and strain. After this lapse, the viscoelastic properties were examined under low amplitude oscillatory shear at 9 °C. The disorder-order transition was also monitored in a micro calorimeter (Setaram DSC III, France) in two heating-cooling cycles from 2 to 90 °C. kC was covalently labeled with RITC and the tagged polymer examined using a BioRad MRC 1024 microscope in fluorescent mode at excitation/emission wavelengths of 543/575 to 640 nm, respectively. The rheological behavior was that of a "soft gel", with G' > G" and both moduli independent of frequency. However, during heating, two peaks appeared in the microDSC thermograph: the first was attributed to a random coil-helix transition without aggregation, and the second to the fusion of aggregates and network break-up. CLSM revealed a three-dimensional network whose continuity depends on the added amount of K+ ion. For gelation to occur, enough K+ ions must be present to induce aggregation of kC double helices so that they can form a continuous three-dimensional network. Otherwise, aggregated and unaggregated double helices coexist in solution without forming a gel.

Monday 11:05 San Carlos I 💿 HP11

Viscoelastic properties of cellulose in 1-buthyl-3-methylimidazolium chloride

Yoshiaki Takahashi, Akihiko Takada, and Kenta Imaichi
Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580, Japan

Viscoelastic properties of cellulose solutions in a ionic liquid, 1-buthyl-3-methylimidazolium chloride (bmimCl) are studied over a wide range of concentration. Cellulose samples mainly used are microcrystalline cellulose and cotton. Due to relatively high viscosity of bmimCl, viscosity data for dilute solutions can be used to determine intrinsic viscosities. At relatively high concentration for cotton solution (about 10wt%), terminal and plateau regions can be observed. The details of viscoelastic properties and their concentration dependence will be reported in this presentation together with a unique viscosity behavior of bmimCl.

Monday 11:25 San Carlos I HP12

Rheology of self-assembling silk fibroin solutions

Rui Zhou and Xue-Feng Yuan

Manchester Interdisciplinary Biocentre, The University of Manchester, Manchester M1 7DN, UK

Silk produced by the domesticated silkworm, Bombyx mori, is readily available in large quantity and has a long history of use in medicine as sutures. It is composed of two structural proteins, heavy (~350 kDa) and light (~25 kDa) fibroin, that form the thread core, together with sericin proteins that 'glue' the fibroin fibres together. The sericins are hydrophilic, and can be easily removed from cocoons to eliminate their adverse effects in medical application. The fibrous proteins exhibit unique mechanical and biological properties, including good biocompatibility, good oxygen and water vapour permeability, biodegradability, and minimal inflammatory reaction. Such distinctive properties have been shown to provide a material option for controlled drug release and for construction of biomaterial scaffolds for tissue engineering. Silk fibroin is composed of highly repetitive amino acid sequences with alternating hydrophobic and hydrophilic blocks along the chain. It can be considered to be nature's counterpart of a synthetic multi-block polyelectrolyte which can self-assemble into micelles, and concentrated solutions of which may form gels, i.e. lyotropic liquid crystal phases. The fibroin heavy chain has long hydrophilic end blocks, and a central block comprising seven hydrophobic blocks spaced by six short hydrophilic blocks. A good understanding of the interplay between the equilibrium phase behaviour of fibroin solutions and fluid flow is a prerequisite for any breakthrough in processing of silk materials. Rheometric characterisations for a range of carefully formulated silk fibroin aqueous solutions with concentration up to 30wt%, and fibroin/poly(ethylene oxide) blends have been carried out in linear and non-linear viscoelastic flow regime. Equilibrium and dynamic phase behaviour are studied. Phase separation and electrospinning techniques are developed to microfabricate silk-based scaffold materials for tissue engineering. The correlations between fluid formulation, rheological properties and processibility of silk fibroin will be reported.

MR-1. Cells and Non-Equilibrium Systems

Organizers: Eric M. Furst and David A. Weitz
Session Chairs: Thomas G. Mason and John C. Crocker

Monday 9:45 Redwood MR1

Microrheology in living cells

Clifford P. Brangwynne[1], Gijsje H. Koenderink[2], Fred MacKintosh[3], and David A. Weitz[1]

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This talk will review the effects of the activity of molecular motors in cells, and their influence on the motion of structural elements within the cell. By analyzing the motor-induced motion of microtubules, insight is obtained about the effects of the motor. These results will be used to discuss the caution that must be exercised when using passive microrheology to study cell mechanics.

Monday 10:05 Redwood MR2

Stress relaxation, stiffening and fluidization of adherent cells

Philip Kollmannsberger and Ben Fabry

Department of Physics, University of Erlangen-Nuremberg, Erlangen, Germany

The rheology of adherent cells is characterized by a creep or stress relaxation response that follows a weak power law over several decades in time. In addition, cells exhibit a nonlinear stress-strain relationship, in particular a pronounced stress stiffening. Stress relaxation processes of living cells in the non-linear range where stress stiffening occurs have been poorly characterized and are not well understood. We used a magnetic tweezer setup with real-time force control to apply forces of 20 nN to beads bound to the cytoskeleton of adherent cells. Cell deformations in response to stepwise increasing and repeated force application were analyzed using a non-linear visco-elastic superposition model that allowed us to dissect stress relaxation processes from stress-stiffening responses. The creep modulus decreased with increasing force, corresponding to a power-law stress stiffening with a slope of ~0.4. In most beads, stresses relaxed according to a power-law in time with a slope between 0.2 and 0.3 that was independent of the stress magnitude. In a smaller fraction of beads, however, we observed a force-induced fluidization and yielding that was accompanied by an increase in the power-law exponent. This increase was indicative either of a total disruption of the beads from the cell when the force was further increased, or of a substantial persistent (plastic) deformation after the force was removed. We interpret our results in terms of a model where dynamic stability and turnover of molecular interactions carrying the mechanical stress are determined by an energy landscape with an exponential distribution of energy well depths and associated trap stiffnesses.

Monday 10:25 Redwood MR3

Nonequilibrium mechanics and stress-fluctuation in the motor-activated cytoskeletons

Daisuke Mizuno[1], Catherine Tardin[2], David Head[3], Fred MacKintosh[4], and Christoph Schmidt[5]

[1]Kyushu University, Fukuoka, Japan; [2]IPBS CNRS, Toulouse, France; [3]Institute of Industrial Science, University of Tokyo, Tokyo, Japan; [4]Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands; [5]III. Physikalisches Institut, Fakultät für Physi, Georg-August-Universität, Goettingen, Germany

Mechanics directly controls many functions of cells: motion, force generation, and mechanosensing. The cytoskeleton is a network of semiflexible filamentous proteins that is responsible for most of the mechanical functions of cells. One of the principal features of the cytoskeleton in vivo is its non-equilibrium character, due to the force generations by the mechanoenzymes (motor proteins). Prior in vitro studies, however, have focused on passive mechanics of cytoskeletons in equilibrium. Mechanism of force generation in cytoskeletons has been also investigated (often with single molecule techniques) separately from the mechanics of cytoskeletons.

Here we show for the first time how non-equilibrium motor activity and the mechanical properties of in vitro model of the cytoskeleton are related to each other. We applied both active and passive microrheology techniques to actin networks driven by myosin II motor protein. While active microrheology directly informs the mechanics of cytoskeletons even out-of-equilibrium, both equilibrium and non-equilibrium stress fluctuation influence the passive microrheology. Thus combination of active and passive microrheology is the prerequisite to elucidate the mechanics of motor-driven cytoskeletons.

The crosslinked actin network can sustain motor driven stress; the network is kept homogeneous and stable under the presence of active myosins. The non-equilibrium stress fluctuation can be elucidated by the violation of a fundamental principle/theorem of equilibrium statistical physics: the fluctuation-dissipation theorem, which is understood as the simple sum of the force generating events by the each independent myosin filaments. We show that nonequilibrium stresses controls cytoskeletal network mechanics: both increasing stiffness by nearly 100 times and qualitatively changing the viscoleastic response of the network in an ATP-dependent manner.

On the other hand, non-crosslinked actin network can sustain very small stress (averagely 15fN/actin filament) driven by motors; system goes through the irreversible contractile process called superprecipitation. Due to the small restoring force from the networks, here we observe more contraction due to the co-operative force-generation where multiple motors working together. We present a quantitative theoretical model connecting the large-scale properties of these crosslinked and non-crosslinked active gels to molecular force generation.

We also present studies on intracellular mechanics of cultured fibroblasts, which show that our physical description of in vitro active cytoskeleton is applicable to in vivo cytoskeletons.

Monday 10:45 Redwood MR4

Episodic dynamics in biomicrorheology

Thomas G. Mason
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We examine how episodic dynamics can affect particle trajectories in biological viscoelastic environments that have considerable complexity: active convection, localized trapping, and random thermal forces. We show that an unsophisticated approach to analyzing such trajectories can lead to a mean square displacement that appears to be effectively diffusive. Moreover, we show that naively using the generalized Stokes-Einstein relation of thermal microrheology to interpret such trajectories and mean square displacements in terms of simple viscosities is inappropriate. We propose an alternative framework for quantitatively analyzing complex trajectories that includes active non-diffusive transport.

Monday 11:05 Redwood MR5

Dynamics of different probe particles to study local micro-environments inside living cells

Michael H. Duits, Siva A. Vanapalli, Yixuan Li, and Frieder Mugele
Science and Technology, MESA Institute, University of Twente, Enschede, The Netherlands

To understand the dynamic behavior of particles inside living cells in relation to intracellular rheology, we performed video particle tracking experiments. Living endothelial cells were examined in untreated form, and after thermal and/or chemical treatments. These interventions were aimed at revealing specific contributions to the particle motions via dynamic driving forces or passive mechanical resistances. Endogenous Granules (EG) and Ballistically Injected Particles (BIP) were used as intracellular tracers, while confocal microscopy was used for visualization. At 37 degrees Celsius the ensemble averaged mean-squared displacement (ea-MSD) showed different time dependence for the two probes. While EGs showed a linear dependence, for BIPs a transition from linear to a plateau at small lagtimes was observed. Moreover, the (normalized) magnitude of the ea-MSD was substantially larger for the EGs. This suggests different (chemical and/or mechanical) local micro-environments for EGs and BIPs. A correlation of these behaviors with the proximity to the cell nucleus or membrane was not found. Also the sets of individual particle trajectories were analyzed. Both the magnitude and the power-law exponent of the MSD showed distributions that were significantly broader for EGs and BIPS than for particles in a viscous liquid, suggesting heterogeneity in the environment for both probes. Depletion of intracellular ATP, generally aimed at 'knocking out' the active processes, resulted in opposite effects on the MSDs of EGs and BIPs. While for EGs the magnitude of the MSD and the fraction of trajectories showing superdiffusive exponents were reduced, for BIPs an increase in MSD magnitude was found. The hypothetic explanation that ATP depletion not only annihilates active processes in the cell, but also alters the cytoskeleton was supported by immunofluorescent labeling of actin filaments before and after ATP depletion. These observations of cytoskeletal network heterogeneities have profound implications for the quantification of global mechanical behavior in living cells.

MP-1. Extension Dominated Flows

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: David James

Monday 9:45 Ferrante I-III MP1

Transient solutions of nonlinear dynamics in film blowing accompanied by flow-induced crystallization

Jae Chun Hyun[1], Hyun Wook Jung[1], Joo Sung Lee[2], Dong Myeong Shin[1], Seung Won Choi[1], and Jeong Yong Lee[1]
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The nonlinear dynamics in film blowing process is simulated employing the governing equations of the system that include the flow-induced crystallization (FIC), i.e., the continuity, the two force balances (axial and circumferential), the energy, the crystallinity, and the constitutive equations of Phan Thien-Tanner (PTT) model coupled with Hookean one. Unlike the hitherto-published simulation results on film blowing, this study doesn't assume the boundary condition of the radius of the bubble at freezeline height having the zero slope with respect to the axial spatial coordinate. Instead, the governing equations of the system yield this important result as part of the solution of the set of the partial differential equations which are defined from the die exit all the way to the nip roll. The reason why the governing equations need to be solved to the nip roll beyond the freezeline height is simple: most of the flow-induced crystallization occurs after the freezeline height and the deformation of the film also persists in the region. Transient solutions of the dynamics in film blowing have been obtained showing close agreement with the experimental results of polymers including LDPE. The instability behavior of the process, draw resonance, has also been portrayed using the FIC-included simulation model of this study, which exhibits better agreement with experiments than the previous model without FIC.

Monday 10:05 Ferrante I-III MP2

Measurement and modeling of flow-enhanced crystallization in bicomponent blown film extrusion

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Multi-layer blown film extrusion is an important industrial process, particularly when one or more of the layers consist of a crystallizable polymer. Inclusion of flow-enhanced crystallization effects in such systems is crucial in understanding the steady-state and dynamic behavior and developing quantitative measures for correlating film properties with processing conditions. We have been modifying our single layer model to account for double layer systems in which one or both components is crystallizable. Model predictions for bubble radius and cystallinity under steady-sate and transient conditions are being compared to data being generated in the test beds at the Center for Advanced Engineering Fibers and Films (CAEFF) at Clemson. The latter involve unique on-line measurements of the layer cystallinity utilizing Raman spectroscopy for polyethylene and polypropylene co-extruded films. An interesting feature with multi-layers is that the higher freezing polymer bears all of the load, whereas the lower Tc polymer solidifies in a partly stress-free state, leading to various morphologies.

Monday 10:25 Ferrante I-III 💿 MP3

Modeling of crystallizing polymer melts in electrospinning

Eduard Zhmayev and Yong L. Joo

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In electrospinning, applied electric field elongates a charged fluid jet to produce nanofibers. Polymer melts can be electrospun nonisothermally in a process, which is more environmentally benign and economically attractive than conventional polymer solution electrospinning. Due to short residence times, high extensional forces, and radially-uniform stress distributions present in this process, electrospinning can provide an attractive framework for the study of flow-induced crystallization.

By incorporating key modifications and simplifications for highly viscous viscoelastic jets with low electrical conductivity, we have developed a nonisothermal thin-filament model for the stable jet region of electrically-driven free-surface viscoelastic flow. The predicted diameter profiles and final diameters for various experimental conditions, such as temperature, flowrate, and applied electric field, agree with experimental results for amorphous polylactic acid melts. This newly developed, nonisothermal model has been extended to the study of crystallization during melt electrospinning. Various approaches for modeling in-flight crystallization kinetics coupled with transport phenomena are presented and compared to experimental results of Nylon-6 melt electrospinning. To account for coupling of the highly elongational flow with crystal morphology evolution, a mesoscale approach based on a lattice model has been developed and preliminary results will also be presented.

Monday 10:45 Ferrante I-III 💿 MP4

Rheological and film-casting properties of well-characterised polyethylenes with different branching structure

Dietmar Auhl[1], Suneel Kunamaneni[1], Christopher W. Seay[2], Christopher D. McGrady[2], Donald G. Baird[2], and Tom C. McLeish[1]

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The aim of our interdisciplinary study is to investigate the complex flow properties of well-characterised branched polyethylenes (PE) in a relevant processing operation like the film-casting process. There is considerable literature dealing with the relationship between rheological flow behaviour and the processing performance of thermoplastic resins. However, not many studies are reported for well-characterised materials and recent molecular constitutive equations. We investigated the influence of branching structure on cast-film properties, e.g. the neck-in and thickness profiles, for a series of well-characterised metallocene (m-PE) and low-density polyethylenes (LD-PE) with various branching levels.

For this study a lab extruder with a matching chill-roll setup has been employed due to the small sample quantities. The materials and flow conditions have been chosen specifically in order to match the shear stresses of polyethylenes with different molecular structures at the die exit. Non-linear flow properties in shear and uniaxial elongation have been determined from constant strain-rate tests and fitted with a multi-mode Pom-Pom model [Inkson et al. *J. Rheol. (1999) 43, 873-896*]. The model parameters are discussed with respect to the molecular analysis of the branching structure determined by size-exclusion chromatography with coupled light-scattering.

The experimental results for the film-flow behaviour are compared to model predictions using the approach of Dobroth and Erwin [T. Dobroth and L. Erwin *Polym. Eng. Sci. (1986) 26, 462-467*] together with the Pom-Pom constitutive equation. Several characteristic quantities for the cast-film dimensions are discussed as a function of branching level and draw ratio.

Monday 11:05 Ferrante I-III MP5

What are universal features in uniaxial extension of entangled polymer melts?

Yangyang Wang and Shi-Qing Wang

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A great number of material processing procedures require basic understanding of extensional deformation and flow behavior of entangled polymer solutions and melts. Recent observations of shear inhomogeneity in entangled polymers [Phys. Rev. Lett. 96, 019001, 169001 (2006); 97, 187801 (2006); Macromol. 40, 8031 (2007); a number of papers to being reviewed by J. Rheol.] suggest that such polymeric liquids are transient solids amenable to cohesive breakdown [J. Chem. Phys. 127, 064903 (2007)]. Lately, we began to ask the question of whether extensional stretching also causes these transient solids to undergo structural failure. Our preliminary investigation indicates that yielding occurs during continuous stretching and after large step strain ["Elastic breakup in uniaxial extension of entangled polymer melts", Phys. Rev. Lett. (2007) volume and page numbers to be updated; manuscript under review by J. Rheol. (2007)]. In the present work, we will examine to what degree the observed elastic yielding is universal by studying the uniaxial extensional deformation of different polymer solutions and melts including thermoplastics such as polystyrene and LDPE and elastomers such as polybutadiene, polyisoprene and SBR, as a function of the degree of chain entanglement and temperature.

IR-1. Interfacial Rheology and Thin Film Flow

Organizers: Jan Vermant and Kausik Sarkar
Session Chairs: Jan Vermant and Kausik Sarkar

Monday 9:45 Bonsai I IR1

Protusion effects of a sphere at an air/water interface

Prajnaparamita Dhar[1], Thomas M. Fischer[2], Vikram Prasad[3], and Eric Weeks[3]
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We study the diffusion of charged beads placed at an interface to probe the protrusion effects due to electrostatic charges on microspheres at an air/water interface. The drag on the sphere immersed in an incompressible viscous monolayer has been calculated numerically where Marangoni forces are shown to contribute significantly to the drag coefficients. The change in the mobility of the sphere with the ionic strength of the solution is analyzed to study the presence or absence of the electrodipping effects. The change in the mobility of a sphere at an interface may be affected by the Marangoni forces, interfacial and bulk viscous effects as well as immersion depth. The mobility of a sphere at an air/water interface is analyzed using the single particle trajectories for a non-viscous interface. Using the numerical results for the single particle theory of the sphere along with the experimental single particle mean square displacement we investigate the effect of electrostatic forces on the protrusion of the sphere. The electrostatic forces on the sphere are altered by varying the electrolyte concentration of the water. Since the surface viscous effects are negligible, and Marangoni effects are maximal, changes in the single particle mean square displacement of the spheres are attributed to the changes in the protrusion. As the electrolyte concentration is changed no effect is observed for large particles while nanoparticles seem to protrude deeper into the water for higher ionic strength. This suggests a size dependence of the beads on the geometric arrangement of the beads at the interface.

Monday 10:05 Bonsai I 💿 IR2

Flow-induced assembly of nickel nanoparticles

Nathan A. Russell, Theodorian Borca-Tasciuc, and Amir H. Hirsa
Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Lead telluride and bismuth telluride exhibit the peak value of about 1 for figure of merit (ZT) of bulk thermoelectric materials; the figure of merit is a measure of efficiency for thermoelectric energy conversion. ZT greater than around 2-3 is necessary for thermoelectric devices to have widespread, practical applications in fields such as regenerative power recovery. Nanoscaled thermoelectric materials have surpassed this criterion, however, the scale-up of these nanostructured materials while maintaining the desired properties has proven to be challenging. Flow-induced assembly of nanoparticles at an air/water interface is a potential candidate to scale-up production of nanostructured thermoelectric materials. Here, we spread nanoparticles on the surface of water using classical techniques developed for Langmuir monolayers. Interfacial shear is produced by an annular Couette flow driven by the constant rotation of an outer cylinder and a stationary inner cylinder. The Reynolds number is large enough to produce strong shearing motion at the interface in order to assemble the particles into a well organized film. These films will subsequently be harvested and stacked accordingly with minimal loss of desired properties. In this paper we investigate flow induced assembly of nickel nanoparticles as a model system.

Monday 10:25 Bonsai I 💿 IR3

Self-assembly and surface rheology of 2D suspension of ellipsoids

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The effect of particle shape in 2D suspensions has been investigated using model polystyrene ellipsoids. Optical video microscopy and interfacial rheology using a combination of surface rheometers were used to understand rheology-structure correlation in these suspensions. Depending on the nature of the interface, ellipsoids of the same surface chemistry give rise to contrasting microstructures at a fluid-fluid interface. The initial structure of a monolayer at a water-decane interface consists of individual particles co-existing with predominantly linear chains, whereas very dense structures were observed at water-air interface. We show that this effect is due to changes in the wetting properties i.e., due to the shift in the three-phase contact line to a position of higher curvature for water-air case. The fundamental building block in these dense networks was a triangle, with three ellipsoids connected at their tips. We show that surface charge, surface coverage and wetting properties can be used effectively to create interfaces with very high surface moduli. These high surface moduli allow for the generation of very stable 'Pickering' emulsions, the stability being controlled by the aspect ratio of the ellipsoids.

Monday 10:45 Bonsai I IR4

Linear and nonlinear interfacial microrheometry

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We describe an interfacial microrheometer that we have developed, and discuss its unique features and advantages. We microfabricate micron-scale ferromagnetic disks, place them on fluid-fluid interfaces, and use external electromagnets to exert torques upon them. By measuring the rotation that results from a known external torque, we compute the rotational drag, from which we deduce the rheological properties of the interface. We describe and demonstrate two modes of operation: linear viscoelastic properties can be measured by exerting small-amplitude oscillatory torques, and non-linear (shear-dependent) viscosities can be measured by measuring steadily-rotating fields. The probe's small size naturally gives rise to large Boussinesq numbers (i.e. high sensitivity to stresses from the interface compared to those from the sub-phases), and the flow field established around the probe involves pure shear without extension. Direct visualization of the probe and interface during measurements enables the measured rheological properties to be directly correlated with the observed microstructural deformations, and 'local' rheologi-

cal measurements to be made in different domains in heterogeneous interfacial systems. We discuss measurements on several interfacial systems: purely viscous interfaces, two-dimensional colloidal suspensions, and model lung surfactant solutions.

Monday 11:05 Bonsai I IR5

Polar fluid model of viscoelastic membranes and interfaces

Alejandro D. Rey
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The polar surface fluid model is used to derive the generalized dynamic shape equation and the interfacial rheological material functions for viscoelastic membranes and curved interfaces, taking viscous bending and torsion modes into full account. The materials modeling approach based on the polar surface fluid leads to the integration of bending and torsion dissipative modes with their elastic counterparts that appear in the dynamic shape equation and in the interfacial rheological functions. The covariant bending and torsion rates derived in this paper are shown to be related to the interfacial co-rotational derivative of the curvature tensor. The dynamic shape equation is used to analyze shape fluctuation in planar geometries, and to establish the role of bending dissipation in shape dynamics. The dynamic shape equation generalizes the static Helfrich shape equation by incorporating bending and torsion dissipation, and it generalizes the dynamic shape equation based on the Boussinesq-Scriven model by incorporating bending and torsion elasticity and dissipation.

Monday 11:25 Bonsai I 💿 IR6

Interfacial shear rheology of coffee samples

Joerg Laeuger and Patrick Heyer
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The aim of the paper is twofold: First, to show that interfacial rheology is a valuable tool to get information on the film formation and therefore the foam stability of coffee, and second, to compare the results obtained by a biconical disc geometry and a Du Nuöy ring. Coffee is a complex dispersion, which for many coffee drinks is topped by a foam structure of tiny bubbles, e.g. the espresso foam - also called espresso cream or "crema". Interfacial rheology does not probe the foam itself, but measures the adsorption of the amphiphilic ingredients and their network formation at the liquid surface. Higher values of the interfacial properties and a faster film formation are expected to correlate with a better foam stability. Measurements on the film formation process and on the interfacial rheological properties of the final film of coffee samples are presented and discussed. Both oscillatory and rotational test have been performed on films with different coffee concentrations. As higher the concentration as faster the film formation process is, whereas the concentration does not have a large effect on the visco-elastic properties of the final films. Different techniques have been used to measure interfacial shear properties. However, a combination of a suitable geometry with a rotational rheometer, which is both extremely sensitive in torque and angular resolution, offers the largest flexibility with respect to the various test possibilities and measuring ranges. Here we would like to focus on two geometries, which have been used in combination with standard types of rotational rheometers. One is the biconical geometry and the other the De Noüy ring. In combination with a rheometer such geometries can be used for performing all kinds of rheological test methods permitted by the rheometer. The presented results show that although with a Du Noüy ring it is possible to measure the qualitative behavior and relative differences only the biconical geometry is sensitive enough to test weak films and to reveal real absolute values for the interfacial shear rheological quantities

SC-1. Particle Level Simulation and Theory I

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Roger T. Bonnecaze and Eric Shaqfeh

Monday 9:45 De Anza III SC1

Microstruture and rheology in sheared suspensions of anisotropic dicolloids

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Large scale simulations are presented for concentrated suspensions of anisotropic dicolloids. The particles under study consist of composite particles formed from two intersecting spheres of arbitrary radii and center-center spacing. Recent experimental efforts have reported synthesis techniques for such anisotropic dicolloids with sizes ranging from 250 nanometers to several microns. Experiments have suggested a range of interesting phase behavior with order-disorder-order transitions as a function of Pe and volume fraction. In the present study, we use high precision Stokesian dynamic simulations and reduced precision near field lubrication models to study the dynamics of sheared suspensions of these anisotropic particles as a function of volume fraction, interparticle forces and Peclet number. We capture the order-disorder-order transitions reported in experiments and investigate systems with a high degree of positional order and varying degrees of orientational ordering. We show how the degree of particle anisotropy affects the degree and alignment of orientational order relative to the shear, gradient and vorticity axes. We show how the changes in microstructural ordering are related to shear thinning, shear thickening and changes in the normal stress.

Monday 10:05 De Anza III SC2

Transient forces in particle based simulations of complex fluids

Wim J. Briels
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In many examples of soft matter liquids a detailed description of the individual particles making up the liquid requires keeping track of prohibitively many degrees of freedom. Examples are synthetic resins consisting of a hard core onto which a thick corona is grafted, many-arm star polymers, but also high molecular weight linear polymers. In order to perform simulations of flow of such liquids in complex geometries a minimum number of degrees of freedom per particle must be used. A possible strategy in this situation is to associate with each particle the position vector of its centre of mass, and to envisage the remaining degrees of freedom as constituting a thermodynamic bath within which the particles move. Since disturbances in the bath caused by displacements of the particles relax on the same time scale as the displacements themselves, a Brownian dynamics propagator with delta-correlated stochastic forces is not appropriate. In order to circumvent the use of frictions and stochastic forces with spatial and temporal memory, we suggest to keep track of the thermodynamic state of the bath by introducing an additional set of variables, one for each pair of particles within a prescribed distance from each other. Deviations of these variables from their equilibrium values, depending on the configuration of the centres of mass, give rise to transient forces in addition to the, usually very soft, potentials of mean force governing the systems thermodynamic and structural proerties. The model will be applied to simulate rheological properties of synthetic resins, star polymers and linear polymers. Besides this imulations of shear banding will be presented.

Monday 10:25 De Anza III SC3

Dynamical heterogeneities in attractive colloids

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Dynamical heterogeneities in glasses are explained in terms of the correlated motion of particles, but their possible connections to any structural feature are still unclear. We study dynamical heterogeneities in colloidal gelation, where a complex slowing down of the dynamics, directly related to the formation of persistent structures, is observed at different volume fractions.

By means of Molecular Dynamics simulations of a model colloidal suspension, we have been able to show that, at low volume fractions, the dynamical heterogeneities are in fact dominated by the clusters of long living bonds[1]. This feature is rather similar to the one observed in irreversible gelation, where the presence of dynamical heterogeneities can be explicitly related to the growing mean cluster size [2]. At higher volume fraction, instead, where crowding of the particles starts to be relevant, dynamical heterogeneities show the typical pattern observed in glassy systems. Interestingly, such behavior can be here well described in terms of a suitable, time-dependent mean cluster size [1].

[1] A. Fierro, E. Del Gado, A. de Candia and A. Coniglio, cond-mat/0707.4071; [2] T. Abete, A. de Candia, E. Del Gado, A.Fierro and A. Coniglio, Phys. Rev. Lett. 98, 088301 (2007).

Monday 10:45 De Anza III SC4

Numerical simulations of suspensions of elastic particles in polymer melts

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Elastic particles are often added to polymer melts as impact modifiers. Unlike rigid fillers, elastic particles can deform during flow and so modify the rheology of the polymer melt. To study the rheology of such multiphase systems we perform direct simulations of the motion of the elastic particles in a viscoelastic matrix under simple shear or extensional flow. We solve the flow in a unit cell containing a small number of particles with doubly periodic boundary conditions on a self-replicating lattice to replicate a suspension on an infinite domain. In shear flow our method is equivalent to the Lees-Edwards boundary condition, while in extension we use the Kraynik-Reinelt cell structure that provides a self-replicating lattice for planar extension. This allows simulations to be carried out to arbitrarily large strains. The continuous phase is modelled using the tube based pom-pom model and Roliepoly models for branched and linear polymers respectively. In nonlinear shear flow, isotropic filler particles deform into ellipses. However, unlike rigid elliptical particles which rotate during shear flow, elastic particles perform a “tank-treading” motion in which the surface of the particle rotates, but bounding shape remains fixed. The shear viscosity is found to be lower than for a polymer filled with rigid particles, however, there is now a phase lag due to the particle elasticity. We will also show comparisons for extensional flows where the filled particles become stretched in the direction of extension.

Monday 11:05 De Anza III SC5

Molecular hydrodynamics in nanoparticle suspensions

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Quantitative characterization of flow behavior at the molecular scale necessitates accounting for the detailed molecular interactions in the system. In this work, we have used molecular dynamics (MD) simulations to study the detailed molecular hydrodynamics in suspensions of nanoparticles in molecular solvents as well as polymer melts. Diffusion and hydrodynamics are fully governed by the intermolecular interactions in such model systems.

In our previous work, MD simulation of a nanoparticle translating near a solid surface showed that the simulation results for friction force on the particle are in qualitative agreement with continuum mechanics predictions. In that work, the quantitative differences between simulation results and continuum theory were explained by the occurrence of the velocity slip at the nanoparticle surface and the interplay between molecular level structure formation and hydrodynamics. A simple, idealized model of the nanoparticle characterized by a smooth external surface and absence of any internal structure was considered in that study. In the current work, a more realistic model of the nanoparticle is considered. The nanoparticle is thus composed of a number of smaller atoms (the same size as the solvent atoms) that are bonded to each other. Such a model allows for the external surface roughness and also enables calculation of the torque on the particle, in addition to the friction force. MD simulations are used to study the translation of this model nanoparticle near a solid surface. The friction force and torque experienced by the nanoparticle in a monomeric solvent are compared with continuum mechanics results and deviations are explained using the coupling between molecular thermodynamics and hydrodynamics. Furthermore, effects of multiparticle interactions are also captured by studying hydrodynamics in concentrated suspensions of nanoparticles. In addition, simulations are also carried out for a system consisting of a nanoparticle that is translating through a polymer melt. The similarities and differences in the particle motion in a simple molecular solvent and a polymeric solvent will be discussed in detail.

Monday 11:25 De Anza III SC6

Rotation of a sphere in viscoelastic fluid under flow

Frank Snijkers[1], Gaetano D'avino[2], Pier-Luca Maffettone[2], Francesco Greco[3], Martien A. Hulsen[4], and Jan Vermant[5]

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The rheological properties of suspensions depend, to a large extent, on the relative motions of the particles and on the subsequent hydrodynamic interactions. Whereas the motion of particles in Newtonian fluids under flow is well understood [e.g. 1], this is not the case for particles in viscoelastic fluids. The rotation speed in the bulk of a Newtonian fluid, in absence of inertia and gravitational effects, is equal to half the shear rate [2]. The situation is less clear for the case of a non-Brownian sphere suspended in a viscoelastic medium during shear flow. Only a few numerical studies [3-5] and two experimental studies exist [6,7]. These authors suggest that the particle rotation slows down compared to the Newtonian case, although a clean quantification of the effect and an elucidation of the role of viscoelasticity are missing. In the present work, we will measure the rotation speed of a single, non-Brownian sphere in shear flow in different, well-characterized, viscoelastic fluids (a Boger Fluid, a single relaxation time surfactant solution, an optically matched shear thinning suspension and a shear thinning viscoelastic polymer solution). A counterrotating rheometer equipped with parallel plates and videomicroscopy are used to measure the rotation speeds over a wide range of shear rates. The particle size and the physical properties of the particles are varied to rule out experimental artifacts. We will compare the experimental results with numerical 3D FEM simulations for selected constitutive models. The effect of medium rheology on rotation speed and streamlines will be discussed with its implications on structure formation [8] and the rheological properties of suspensions in viscoelastic liquids.

[1] HL Goldsmith, SG Mason, in Rheology: Theory and applications vol 4, ed. FR Eirich, Academic Press, New York and London, 85-250, 1967; [2] BJ Trevelyan, SG Mason, J. Coll. Sci., 6, 354-367, 1951; [3] WR Hwang, et al. J. Non-Newt. Fluid Mech., 121, 15-33, 2004; [4] NA Patankar, HH Hu, J. Non-Newt. Fluid Mech., 96, 427-443, 2001; [5] F Greco, et al., Phys. Rev. Lett., 95, 246001 1-4, 2005 and Erratum, 98, 109904-1, 2007; [6] F Gauthier,et al. Rheol. Acta, 10, 344-364, 1971; [7] M Astruc, et al., Rheol. Acta, 42, 421-431, 2003; [8] R Scirrocco et al.,J. Non-Newt. Fluid Mech., 117, 183-192 (2004).

GR-1. General Rheology

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Robert K. Pru'homme

Monday 9:45 Bonzai III GR1

On the use of Laplace transform inversion for reconstruction of relaxation spectra

Michael Renardy

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We discuss the use of Fourier transforms to construct approximate inversion formulae for the Laplace transform and apply this technique to recover the relaxation spectrum from ``data" for the relaxation modulus. We show that regularization by a Gaussian, as proposed by Davies and Anderssen yields reasonable results even for data with significant noise. We also show that, in principle, other choices of regularization allow the relaxation spectrum to be reconstructed from data which are taken in any interval of time or frequency, however short and wherever located. We construct formulae which would do this, based on polynomial approximation of a function in an exponentially weighted space. This algorithm, however, turns out not to be practical, and we elucidate the reasons for that.

Monday 10:05 Bonzai III GR2

Constitutive equation for polymer networks with phonon fluctuations

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Recent research [X.Xing et al. Phys.Rev.Lett 98, 075502, (2007)] has provided an expression for the Helmholtz free energy related to phonon fluctuations in polymer networks. This expression is used to develop a general nonlinear constitutive equation. From the constitutive equation one can calculate stress-strain curves in entirely general deformation fields. Constitutive equations for the Sliplink Model and the Tube Model are derived and stress-strain curves are calculated and compared with each other and data from Xu and Mark [Rubber Chem. Technol. 63, 276 (1990)] and Wang and Mark [J.Polym.Sci.B 30, 801 (1992)]. Elastic moduli are derived for the considered models and compared to moduli determined from the network characteristics.

Monday 10:25 Bonzai III GR3

A new approach to determine the nonlinear parameter of the Giesekus constitutive model

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Some of the latest investigations of weakly viscoelastic solutions in complex flow geometries put in evidence the capabilities of the differential Giesekus model to properly reproduce the experimental flow spectrum. One major difficulty in using the Giesekus model is the determination of the material constant α_i, the so-called "mobility" parameter (which is responsible for the non-linearity of the model). Usually, the parameter α_i is obtained by fitting the shear viscosity function and dynamic moduli, and only in few cases from pure extensional tests. In the present paper the authors propose a novel technique to compute α_i, based on the decomposition of the oscillatory data and using the Fourier transform analysis. We use large amplitude oscillatory shear for generating the nonlinear response, which is then analyzed via Fourier transform for isolating the nonlinear effects. In the frequency domain, the intensity of the third harmonic is altered by the relaxation time (spectrum) and the nonlinear parameter (or parameters, in the case of multimode models). When the relaxation time is fixed, we can determine the α_i parameter that provides the same nonlinear results. We believe that this method is more appropriate for a realistic value of the nonlinear parameter. The numerical technique is applied to the rheological modeling of aqueous polyacrylamide solutions. We also aim to establish the dependence of the α_i parameter on the polymer concentration.

Monday 10:45 Bonzai III GR4

Energy elastic effects in flowing polymeric liquids and the concept of nonequilibrium temperature

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Entropy elasticity of rubbers serves as a starting point for most of the current models to describe the flow of polymeric liquids with an internal conformation tensor, while consideration of energetic effects is scarce. Such exclusive subscription to entropy elasticity can be considered a little surprising, in particular in view of microscopic modeling where potential forces between (united) atoms play a dominant role. In this regard, it is interesting to discuss the possible ramifications of energy elasticity on the flow behavior of polymeric liquids. After discussing previous approaches in literature for capturing energy elastic effects, we develop a thermodynamically consistent model in terms of the momentum density, the local entropy density, the mass density, and the conformation tensor as dynamic variables. The choice of the local entropy as a variable in contrast to temperature or total entropy is of primary importance, as will be explained in due detail. Specifically, we avoid working with a temperature concept that is ill-defined in flow. In order to render the conclusions of the model more specific, a microscopically motivated toy model with energetic effects is introduced, for which both the coarse-grained energy and entropy are calculated in a generalized canonical ensemble.

Monday 11:05 Bonzai III GR5

A new closure approximation for the fourth moment of a representative microstructure vector and its consequence on partially extending strand convection models

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The partially extending strand convection model of Larson (1984) is analyzed from the framework perspective constructed by Pasquali and Scriven (2004) and some of the drawbacks are pointed. A decomposition theorem presented by Thompson (2007) is used to provide a new closure approximation for the fourth moment of a representative microelement vector and find modified versions, which are more physically consistent, of models that use the same classical closure approximation. The new class of models for the evolution equation of the second order conformation tensor is presented with the same framework (Pasquali and Scriven (2004)). The concept of the natural convected time derivative (Thompson (2007)) is used in order to split the general evolution equation into two parts: a stretching-evolution equation and a rotation-evolution one. This new formulation gives an alternative simulation algorithm that can be coupled with the matrix-logarithm approach presented by Fattal and Kupferman (2004).

Monday 11:25 Bonzai III GR6

Polymer rheology and the hdrodynamic theory of transient elasticity

Harald Pleiner[1], Oliver Mueller[2], Mario Liu[3], and Helmut R. Brand[4]
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A simple model based on ``transient elasticity" is proposed, solved analytically, and shown to account for a broad range of polymers' non-Newtonian behavior -- including shear thinning, elongational hardening, rod-climbing, the Cox-Merz and First Gleissle Mirror Rule. This suggests *transient* elasticity is not merely an aspect of polymer rheology, but rather its underlying physics.Although undoubtedly complex and non-Newtonian, the flow properties of superfluids and nematic liquid crystals are taken to be well understood in their essence. This is different for the rheology of polymer solutions or melts, widely considered less transparent by physicists. A probable main reason is, the first two systems have a concise characterization, a *defining physics* that the third lacks: Taking superfluid He4 as an isotropic fluid breaking the phase symmetry spontaneously, and nematic liquid crystals as uniaxial fluids breaking rotational symmetries are each a concise macroscopic characterization of these two systems. It fixes the additional thermodynamic variables and uniquely determines the structure of the associated hydrodynamic theory – including especially the explicit form of the stress tensor – yielding a complete account of their macroscopic behavior. The prevalent understanding of polymers lacks such a single defining physics, and is based mainly on a collection of experimental observations, chosen for their ``non-Newtonian-ness," or the distance from how water is known to behave. In addition to linear visco-elasticity, the more prominent ones are: Shear-thinning, elongational hardening, or rod climbing or the Weissenberg effect. Water, in contrast, is purely viscous, sports a viscosity that is shear-independent for both geometries, and dips slightly around the shaft. There are many textbook models, ranging from Maxwell, Jeffrey, Oldroyd to the intricate KBKZ, that are designed by skillfully combining fluiddynamic insights, elasticity theory and the frame-indifference principle, to account for these effects. Starting all from momentum conservation, they typically provide a constitutive relation that specifies an objective time derivative of the stress tensor as a function of the stress istelf and the flow. Although no model is all-embracing, or generally accepted as authoritative, the more sophisticated ones are well capable of quantitatively accounting for many experiments. This paper does not attempt to tailor yet another constitutive relation, to further improve the fit with select experiments. Rather, it suggests to consider visco-elasticity – more precisely transient elasticity – as the single defining physics for polymers. In addition, the associated hydrodynamic theory – including explicit expressions for the stress tensor and the conserved energy (or equivalently, for the free energy) – then provides the proper frame work, within which a realistic and complete theory of polymer rheology may be found.

CF-1. Flow Instabilities I

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Matteo Pasquali

Monday 9:45 Steinbeck CF1

Field measurement techniques applied to rheometry of secondary flows of LDPE and correlation to viscoelastic models

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In this study, the secondary flow of a low-density polyethylene melt was investigated in the entrance region of a flow channel by means of field measurement techniques: Laser Doppler Velocimetry (LDV) and Flow Induced Birefringence (FIB). The flow channel used was a transparent slit die with a planar contraction of 14:1. LDV measurements give access to the local planar velocity field, whereas FIB measures the cumulated phase retardation of the transverse transmitted light. Center plane velocity field analysis showed that it exists a boundary which divides the flow in a shear dominant flow within the vortex and an elongational flow outside the vortex. It was shown, as previously observed with LDV for long-chain branched polyethylenes [1], that the centre plane vortex size A is strongly influenced by both temperature T and flow rate Q. Moreover, it was found that the vortex size as a function of T (resp. Q) runs through a maximum when Q (resp. T) is kept constant. The same dependence with T and Q was also observed for the FIB patterns, in which one can identify a boundary line which exhibits a strong contrast of the birefringence pattern. This contrast could be related to the fact that molecular conformations (and consequently the birefringence pattern) change locally due to a different thermomechanical history, which indeed would occur closely to the vortex boundary. The vortex size dependence on T an Q was correlated to the relative magnitude of shear thinning and strain hardening phenomena in such complex flows, as suggested by Schwetz et al. [1]. This analysis was done by performing an inverse analysis on non-linear parameters of pom-pom like constitutive equations by using LDV and FIB fields to build a suitable cost function. As this study implies that the flow characteristics are invariant in the transverse direction, 3D flow analyses were performed in order to quantify this assumption: - 3D LDV measurements, by measuring several velocity fields at different transverse positions, - 3D finite elements computations [2] for the set of pompom parameters found in the previous inverse method. These analyses showed that this assumption was quite acceptable, as already shown in [3].

[1] Schwetz, M., H. Münstedt, M. Heindl, A. Merten, J. Rheol. 46 (4), 797-815 (2002); [2] Silva L., Valette R., Coupez T., J. Non-Newt. Fluid Mech., submitted; [3] Clemeur N., Rutgers R.P.G., Debbaut B., J. Non-Newt. Fluid Mech., 123 (2-3), 105-120 (2004).

Monday 10:05 Steinbeck CF2

Suppression of interfacial and free-surface instabilities in the flow of polymeric liquid layers

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Multilayer and free-surface flows of Newtonian and polymeric (viscoelastic) liquids are well-known to be prone to interfacial instabilities caused by viscosity and elasticity contrasts between the different layers. Such instabilities during melt processing often have an adverse impact on the quality (e.g. mechanical and/or optical properties) of the final product, and a clear knowledge of when this instability occurs and how it can be controlled is critical in the design of these operations. In this work, we use analytical and computational tools to evaluate the feasibility of using soft solid coatings to suppress interfacial instabilities in Newtonian and viscoelastic liquids. We model the liquids using upper-convected Maxwell (UCM) and FENE-P constitutive relations, while the solid layer is modeled using linear elastic and neo-Hookean models. We show using long-wave asymptotic analyses and numerical solutions that under appropriate conditions (viscosity ratios, relaxation times) the interfacial instability in two-layer and free-surface flows can be completely suppressed at all wavelengths when the solid layer is made sufficiently deformable. We also show that under other parametric conditions where the interfacial mode is stable in rigid channels, the soft solid layer could destabilize the interfacial mode. The nature of suppression by the soft solid layer is shown to be quite generic and is independent of the constitutive nature of the liquid and the type of flow (plane Couette/pressure-driven or free-surface flows). Thus, the present study shows that soft solid layer coatings could potentially provide a passive method for the suppression of interfacial instabilities in multilayer flows of polymeric liquids.

Monday 10:25 Steinbeck CF3

Experimental and computational identification of a polymer melt flow instability

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Entangled polymer melts exhibit a variety of flow instabilities that limit production rates in industrial applications. We study one such flow instability, in a contraction-expansion geometry, through both experiment and numerical calculation. The experiments investigate the flow of monodisperse linear polystyrenes in a multi-pass rheometer, and we present observations of the instability referred to as “gross melt fracture” or “volume defects” in the literature, which is first observed at the slit outlet and subsequently produces large-scale fluid motions upstream. The numerical study uses linear stability theory with a semi-staggered finite-volume scheme, and models the fluid using the *Rolie-Poly* constitutive equation. The numerical results confirm the instability and we are able to identify important parameters for instability within the model. This gives a physical insight into the underlying mechanisms involved.

Monday 10:45 Steinbeck CF4

Co-extrusion instabilities modelled with a single fluid

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Industrial processes involving co-extrusion of multiple fluids to produce multi-layered products are rife with instabilities. We consider a simple indicative instance of co-extrusion, in which there is only a single fluid involved in the flow, but two different channel branches impose differing flow histories on it. The channels merge and, ideally, a smooth film is extruded with two layers having different stress histories.

In our experimental work, the film is visualised outside the die, looking through the thin film. A wavelike instability is observed with a well-defined wavelength in the flow direction and a "zig-zag" like structure, indicating that the extra flow caused by the instability is three-dimensional.

Suggested mechanisms for the instabilities seen in coextrusion include a jump in viscosity and/or first normal stress difference across a flat interface, and a coupling of normal stresses with streamline curvature in the region where the two streams merge. Using a numerical linear stability tool, we will investigate this instability (using a single fluid model throughout) and shed light on which of the known mechanisms is the most likely culprit here.

Monday 11:05 Steinbeck CF5

Numerical studies of axial instability in contraction flow

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It is known that the instabilities in axisymmetric contraction flows of polymers start with development of axisymmetric, non-rotational disturbances. Our studies of this instability are based on the extension of previous approximate theory of steady contraction flow [1]. This theory matches at the die entrance a "jet-like" viscoelastic flow in reservoir with developing viscoelastic shearing flow in the die. A set of PDE's for mass and momentum conservation, along with a viscoelastic constitutive equation and appropriate initial/boundary conditions was numerically analyzed employing finite difference method. The instability which occurs in the reservoir jet-like flow, reminds a draw resonance in melt spinning. Then unstable fluctuations formed in the reservoir propagate into capillary with their axial decaying. Linear and non-linear stability analyses have been performed to describe the fluctuations in the whole region of contraction flow up to the die exit. In this problem, a critical Deborah number established for onset of instability strongly depends on contraction ratio. The results of these numerical studies have been compared with existing experimental data.

[1] Jeong, J. and Leonov, A.I., A Quasi-1D Model for Fast Contraction Flows of Polymer Melts, 2004, J. Non-Newtonian Fluid Mech., 118, 157-173.

Monday 11:25 Steinbeck CF6

On extensibility effects in the cross-slot flow bifurcation

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The flow of finite extensibility models in a two-dimensional planar cross-slot configuration is studied numerically, using a finite-volume method, with a view to quantify the influences of the level of extensibility, concentration parameter, and sharpness of corners, on the occurrence of a bifurcated flow pattern. This work extends previous studies [1,2], in which the viscoelastic flow of upper convected Maxwell and Oldroyd-B fluids in a cross-slot was shown to undergo through a supercritical instability at a critical value of Deborah number, by providing further numerical data with controlled accuracy mapping the effects of the parameter in FENE-CR and FENE-P models, for a channel-intersecting geometry having both sharp, slightly and markedly rounded corners. The results show the phenomena to be largely controlled by the elongational properties of the constitutive model, with the critical Deborah number for bifurcation tending to be reduced as extensibility increases, and the sharpness or otherwise of the corners to have only a marginal influence on the triggering mechanism leading to the pitchfork bifurcation, which seems essentially to be restricted to the central, stagnation point region.

[1] R.J. Poole, M.A. Alves, P.J. Oliveira, Purely elastic flow asymmetries, Phy. Rev. Let. 99 (2007)164503; [2] R.J. Poole, M.A. Alves, A.A. Afonso, F.T. Pinho, P.J. Oliveira, A new viscoelastic benchmark flow: bifurcation in a cross slot, J. Non-Newt. Fluid Mech. (2007) (submitted).

MF-1. Microfluidics with Polymers

Organizers: Todd M. Squires and Annie Colin
Session Chairs: Susan Muller and Satish Kumar

Monday 9:45 Portola MF1

Nanofluidic t-junctions for single molecule DNA mapping

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Controlled trapping and stretching of DNA molecules is critical for single molecule genomic and polymer physics studies. To date, most devices are based on hydrodynamic stretching of DNA. In contrast, we exploit the fact that DNA is a homogeneously charged polyelectrolyte and so will migrate in an electric field. Here we present T-junction and cross-slot devices which can trap and stretch DNA using electric field gradients. The devices do not require special end-functionalization of the DNA. The purely elongational nature of the electric field allows us to use thin nanofluidic channels. We show that two physical mechanisms of stretching can occur depending on the length of the DNA relative to the channel width in the junction region. In one case the governing dimensionless group is a Deborah number and in the other a Peclet number. Stable trapping and stretching of DNA molecules up to lengths of 485 kilobasepairs is demonstrated. Applications in single molecule mapping will also be demonstrated.

Monday 10:05 Portola MF2

Use of stagnation point flows for DNA trapping, manipulation, and target sequence detection

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We have developed a method amenable to manipulation of single molecules of double-stranded genomic DNA for detection of specific sequences along the DNA backbone. Fluorescent polystyrene beads are surface-functionalized with site-specific probes and incubated with fluorescently labeled double-stranded lambda-DNA. The solution is introduced into a microfluidic cross slot where the tagged DNA molecules are trapped and elongated at the stagnation point of the planar extensional flow. The degree of elongation can be controlled using the flow strength in the device, as demonstrated by Perkins, Smith, and Chu (Science 1997). Beads bound along the stretched DNA may be directly observed, and their locations along the backbone determined, using fluorescence microscopy. Previously, we have demonstrated the feasibility of this method for detection of specific sequences, for single-molecule kinetic and binding studies, as well as for single-molecule sorting (R. Dylla-Spears, L.L. Sohn, and S.J. Muller, AIChE Annual Meeting, Salt Lake City, November 2007). We have now begun to investigate single-molecule binding statistics and how these vary with flow strength.

Monday 10:25 Portola MF3

Elongation deformation of DNA polymers in micro flow

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Deformation behaviors of DNA polymer in the micro flow field have been directly observed utilizing a fluorescence microscope. Length of the individual DNA was measured under the flow. We found that the DNA polymers were extended by elongational flow but the length of DNA had broad distribution. In order to clarify the cause of the broad distribution, we have observed the detailed deformation behavior of DNA polymers under the flow and it was clarified that there were some patterns in the form of molecules. Moreover, to clarify rheological properties of a concentrated polymer solution with entanglement of polymers, deformation behavior of the individual molecule is considered. Aqueous solutions were prepared by mixing unstained DNA solution with fluorescently-stained DNA as model system of the concentrated polymer solutions. It was considered about relation to the deformation behavior of individual molecule which observed in the solution with entanglement structures and the rheological properties measured by mechanical and optical technique.

Monday 10:45 Portola MF4

Conformation and diffusion of a single polyelectrolyte chain in confined spaces of nano/microchannels: Simulation and experiment

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Understanding the behavior of a confined polyelectrolyte has direct relevance in design and manipulation of micro/nanofluidic devices, as well as transport in a biological system [1]. Brownian dynamics simulations with the models in bulk solutions and under confinement in a slit channel between two plates revealed an interesting crossover behavior from the 3D chain to a 2D one. A coarse-grained modeling is based on the FENE spring of Warner with long-range electrostatic and Rotne-Prager hydrodynamic interactions between pairs of beads [2]. We also consider steric and electrostatic interactions between the bead and the confining walls of different charge condition. Relevant model parameters are determined from previous rheology data on the anionic xanthan [3]. Both flexible and semiflexible models are developed accompanying zero and finite intrinsic persistence lengths, and then conformational changes of the chain induced by confinements and their dependence on the screening effect are characterized. Depending on the intrinsic rigidity and the medium ionic strength, the polyelectrolyte can be classified as flexible, semiflexible, or rigid. Confined flexible and semiflexible chains exhibit a non-monotonic variation in size, as measured by the radius of gyration and end-to-end distance, with changing slit width. The rigid chain does not have minima but exhibits a sigmoidal transition. The size of confined semiflexible and rigid polyelectrolytes can be well described by the wormlike chain model once the electrostatic effects are taken into account by the persistence length measured at long length scale [4].

For experimental verifications, single molecule visualization is performed on fluorescently labeled xanthan using an inverted epi-fluorescence microscope equipped with high-resolution CCD camera. Both the conformation and diffusivity of single xanthan molecules are characterized with variations of the chain confinement, wall charge, and solution environments. Applying the MEMS process, we prepared a suitable microchamber for the bulk space, and the polydimethylsiloxane (PDMS)-glass channels were fabricated with the widths ranging 0.2-20 micrometer for the confined system. The center-of-mass displacement is determined as a function of the time elapsed between images, where the radius of gyration can be estimated. The diffusivity calculated for each individual molecule is an ensemble property of many displacements and lag-times in each Brownian trajectory [5]. Finally, we will present the scaling predictions to describe the source of the observed free-draining diffusion dynamics.

[1] Y.-L. Chen, M.D. Graham, J.J. de Pablo, G.C. Randall. M. Gupta, P.S. Doyle, Phys. Rev. E 70, 060901R, 2004; [2] J. Rotne, S. Prager, J. Chem. Phys. 50, 4831, 1969; [3] M.-S. Chun, O.O. Park, Macromol. Chem. Phys. 195, 701, 1994; [4] J. Jeon, M.-S. Chun, J. Chem. Phys. 126, 154904, 2007; [5] B. Maier, O. Radler, Phys. Rev. Letts. 82, 1911, 1999.

Monday 11:05 Portola MF5

Polyelectrolyte adsorption in shear flow with hydrodynamic interaction: Kinetic theory and Brownian dynamics simulations

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The effect of hydrodynamic interaction on the adsorption of a polyelectrolyte molecule onto a wall in shear flow is investigated using kinetic theory and Brownian dynamics simulations. A bead-spring dumbbell model is used in the kinetic theory, while both bead-rod and bead-spring chains are investigated in the Brownian dynamics simulations. In the kinetic theory, bead-bead and bead-wall electrostatic interactions are taken into account using screened Coulombic interactions, and hydrodynamic interaction is incorporated using the approach proposed by Ma and Graham [Phys. Fluids. 17, 083103 (2005)]. An analytical expression for the concentration profile of the polyelectrolyte is derived which predicts a competition between bead-wall hydrodynamic interaction and bead-wall electrostatic attraction. The behavior of the concentration profile is explored as a function of the Weissenberg number, surface (wall) charge density, charge on the beads, and screening length. The charge on the beads assists migration of the dumbbell away from an uncharged wall, whereas for an oppositely charged wall it increases the probability of finding the dumbbell close to the wall. In some cases, the concentration profile shows a very sharp peak near the wall whose distance from the wall increases with dumbbell size, indicating the possibility of size-based separation. The results of the Brownian dynamics simulations are consistent with the kinetic theory, and are used with the kinetic theory to develop a criterion for the critical shear rate needed to desorb an adsorbed polyelectrolyte molecule. The simulations are also used to explore the effects of non-electrostatic interactions, and yield results in qualitative agreement with experimental observations. The results of this work are expected to be of interest for applications related to microfluidics, materials science, and biophysics.

Monday 11:25 Portola MF6

Bending dynamics of individual single-walled carbon nanotubes

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Understanding the dynamics of single-walled carbon nanotube (SWNTs) motion is crucial for establishing potential applications of nanotube architectures for material and biological sciences. Here we present analysis of the bending dynamics of individual SWNTs in water at thermal equilibrium. Intrinsic SWNT near-infrared emission is used to visualize motions of semiconducting carbon nanotubes and deduce their diameter. The variance of the curvature fluctuations induced by Brownian motion is analyzed to obtain the persistence length (or bending rigidity); we find that the persistence length ranges between ~20 and ~100 micrometers and that it scales with the cube of the SWNT diameter, as expected for a hollow pipe. Additionally, the relaxation times of the slowest bending modes are measured through the autocorrelation of the SWNT shape. The measured relaxation times agree excellently with those predicted for a semiflexible chain. These findings indicate that SWNTs are ideal model semiflexible objects.

EM-1. Free Surface Rheometry

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: Gareth McKinley

Monday 9:45 De Anza I EM1

Linear viscoelastic rheology and extensional flow behaviour of low viscosity viscoelastic polymer solutions and inkjet fluids

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Experimental protocols to explore the viscoelastic properties of low viscosity fluids have been developed and tested on model polymer solutions and inkjet fluids. In order to measure the linear viscoelastic response of dilute solutions, a Piezoelectric Axial Vibrator system (developed by Prof. Pechhold at university of Ulm, Germany) has been used to probe elastic (G') and viscous (G") modulus in the frequency range 1-10 kHz. The data provided reliable information for short time scale relaxation behaviour for polymer solutions and also inkjet fluids.

Extensional and non-linear behaviour for the fluids have been probed using a new in-house built filament stretch apparatus that is capable of operating at filament stretch speeds in excess of 1 m/s. Using high-speed camera, it was possible to establish differences in the extensional behaviour for a range of the test fluids.

Both experimental protocols demonstrate the viability of obtaining reliable viscoelastic measurements for fluids where the base viscosity is close to that of water. Using these techniques, it is for example possible to differentiate between apparently identical inks that have the same shear viscosities, but show different jetting behaviour during printing. The results have been compared and validated with those obtained from real inkjet printer heads.

Monday 10:05 De Anza I EM2

Formation and pinch-off of viscoelastic filaments: Numerical analysis and ink jet experiments

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Several modern printing and patterning applications involve the production of drops of complex viscoelastic liquids, e.g., micro-arraying of genomes, printing of biological cells, and fabrication of flexible electronics. Ink jet printing, aside from its conventional use, is being applied as

the preferred dispensing mechanism in many of these emerging applications (de Gans et al. 2004). A clear understanding of the formation and pinch-off of viscoelastic filaments into drops is critical in the analysis and better design of these processes. In addition, the dynamics in the region close to where pinch-off occurs is known typically to exhibit behaviors rich in physics such as universality and self-similarity (Eggers 1993). Most studies to date have used the 1-D slender filament approximation to probe the self-similar dynamics of thinning viscoelastic filaments. This approximation is clearly invalid in regions where slenderness is lost. Here, we present a full 2-D numerical analysis of the problem in which viscoelasticity is captured using the conformation tensor formalism (Pasquali and Scriven 2002) and the governing equations are solved using a fully-coupled finite element method that has been well benchmarked against experiments (Chen, Notz, and Basaran 2001, 2002). The dynamics of thinning viscoelastic filaments in the low capillary number regime is also studied. The results from this study are valuable in assessing experiments that are based on the filament breakup of low viscosity, water-like liquids (e.g., the filament stretching rheometer (FSR) and the capillary breakup extensional rheometer (CaBER)). Experimentally, formation of drops of polymeric materials is studied using the drop-on-demand (DOD) ink jet dispensers at room and elevated temperatures and the potential of the DOD technology in applications such as deposition of drugs on different substrates is explored.

Monday 10:25 De Anza I EM3

Measurement of rheological properties under high shear rate induced by collision of microdroplets

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A new experimental setup of generating a microdroplet was invented. Using the nozzle made of glasses, which is the only part of contacting region to sample liquids, we generate a droplet of any liquid. This technique can be applied to the manipulation system for various fields and the measurement of fluid properties. The Macroscopic behavior of a microdroplet with approximate radius of 10 µm is determined by the surface tension and the viscosity rather than the gravity and inertia. Since the shape of a droplet shot into the air is almost sphere, its oscillation is easy to analyze. The characteristic time scale of the droplet's behavior is in the order of a few microseconds, within which we can observe the dynamic properties. The initial velocity of a droplet is adjustable from 1 m/s to 10 m/s. If the fastest droplets collide head-on, the induced shear rate in the coalescing fluid is approximately 10^6 s^{-1}. Note here, the obtained microscope images at a certain moment coincide even for such fast phenomenon because it is not involved in the turbulent flow. In fact, our system has the Reynolds number as small as 100 under the highest shear rate. Though the collision process causes very high shear rate, its dynamics was described by the static values of surface tension or viscosity. Numerical calculations also were performed based on the Navie-Stokes equation and the results were in very good agreement with the observed images, suggesting a reliable measurement of the fluid properties from the collision dynamics. We have another interest in the orientational dynamics in the microdroplet of liquid crystal. The molecular orientation of a particular direction should be strongly induced by the high shear on the collision process. From the observation in crossed polars, the instant luminousness was discovered even in the droplets of isotropic phase.

Monday 10:45 De Anza I EM4

Pulse jets, rims, and elastic-liquid sheets: Rheology of high strain rates and rupture criteria

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Collisions of pulse jets of viscous and elastoviscous liquids with small conical/disk target were studied experimentally. The tested liquids were Newtonian silicone oils of the shear viscosities from 0.005 up to 10 Pa*s, aqueous solutions of polyethylene oxide (PEO) of molecular mass 0.5-5M at concentrations 5-100 ‰ , and 38 ‰ solution of polysterene-butyl metha-acrylate (PSBMA) in tri-butyl phosphate (TBP). The jet impact velocity was 10-100 m/s, and the jet diameter was 1, 2 and 3 mm. The jet was directed vertically upward and it was coaxial with the conical target. The target was a cone, 120 degrees included angle, of 4 mm in base diameter, or a similarly dimensioned circular disc positioned normal to the flow direction. The impacts were carried out within an evacuated down to 5 kPa chamber. The collision was observed by means of technique Phantom7 high-speed video camera. The resulting flow was axisymmetrical. In the case of the Newtonian liquids and conical target the flow was conical in the observation field 150×300 mm during pulse jet impact on the target. The forward rim of the film was a thin liquid torus. This toroidal rim expanded with constant velocity and propagated in vertical direction also with constant velocity. Even under low air pressure the low viscous liquid films demonstrated flaging instability and were subjected to break up. However the flow of the 10 Pa·s oil took place without lost of continuity that demonstrates the stabilizing role of the viscosity in film flows. The behavior of polymeric liquids was significantly different. First of all we observed longitudinal jet splitting into a number of liquid edges (fibrils) for certain polymer solutions. The effect was more pronounced for disk-like targets. Secondly, we observed the formation of films with bell-like shapes. If a concentration was high enough the expansion of the forward rim at certain moment was reversed into a radial retraction. Finally all liquid was accumulated at the vertical rod, used as a target holder. The film retraction was caused by elastic stresses developed in the liquid due to extension of liquid elements in direction of film's “parallels”. Thus the rim trajectory (as well as of all other film elements) is governed by competition of elasticity and inertia. Estimations of the forming elastic stress based on analysis of the rim trajectory, within a framework of stress-inertia balance, give values up to 1 MPa, with correspondent elastic modulus of order 1 kPa. The latter value in few orders of magnitude greater than ones obtained with standard dynamic shear methods at low strain rates. Also we observed spontaneous hole formations in the film and following film break up with formation web-like intermediate liquid structures. For a jet of 2 mm in diameter the film break up happens at jet velocity higher than 40 m/s for all tested polymeric liquids.

Monday 11:05 De Anza I EM5

Evaluation of planar elongation viscosity by drag force acting on a bullet bob

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A new measurement method of planar elongation viscosity for low viscous fluids is developing. A bullet shaped bob is pushed into a sample liquid held in a cylindrical cup with a constant velocity and the drag force acting on the bullet bob is measured. The bullet bob is designed to generate steady planar elongation flow in the gap between the bob and the cup. The flow between the bob and the cup is axisymmetric but it is possible to approximate to the two-dimensional flow when the gap is narrowing compared with the radius of the bob. This flow field has an advantage for two-dimensionality compared with the traditional two-dimensional flow cell because it does not have side walls. The recent commercial rheometer contains a very fine transducer to measure the thrust force. They also have a tool gap control system which can move the flow cell up and down with a constant speed. Then, only the bullet bobs are required for carrying out this method if such rheometer can be used. In case of the cylindrical bob, the flow between the bob and the cup becomes two-dimensional Poiseuille flow on Newtonian fluids, not the elongation flow. Then, the shear viscosity can be evaluated by the drag force acting on the cylindrical bob. In case of viscoelastic fluids, the first normal stress difference generates in the gap and the drag force is changed by it. Therefore, the first normal stress difference can be estimated by the drag and the shear viscosity measured by the traditional rotary method of the cylindrical bob system. For the trial test, the bullet bobs and the cylindrical bobs were made. Some of the bullet bobs were designed to generate different elongation rate at the same moving speed. The others were designed for the evaluation of effect of the bob length. The cylindrical bobs which have the same diameter but different height were designed for evaluation of the effect of the entry flow loss. The standard Newtonian viscous fluids, polymer solutions, M1 fluid, etc. were used as a test sample. From the results of the cylindrical bob, the shear viscosity can be accurately evaluated by the drag force in case of Newtonian fluids. The first normal stress difference of the polymer solutions in low shear rate region were also evaluated but it is thought that the more theoretical discussion should be needed. From the results of the bullet bobs, it was confirmed that the drag force measured by the different bobs was a function of the planar elongation rate. The planar elongation viscosity was evaluated for each test fluids and compared with the results measured by other methods. This study is the first step of the development and it contains uncertain assumptions in the designing of the bob and calculation. However, this method has a lot of advantage, such as the simplicity for execution of experiment, applicability for various materials, convenience by use of the existing commercial rheometer, etc. It is thought that this method has the possibility of becoming the standard of the plane expansion viscosity measurement.

Monday 11:25 De Anza I EM6

A conveyor belt setup for studying gravitary free surface flows of complex fluids

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We present a new experimental setup dedicated to understanding the dynamics and mechanical properties of gravitary free surface flows made of complex materials. Our study is motivated by the need of improving the modelling of hazardous natural flows such as debris flows, mud flows, avalanches,... Due to the extreme heterogeneity of the materials involved in these phenomena, classical laboratory rheometers are not suitable. Our experimental setup consists of a 3-m long inclined channel whose bottom is constituted by an upward-moving conveyor belt. The belt is driven by an electrical motor allowing to reach running velocities in the range 0-1.6 m/s. Channel section is rectangular, with an adjustable width in the range 0-0.5 m. The two side banks are fixed in the laboratory frame. To enforce fluid recirculation, channel upper end is closed by a fixed rigid wall perpendicular to the bottom. The inclination of the whole setup can be adjusted in the range 0-30°. In terms of instrumentation, flow characteristics are monitored using ultrasonic height sensors and optical pattern projection techniques. Series of experiments have been conducted with different types of complex materials: viscoplastic fluids (carbopol, kaolin slurry), dry granular materials, fluid-grain mixtures. For all these materials, we observed the existence of specific ranges of belt velocity and slope angle in which stationary surges with immobile front spontaneously develop. Inside these surges, fluid velocities are oriented upward in the vicinity of the conveyor belt and downward in the vicinity of the free surface, so that the average velocity everywhere equals to zero. Interestingly also, only a small portion of the flow appears affected by the upper boundary condition. We report on the detailed morphology of the surges (front shape, appearance of a zone of uniform flow depth), and on the evolution of these characteristics as a function of belt velocity and slope angle. In particular, we show how flow height measurements in our setup can be related to the rheological properties of the used materials. We also demonstrate that our results provide convenient and well-documented benchmarks to test the long-wave models classically used for natural free surface flows.

CF-2. Computational and Multiscale Modeling I

Organizers: Antony N. Beris and Jan K. Dhont
Session Chairs: Francesco Chinesta and Bamin Khomami

Monday 9:45 Colton I-III CF7

Hi fidelity multiscale flow simulation of dilute polymeric solutions in complex kinematics flows

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Modeling flow of dilute polymeric solutions in complex kinematics flows using closed form constitutive equations or single segment elastic dumbbell models has attracted considerable attention in the past decade. However, to date most simulations in complex kinematics flows have not been able to quantitatively describe the experimentally observed flow dynamics, such as vortex growth, free surface and/or interface motion, or the measured frictional drag properties. This lack of quantitative prediction of experimental findings can be attributed to the fact that single segment elastic dumbbell models as well as closed form constitutive equations obtained by invoking various closures such as the FENE-P, FENE-LS can at best qualitatively describe the polymer dynamics and rheological properties of dilute polymer solutions as evinced by recent fluorescence microscopy studies of model macromolecules. However, multi-segment bead-rod and bead spring descriptions of dilute polymeric solutions have been shown to describe both single molecule dynamics as well as the solution rheological properties. These findings clearly underscore the fact that a multi-segment description of the macromolecule that contains sufficient information regarding the internal degrees of freedom is required for quantitatively accurate modeling of dilute polymer solutions under flow. Motivated by this fact, we have developed a highly accurate and CPU efficient algorithm for multiscale simulation of dilute polymeric solutions in complex kinematics flows using a bead-spring chain description. In this study, we have used this algorithm to model flow of a dilute polymeric solution through 4:1:4 axisymmetric contraction/expansion geometry utilizing single and multi-segment bead-spring descriptions as well as the FENE-P closed form constitutive equations. It should be noted that this geometry has been selected not only because it contains many important features of typical polymer processing flows, namely, contraction/expansion as well as recirculation but also due to the fact that a wealth of experimental data is available in terms of vortex dynamics and frictional drag properties. In this presentation, we will discuss the influence of various model parameters, such as internal degrees of freedom, finite extensibility, closure approximation, and stress-conformation hysteresis on the predicted vortex dynamics and the frictional drag properties of the flow over a wide range of De. In turn, a unified approach for process level simulation of dynamics of dilute polymeric solutions will be suggested.

Monday 10:05 Colton I-III 💿 CF8

Towards a Fokker-Planck rheometer

Francisco Chinesta[1], Amine Ammar[2], and Roland Keunings[3]
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Models of kinetic theory provide a coarse-grained description of molecular configurations wherein atomistic processes are ignored. They are meant to display in a more or less accurate fashion the important features that govern the flow-induced evolution of configurations. Over the last few years, different models related to dilute polymers have been evaluated in simple flows by means of stochastic simulation or Brownian dynamics methods. Kinetic theory models can be very complicated mathematical objects some times defined in highly multidimensional spaces including the physical space, the time and the conformational space. It is usually not easy to compute their rheological response in rheometric flows, and their use in numerical simulations of complex flows has long been thought impossible. The traditional approach has been to derive from a particular kinetic theory model a macroscopic constitutive equation that relates the viscoelastic stress to the deformation history. However, this approach noticed some limitations that pushed researchers to propose novel multi-scale approaches. In this context, micro-macro methods of computational rheology that couple the coarse-grained molecular scale of kinetic theory to the macroscopic scale of continuum mechanics have an important role to play (Keunings, Rheology Reviews, D.M. Binding and K. Walters (Edts.), British Society of Rheology, 67-98, 2004). In the last years we have proposed novel strategies of the kinetic theory models based on the use of model reduction and separated representations applied to their Fokker-Planck description. These strategies have been successfully applied to solve a large variety of models (linear and non-linear, steady and transient) describing suspensions (short fibers, nano-tubes, ferrofluids, colloids); polymer solutions (dumbbell and multi-dumbbell models); entangled polymers based on the reptation picture (Doi and Edwards, Ottinger, ...) or in the network description; liquid crystalline polymers; associative polymers; aggregating systems; ... In this work the main ideas involved in these advanced computational techniques will be revisited, highlighting the generality of the approach to be applied in a large variety of models described within the Fokker-Planck formalism. At present the Fokker-Planck equations are solved by assuming a known flow kinematics (like in a hypothetical Fokker-Planck rheometer) but some preliminary results also proves the possibility of coupling the Fokker-Planck solver with a flow kinematics solver to perform complex fluid flow simulations.

Monday 10:25 Colton I-III CF9

Single-chain dynamics of linear polyethylene liquids under shear

Jun M. Kim, Brian J. Edwards, Bamin Khomami, and David J. Keffer
Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

In this presentation, we have performed nonequilibrium molecular dynamics and Brownian dynamics simulations to investigate the dynamics of individual chains comprising linear polyethylene liquids under shear. Plots of the distribution function vs. the magnitude of the chain end-to-end vector exhibit Gaussian behavior at low shear rates, but display a bimodal distribution at high shear rates. By dividing this distribution into four bins with respect to the magnitude of the end-to-end vector, it was possible to examine the chain conformations in each bin, and to compare the results with those of the corresponding Brownian dynamics simulation of bead-rod chains at the same Weissenberg numbers. We generated time correlation functions <Rx(t)Rx(t+t)> and <Rx(t)Ry(t+t)>, where the Ri denote components of the end-to-end vector, and extracted the frequencies of the correlations using a fast Fourier transformation. There were three time scales observed in this study, one of which was the Rouse time. The other two were derived from the two correlation functions mentioned above. These two time scales were approximately the same at low shear rates, and were larger than the Rouse time. However, at high shear rates, the two time scales were significantly different, although each was substantially less than the Rouse time. At the highest shear rate examined, the two time scales had attained a common value. It is postulated that the RxRx correlation corresponds to stretching modes within the liquid, and that the RxRy correlation corresponds to rotational modes. Implications of these observations will be discussed during the presentation.

Monday 10:45 Colton I-III 💿 CF10

A fluid particle method for the discretization of the Oldroyd-B model with thermal fluctuations

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Micro-rheology is an experimental optical technique that probes the viscoelastic response of a fluid by optically measuring the Brownian motion of suspended colloidal particles. A simulation technique for these type of problems requires the consideration of thermal fluctuations which are the ultimate responsible for the diffusion of the colloidal particles. There are not many simulation techniques that have considered the introduction of thermal fluctuations in viscoelastic fluids. Lattice Boltzmann, which has been generalized to include thermal fluctuations in the Newtonian case, has been also generalized to describe viscoelastic behavior, but without thermal fluctuations. Another approach, CONNFFESSIT, is intrinsically stochastic but requires the averaging of many realizations in order to obtain smooth macroscopic results, thus increasing the computational resources required.

Dissipative Particle Dynamics is a natural method for dealing with the simulation of polymers in which thermal fluctuations are naturally incorporated. Despite its great success for studying problems at the mesoscopic level, DPD suffers from a number of conceptual shortcomings which can limit its applicability, the worst one being the unclear definition of the particle length size which prevents an "a priori" control of the external spatio-temporal scales. In order to solve these problems, a new formulation of DPD (denoted as Smoothed Dissipative Particle Dynamics; SDPD) has been recently proposed [1] where an additional extra variable for every fluid particle, c.f. a thermodynamic volume, is considered, thereby providing a unique definition of the particle size.

In this talk, the SDPD method will be briefly reviewed and a new fluid particle model for viscoelastic liquids will be presented, in which the state of the polymer molecules is represented by a conformational tensor. The motivation to consider the conformation tensor is that we will obtain a model in which thermal fluctuations may be switched on and off by appropriate selection of the size of the fluid particles. When the underlying polymer molecules are modeled by Hookean dumbbells, the resulting fluid particle model turns out to be a Smoothed Particle Hydrodynamics discretization of the well-known Oldroyd-B model [2] and allows for a simple introduction of thermal noise with clear physical meaning [3].

[1] P. Espanol, M. Revenga, Phys. Rev. E, v. 67, 026705 (2003); [2] M. Ellero, R.I. Tanner, J. Non-Newt. Fluid Mech., v. 132, 61 (2005); [3] M. Ellero, P. Espanol, Phys. Rev. E (2007) under submission.

Monday 11:05 Colton I-III CF11

3D viscoelastic flow of a falling sphere in a Couette flow

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In this paper we study the flow of a viscoelastic fluid in a Couette with a falling sphere. As already experimentally observed by van den Brule and Gheissary, the settling velocity of a sphere is reduced by elastic effects of the fluid, i.e. presence of normal-stress differences, and the effect becomes increasingly higher with increasing shear rates experienced by the falling sphere. The log conformation representation, as proposed in Fattal et al., has been implemented in a three-dimensional finite element context using the DEVSS-G/SUPG formulation. Our computations, using a Giesekus viscoelastic model, confirm an increase of the drag with an increasing shear rate. The seperate and combined effects of elasticity and shear-thinning on the settling velocity are discussed in detail. The results also serve as a benchmark for other numerical models to compute three-dimensional viscoelastic flow.

Monday 11:25 Colton I-III CF12

Numerical solution of the PTT constitutive equation for three-dimensional unsteady free surface flows

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This work deals with the development of a numerical technique for simulating three-dimensional viscoelastic free surface flows using the nonlinear constitutive equation PTT (Phan-Thien-Tanner). In particular, we are interested in flows possessing moving free surfaces. The equations describing the numerical technique are solved by the finite difference method on a staggered grid. The fluid is modelled by a Marker-and-Cell type method and an accurate representation of the fluid surface is employed. The full free surface stress conditions are considered. The PTT equation is solved by a high order method which requires the calculation of the extra-stress tensor on the mesh contours. To validate the numerical technique developed in this work an analytic solution for fully developed flow in a tube, using Cartesian coordinates, was derived. Fully developed flow in a pipe was simulated and the numerical solutions were compared with the respective analytic solutions. Results of complex free surface flows using the PTT equation such as the transient extrudate swell problem and a jet flowing onto a rigid plate are presented. An investigation of the effects of the parameters ε and Θ on the extrudate swell and jet buckling problems is given.

Monday Afternoon – 4 August 2008

KL-1. Keynote Lecture 1

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Alexei Likhtman

Monday 1:15 Steinbeck KL1

Dynamics of entangled polymers

Michael Rubinstein[1], Sergey Panyukov[2], David Shirvanyants[1], Michael Lang[3], and Dimitris Vlassopoulos[4]
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Topological entanglements lead to most interesting and most complicated effects in polymer dynamics. Confining tube models allow quantitative description of these effects, but require several input parameters, such as tube diameter and primitive path length. I will analyze assumptions that enter into the definitions of these parameters and describe the consequences if these definitions are modified. The dominant modes of polymer motion within the framework of the confining tube model are reptation, tube length fluctuation, and constraint release. Typical tube length fluctuations with root mean square average amplitude are believed to be important in dynamics of linear polymers, while rare large fluctuations, called arm retractions, dominate motion of branched polymers. I will explain how these rare large fluctuations can be important for linear polymers as well. The ultimate test of tube models is its ability to describe the dynamics of non-concatenated, but entangled ring polymers. Neither reptation, nor arm retraction are applicable for entangled rings, that seemed to have no rubbery plateau. I will describe tube model for ring polymers that predicts power law frequency dependence of storage and loss moduli. This prediction is in good agreement with results of recent experiments. Melts of non-concatenated but entangled rings relax relatively fast compared to melts of linear chains with the same molecular weight. Linear chains added in trace amounts to melts of rings thread through ring polymers, slowing down their diffusion and relaxation and leading to the re-appearance of the plateau in the stress relaxation function. This effect begins at compositions below the overlap of linear chains as soon as tenuous network of rings threaded by linear chains percolates through the melt. This model explains the experimentally observed extreme sensitivity of entangled rings to trace amounts of linear chains.

KL-2. Keynote Lecture 2

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Jan Vermant

Monday 1:15 Serra I KL2

Multiphase flows in microfluidic devices: Drops, vesicles, and cells

Howard A. Stone
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Microfluidic approaches are proving to be very useful for shedding new insights into multiphase hydrodynamics in confined systems and cellular-scale hydrodynamics. We will survey several multiphase microfluidic contributions from my research group, including particle-covered drops and bubbles, making double emulsions consisting of bubbles inside an aqueous droplet which itself is suspended in oil, and size separation of giant unilamellar vesicles using electrohydrodynamic flows. If there is time, we will show how microfluidic methods provide a route for investigating mechanochemical transduction processes in red blood cells.

HS-2. FIC/Composites/Imm. Polymer Blends

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chairs: Richard S. Graham and Pier-Luca Maffettone

Monday 2:30 San Carlos IV 💿 HS7

Rheological modeling of flow-induced crystallization in polymer melts and limitations on classification of experiments

Rudi J. Steenbakkers, Gerrit W. Peters, and Han Meijer
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A model has been developed, which provides a coupling between the kinetics of flow-induced crystallization and the relaxation behavior of the high molecular weight chains in a polymer melt. Stretch of these chains is found to be the key factor in the formation of nucleation precursors. Orientation is not sufficient. This is demonstrated by combining simulations and experiments with different materials, under varying flow conditions and at different temperatures. Saturation of the number density of flow-induced precursors and resulting nuclei, which is an essential element of the model, is also observed in experiments. The saturated number density is shown as a function of characteristic Weissenberg numbers, based on the reptation time and on the Rouse time of the high molecular weight chains. In some experiments, a large effect of flow is observed while the Weissenberg number based on the Rouse time is smaller than unity. This apparent disagreement with the model is discussed, showing that classification of flow-induced crystallization experiments based on Weissenberg numbers is difficult, if not impossible. When longitudinal growth of precursors is included, the saturation part of the model should be reformulated, depending on whether only chains of high molecular weight or chains of all molecular weights are involved in the growth process. Based on rheological measurements on crystallizing melts, the latter appears to be the case.

Monday 2:50 San Carlos IV HS8

The specific work of flow as a universal parameter to control formation of shish-kebab morphology in polymers

Oleksandr O. Mykhaylyk[1], Pierre Chambon[1], Richard S. Graham[2], Patrick Fairclough[1], Peter D. Olmsted[3], and Anthony J. Ryan[1]

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The majority of polymers are semicrystalline and inevitably these crystals are oriented by flow during processing. Two different morphologies can be found in crystallized polymers: spherulites forming at quiescent conditions and shish-kebabs appearing under shear flow. It has been established in the recent years that the longest chains in a polymeric ensemble play a catalytic role in the formation of shish recruiting other chains into the formation of shish-kebab morphology. A universal parameter for the formation of shish-kebab structures, the specific work of flow, and a method by which it can be measured for any given ensemble of polymers are presented in this report. The magnitude of the specific work required to create shish-kebab structures depends on both the chemical structure of the polymer and its molecular weight distribution as these both affect the longest relaxation time (Rouse time) associated with the longest chains in the polymer ensemble. Model linear-linear hydrogenated polybutadiene blends as well as industrial materials (low-density polyethylene and isotactic polypropylene) have been investigated by both small-angle X-ray scattering (SAXS) and birefringence methods. The critical parameters of specific work of flow responsible for the formation of shish-kebab structure in these polymers have been established and measured. It has been also found that shish nuclei can be formed and exist at temperatures above the nominal melting points of the studied polymers. The phenomenon of elastic turbulence has been identified in semicrystalline polymers crystallized under shear where complex oriented structure caused by elastic instabilities is pinned by the process of crystallization and persists down to room temperature. Different stages of instabilities (similar to instabilities observed in dilute solutions of high molecular weight polymers using colouring particles) towards development of elastic turbulence have been identified in sheared polymers using technique of post-crystallization characterization of the sheared samples (SAXS and birefringing measurements). It is also demonstrated that the orientation of the lamellar structure tilted to the flow direction observed in many time-resolved scattering experiments on shear-induced crystallization is actually a result of a spiral flow caused by elastic turbulence.

Monday 3:10 San Carlos IV HS9

Flow-induced crystallization of bimodal blends of ethylene copolymers and high density polyethylene

Diana S. Smirnova and Julia A. Kornfield

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Ethylene copolymers have been studied heavily under quiescent conditions because of their inhibited abilities to form organized structures. Since short chain branches act as crystal defects resulting in decreased crystallinity, any amount of comonomer changes the morphology, and hence physical properties. Since final polymer products are obtained through processing, it is technologically relevant to understand the behavior of ethylene copolymers under flow. In particular, we are interested in probing the effect of short-chain branching on morphological development following shear. Specific molecular characteristics (i.e. molecular weight, topology) can be isolated through the study of bimodal blends. Bimodal blends containing small concentrations of high molecular weight, high density polyethylene (HDPE, Mw = 526 kg/mol, Mw/Mn = 3) in an ethylene-co-hexene matrix (Mw = 50 kg/mol, Mw/Mn = 2, 5 mol % hexene) were sheared to expose the effect of short-chain branching of the matrix. HDPE concentrations were selected to be above and below the overlap concentration of the material (c* ~ 0.6%), but maintained below 1% such that the rheology of the blends was not significantly altered from that of the copolymer matrix. DSC traces were collected to ensure that co-crystallization between the two blend components occurs. A Linkam shear stage was used to apply a shear strain of 300 units while varying shear rates between 0 and 30 s-1. Structural development was followed by in-situ small angle x-ray scattering (SAXS) and later by rheo-optical measurements (turbidity and birefringence). It has been found that the copolymer matrix alone exhibits poor spherulite formation both under quiescent conditions and following flow. No oriented growth was observed even under the strongest shearing conditions used. Under quiescent conditions, the presence of HDPE induces the formation of small spherulites that can be discerned by small angle light scattering (SALS), increased crystallization kinetics, and increased crystallinity. Following shear, oriented growth was observed in the blends, even those with HDPE concentrations that are below that of overlap. However, even the most oriented samples exhibited a significant amount of isotropic growth.

Monday 3:30 San Carlos IV HS10

Strain-induced crystallization of poly(L-lactide) tubes under uniaxial and biaxial deformations

James P. Oberhauser[1], Lothar W. Kleiner[2], Janos B. Bebok[2], Vincent J. Gueriguian[1], and Fuh-Wei Tang[3]

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The coupling between microstructure and macroscopic material properties is a universally recognized materials science concern, and for polymeric materials, the relationship between applied deformation and microstructure is of added importance since nearly all polymer processing applications involve flow and thus deformation of the molecular structure. More narrowly, a diverse range of commercial products of tubular geometry rely upon a high degree of uniaxial (i.e., radial) or biaxial (i.e., mixture of radial and axial) orientation to imbue the requisite mechanical properties, including radial strength, modulus, and creep resistance.

These features are particularly true of a proposed new class of bioabsorbable coronary stents based upon semicrystalline biopolymers, which must possess sufficient radial strength to resist the pressure applied by the arterial wall for some finite time frame after deployment. At the same time, the device must retain some ductility so that it may be crimped onto a balloon catheter during production. Much of the radial strength derives from the degree of crystallinity and the crystalline orientation state, while ductility is influenced by the degree of crystallinity as well as the amorphous phase orientation. Complicating the picture is the fact that the device undergoes hydrolytic degradation *in-vivo*, which can potentially compromise its structural integrity. The spacing between crystalline lamellae and the density of tie chains in the amorphous phase bridging crystalline lamellae directly influences the time scale on which radial strength is lost during hydrolytic degradation, since the amorphous phase is more permeable to water and tends to degrade preferentially. Thus, the physics of strain-induced crystallization govern the microstructural evolution during processing and, ultimately, critical mechanical and degradation properties.

We will present results for poly(L-lactide) tubes in an largely amorphous initial state that are then subjected to controlled thermal and deformation histories in a radial expansion process that resembles blow molding. The expansion temperature and pressure (i.e., applied stress) as well as the radial and axial strain will be varied to induce a range of crystalline and amorphous morphologies. Microstructure will be evaluated across a spectrum of length scales, including that of the crystal lattice and crystalline orientation (WAXD), crystalline and amorphous orientation (Raman spectroscopy), lamellar spacing (SAXS). Polarizing optical microscopy (POM) and transmission electron microscopy (TEM) will also be employed to provide visual images of microstructure. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), radial strength, and gel permeation chromatography (GPC) testing will also be performed at various time points during *in-vitro* hydrolytic degradation to evaluate the relationship between initial crystalline/amorphous structure and radial strength throughout the degradation process.

Monday 3:50 San Carlos IV HS11

Rheology, morphology and temperature dependency of nanotube networks in polycarbonate/multiwalled carbon nanotube composites

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We present several issues related to the state of dispersion and rheological behavior of polycarbonate/multiwalled carbon nanotube (MWCNT) composites. The nanocomposites were prepared by diluting a commercial masterbatch containing 15 wt % nanotubes using optimized melt-mixing conditions. The state of dispersion and the nanoparticle orientation were then analyzed by scanning and transmission electron microscopy (SEM, TEM) and also atomic force microscopy (AFM). Rheological characterization was used to assess the final morphology. The results of frequency sweep tests at different temperatures and gaps for nanotube concentrations ranging from 0.2 to 5 wt % did not reveal any significant effect of the gap (or apparent slippage) down to a 500 µm gap. Interestingly, Cole-Cole plots showed that by increasing the temperature, the nanotubes behaved more as rubber-like. Further, it was found that the percolation threshold decreased significantly with increasing temperature and finally reached a constant value. This is described in terms of the Brownian motion, which increases with temperature. However, by increasing the nanotube content, the temperature effects on the complex viscosity at low frequency decreased significantly. This suggests that the nanotubes form a thermal network that results in a significant increase in thermal conductivity and hinders the accumulation of heat in the system. Finally, the nanotube percolation thresholds were found to be approximately equal to 0.3, 0.7 and 2 wt % for rheological, thermal and electrical conductivity measurements, respectively.

Monday 4:10 San Carlos IV HS12

Multifunctional elastomer nanocomposites from functionalized graphene single sheets

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We present the effects of incorporation of completely exfoliated graphene nanoplatelets on the physical properties of rubber nanocomposites. The functionalized graphene sheets (FGS) with very high aspects ratios (100-10000) and specific surface areas (1800 m^2/g) are obtained through rapid thermal expansion of graphite oxide. Both thermoset and thermoplastic elastomer-FGS nanocomposites offer better or equal mechanical, electrical and gas barrier properties compared to nanotube, clay and carbon black (CB) filled systems. For example, the tensile tests show that both modulus and strength increases by ~ 400 % in styrene-butadiene rubber (SBR) with 2 wt % FGS loading. WAXS measurements coupled with tensile tests reveal that the incorporation of FGS into natural rubber (NR) significantly shifts the onset of strain-induced crystallization to lower elongations compared to neat and CB filled matrix. The rheological and electrical percolation is achieved at low volume fractions (<1 vol %) of FGS in various systems due to its high aspect ratio. The gas barrier properties of FGS filled elastomers are studied and the results are compared to the available models. The effects of processing methods (melt vs. solution), surface area of FGS and degree of surface functionality on the filler dispersion and physical properties will be discussed.

Monday 4:30 San Carlos IV HS13

Strain and morphology induced non-linearities in the viscoelastic behavior of filled polymer systems

Jean L. Leblanc
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Polymers are by nature non-linear materials in this sense that, except in special, limiting conditions, their behavior never conform to a straight proportionality between stress and strain (or rate of strain). In the limit of very small strain (or very slow rate of strain) however, pure polymers exhibit linear viscoelasticity, then as strain (or rate of strain) increases, strain-induced non-linearities are common observations. With filled polymer systems, a more complex behavior is observed since, in addition to strain induced non-linearity, one has to consider additional morphology-induced effects. A variety of filled polymer compounds in the molten state were studied through LAOS (large amplitude oscillatory strain) experiments, using a closed cavity torsional dynamic rheometer, suitably equipped to record strain and torque signals and analyzed it through the so-called Fourier Transform rheometry technique. The variation of odd torque harmonics is the "non-linear viscoelastic signature" of the material in the conditions of the experiments. Filled polymer systems exhibit quite typical "non-linear signatures" which result from the superimposition of strain and morphology induced non-linear effects, as readily considered in developing a mathematical model that meets very well experimental data and gives access to typical features of the viscoelastic behavior of such heterogeneous materials.

Monday 4:50 San Carlos IV HS14

The rheological behaviour of glass-filled high and low density polyethylenes

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This study focuses on some recent results, both experimental and theoretical, on the effects of the addition of glass beads to the linear and non-linear rheology, and hence melt processability, of two commercial shear-matched polyethylenes. The addition of the glass beads leads to interesting structural aspects such as cavitation, particularly in non-linear extension. The beads were coated with a commercial coupling agent prior to blending using a solvent procedure. First, a set of linear and non-linear rheology measurements were carried out on both the pure PE and glass bead/PE blends. Time-temperature superposition was used to obtain the complex viscosity behaviour over a wide range of frequencies for all samples. The presence of the glass particles was found to raise the viscosity. The increase was found to be predicted satisfactorily by the empirical Kreiger-Dougherty relationship for the low density polyethylene, with an additional novel horizontal shift factor for the frequency. This second factor adjusts for the enhanced strain in the matrix due to the presence of the rigid glass beads, and hence the earlier onset of shear thinning. The divergent results from filled HDPE are explained through SEM analysis of the matrix. Non-linear measurements, in both shear and extension, were also carried out. The use of the same shifting factors gave good agreement at small strains in both cases, but divergence occurred at higher strains. Currently this is thought to be due to two distinct effects. First, the presence of the glass beads affects the development of molecular orientation during flow, reducing the overshoot in non-linear shear and the amount of strain hardening in non-linear extension. Second, post analysis of the samples from the extensional tests by SEM, showed the presence of cavities in the PE matrix; this may be the major contributor to the transient shear and strain hardening reduction.

Monday 5:10 San Carlos IV HS15

Effect of particles on rheology and morphology of immiscible PI/PDMS polymer blends

Prachi Thareja and Sachin Velankar
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We present the effects of interfacially-active particles on the rheology of immiscible polymer blends of polyisoprene (PI) and polydimethylsiloxane (PDMS) with a droplet-matrix morphology. Various commercially available particles are used viz. polytetrafluoroethylene (PTFE), iron oxyhydroxide (FeOOH), iron and titanium dioxide (TiO2). All these particles adsorb at the PI/PDMS interface, and such addition of these particles is expected to significantly affect the breakup and coalescence of drops, and hence the rheology of the blends.

20 wt% PI-in-PDMS blends and 20 wt% PDMS-in-PI blends, both containing 0.5 volume% particles were sheared at successively lower shear stresses. Steady shear viscosities, recoveries upon cessation of shear, and dynamic oscillatory properties upon cessation of shear were measured. All blends showed a relaxation process that corresponded to deformation and relaxation of drops, and the kinetics of this relaxation process gives information about the effect of particles on the droplet dynamics. In all cases, decreasing stress caused an increase in the relaxation time of this process, suggesting droplet coalescence. Thus, although all the particle types adsorb at the interface, none is able to prevent coalescence. Indeed, in some cases, e.g. iron particles added to PI-in-PDMS blends, addition of particles causes a large increase in the relaxation time, suggesting that the particles *promote* coalescence. We speculate that promotion of coalescence in this system is analogous to anti-foaming action of hydrophobic particles added to aqueous foams.

SG-2. Glass Transition Dynamics

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Mike Roland

Monday 2:30 San Carlos II SG7

The role of molecular length and connectivity in the relaxation scenario of supercooled liquids

Johan Mattsson, Rikard Bergman, Per Jacobsson, and Lars Börjesson
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An outstanding question in our attempts to understand the glass transition and its related dynamics is to find the links between molecular architecture, intermolecular interactions and molecular dynamics. We here present systematic broad band dielectric spectroscopy studies of the dependence of chain-length on the supercooled dynamics performed for different oligomeric systems stretching in size from the monomer to the polymer. In addition to the effects of a chain-length variation, we investigate systematically how the supercooled dynamics changes with the degree of hydrogen bonding in the systems. Intriguingly, we are able to establish a direct link between the supercooled dynamics of a class of hydrogen bonded liquids and water. The results have direct implications for the mysterious behaviour of supercooled water within the experimentally inaccessible temperature region, the so called 'no man's land'.

Monday 2:50 San Carlos II SG8

Scaling of the structural relaxation in supercooled fragile liquids and simulated liquid silica

Arnaud Le Grand[1], Catherine Dreyfus[2], Claire Bousquet[2], Robert Pick[2], Jacek Gapinski[3], A Patkowski[3], and Werner Steffen[4]
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After a first study on supercooled o-terphenyl [1], recent studies of fragile supercooled glassforming liquids has shown that their dynamics and, more specifically, their “relaxation time” depends on a single control parameter, $\Gamma(\rho, T, n)$, where ρ is the mass density; T, the absolute temperature and n, a positive number usually ranging from ~3.5 to ~ 8. In particular [2], we have extended this finding to other fragile glassforming liquids using light scattering data and we have proposed a simple form for $\Gamma(\rho, T, n)$, which depends only on three material-dependent parameters, reproducing relaxation times over 12 orders of magnitude. Summarizing these results, we also we generalise n to a local parameter, Q_1, which is equal to n when n_{loc} is independent of ρ and T. Numerical results obtained from simulation with the BKS model of liquid SiO_2 allow to determine n_{loc} over the large 2500 K < T < 7000. In the 2 $gm/cm^3 < \rho < 3.5\ gm/cm^3$ range, n_{loc} varies very little with the density but changes with the temperature from –1 to ~0.5 [3]. Also, it linearly correlates with a parameter describing a local orientation, whose varies with the change in the Si-O-Si bonding with temperature.

[1] C. Dreyfus, A. Aouadi, J. Gapinski, M. Matos-Lopes, W. Steffen, A. Patkowski, and R. M. Pick, Phys. Rev. E 68, 011204 (2003); [2] C. Dreyfus, A. Le Grand, J. Gapinski, W. Steffen and A. Patkowski, Eur. Phys. J. B 42, 309-319 (2004); [3] A. Le Grand, C. Dreyfus, C. Bousquet, and R. M. Pick Phys. Rev. E 75, 061203 (2007)

Monday 3:10 San Carlos II SG9

Impact of the application of pressure on fundamental understanding of glass transition

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Many remarkable dynamic properties of glassforming materials have recently been discovered experimentally by the application of elevated pressure. These properties turn out to have great impact on the research frontier of glass transition because they are general and fundamental. We review some of these experimental facts and show that they originate from intermolecular interaction and many-body relaxation dynamics of the structural relaxation. While these properties are either not explained or not explainable by convention theories and models of glass transition, they can be rationalized by the coupling model of the author.

Monday 3:30 San Carlos II 💿 SG10

Empirical description of the frequency response of glass transition related relaxation processes

Rikard Bergman
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Although the most prominent feature of the liquid to glass transition is the slowing down of the main structural relaxation, the alpha-relaxation, increasing interest is focussed towards secondary- or beta-relaxations. The beta relaxations are observable below the glass transition and have a much weaker and simpler (Arrhenius) temperature dependence compared to the dramatic non-Arrhenius behaviour of the alpha-relaxation. Typically, at some temperature in the supercooled regime, the relaxation times of the beta relaxation approach that of the alpha relaxation and the relaxation processes merge. We here compare different ways of analyzing the frequency domain susceptibility data in the merging region. In particular, we focus on the relaxation dynamics of a particular class of glass-formers, so called type A or wing glass-formers, where the beta-relaxation shows up only as a high frequency excess wing on the high frequency flank of the alpha relaxation. Based on certain straightforward assumptions we arrive at an empirical susceptibility equation that is shown to describe experimental data of wing glass-formers exceptionally well.

Monday 3:50 San Carlos II 💿 SG11

Effect of crosslinking on segmental and secondary dynamics of polyvinylethylene

Riccardo Casalini[1] and C. M. Roland[2]
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The local segmental and secondary dynamics of polyvinylethylene (PVE) networks having different cross-linking density have been studied as a function of temperature and pressure, using broad band dielectric measurements and pressure-volume-temperature measurements. The increase of cross-linking density increases the glass transition and the fragility. These increases are found to be associated with a larger relative contribution of temperature to the segmental dynamics, as measured by the ratio of the apparent isobaric and isochoric activation energy. On the other hand the effect of cross-linking on the non-cooperative secondary relaxation is found to be opposite to that on the segmental dynamics, with a speeding up of the secondary dynamics.

Monday 4:10 San Carlos II 💿 SG12

Heat capacity and entropy at the glass transition

Ranko Richert
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Heat capacity is a decisive quantity for identifying the glass transition temperature and the dynamics which control structural relaxation and viscous flow of supercooled liquids. Dielectric relaxation data of monohydroxy alcohols are used to demonstrate that $C_p(\omega)$ is a more fundamental property than is its dielectric counterpart, $\varepsilon(\omega)$. The heat capacity C_p determined via differential scanning calorimetry is also a standard approach to the excess entropy $S_{exc}(T)$ of a liquid. According to the Adam-Gibbs model, the configurational entropy $S_{cfg}(T)$ can explain the Vogel-Fulcher-Tammann (VFT) type temperature dependence of viscosity and relaxation times [1]. However, there is speculation regarding the amount of the configurational contribution to the excess entropy (level of liquid over crystal).

Frequency resolved non-linear dieletric relaxation experiments at fields up to 450 kV/cm are used to show that viscous liquids are not only dynamically but also thermodynamically heterogeneous [2]. The understanding of the nanoscopic heat-flow is quantitative and allows us to extract the configurational contribution to heat capacity and entropy. It is found that the excess heat capacity is largely configurational only for liquids that are not fragile in terms of the strong-fragile pattern [3].

[1] R. Richert, C. A. Angell, J. Chem. Phys. **108**, 9016 (1998); [2] R. Richert, S. Weinstein, Phys. Rev. Lett. **97**, 095703 (2006); [3] L.-M. Wang, R. Richert, Phys. Rev. Lett. **99**, 185701 (2007)

Monday 4:30 San Carlos II SG13

Relating structure, dynamics and rheology of soft micellar glasses

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For kinetically frozen poly(ethylene propylene)-poly(ethylene oxide) (PEP_m-PEO_n) block copolymer micelles we have shown, that the architecture of the individual micelle can be adjusted between the limits compact sphere like ($m \sim n$) and star-like ($m \ll n$) [1]. At the same time the (repulsive) micellar interactions vary from hard sphere like to ultra soft. Therefore PEP-PEO block copolymer micelles are an excellent model system for soft colloids. Special emphasis will be on star-like micelles [2-5] with varying functionality f, since these are hybrids combining colloidal and polymeric characteristics, which therefore crucially affects the rheological properties. In particular we want to relate rheology to the microscopic structure and adress the following points.

i) **Jamming transitions in concentrated micellar solutions.** For star-like micelles with large functionalities, $f \sim 120$, the (mesoscopic) self diffusion coefficient as independently obtained by dynamic light scattering and pfg-nmr as well as the (macroscopic) zero shear viscosity diverge on approaching the overlap concentration c*. Dynamic mechanical experiments show that for c=c* a real solid phase (G`>G`` for all ?) is formed. In contrary, for intermediate functionalities, f˷80, the zero shear viscosity continuously increases on crossing c* and finally diverges at a much higher characteristic concentration cc˜3c*. A solid phase is only formed in an extremely small concentration range and thereafter a re-entrant melting occurs which recovers the flow properties of sample with c<c*.

ii) **Rheo-SANS experiments.** The microscopic structure of micellar solutions can be probed on a nanometer scale by small angle neutron scattering (SANS). Performing insitu SANS experiments (Rheo-SANS) allows us to directly investigate on a local scale the structural response of ordered/disordered micellar phases to applied external shear. Whereas the macroscopic rheological properties viscosity and complex modulus G* drastically change upon increasing steady or oscillatory shear, the microscopic structure given by the principal peak in the structure factor S(Q) remains nearly unchanged.

[1] J. Stellbrink, G. Rother, M. Laurati, R. Lund, L. Willner and D. Richter, J. Phys.: Cond. Matter, 16, S3821-S3834, 2004; [2] M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, Phys. Rev. Letters, 94, 195504, 2005; [3] R. Lund, L. Willner, J. Stellbrink, A. Radulescu and D. Richter, Macromolecules, 37, 9984-9993, 2004; [4] M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, Phys. Rev. E, 76, 041503, 2007; [5] R. Lund, L. Willner, J. Stellbrink, P. Lindner, and D. Richter, Phys. Rev. Letters, 96, 068302, 2006.

HP-3. Entangled Polymers I

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Christian M. Bailly and Jay D. Schieber

Monday 2:30 San Carlos III HP13

Finding tube dynamics in a class of slip-links models

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The slip-spring [1] is a single chain model that contains similar physical assumptions as the tube model but expressed in discreet notation. The advantage of the slip-spring model is that its statics and dynamics are precisely formulated, and the number of assumptions is limited. The model is able to describe the smooth transition from entangled to unentangled dynamics, which makes it suitable for the prediction of mildly entangled materials, including results from molecular dynamics simulations.

We have compared in detail a set of selected observables in the linear regime from both the tube and slip-spring models. This comparison suggests that the dynamics in the latter can be seen as a sum of Rouse dynamics along a 1D path, plus constrained lateral fluctuations [2], which are usually not included in the tube model. The 1D path and the average of the lateral fluctuations can be thought of as the primitive path and the radius of the tube. For the same range of observables, the slip-spring model shows a better and more consistent agreement than the tube theory when compared with results from equilibrium molecular dynamics simulations of linear chains up to 7-10 entanglements [3]. A key question is how to define geometrically the primitive path using only observable quantities, like the coordinates of the monomers, and without recurring to complex constructions. It is also desirable to be able to do the inverse mapping and reproduce the monomer dynamics from those of the defined path. A proper definition of a primitive path in the slip-spring model can also be used to study the tube dynamics in multi-chain simulations. In this talk, we discuss all these issues and suggest possible directions to solve the problem.

[1] Likhtman, A.E., *Macromolecules* 2005, **38**, 6128-6139; [2] Ramirez, J, Sukumaran, S.K. and Likhtman, A.E., *Macromol. Symp.* 2007, **252**, 119-129; [3] Likhtman, A.E., Sukumaran S.K. and Ramirez J., *Macromolecules* 2007, **40**, 6748-6757

Monday 2:50 San Carlos III HP14

Slip-link simulations and comparison to single molecule studies of entangled DNA in shear and extensional flow

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The dynamics of entangled polymeric systems is most often inferred from the changes in macroscopic properties such as viscosity, birefringence, etc. Such observations may be inadequate to distinguish different models of entangled polymer dynamics in the “fast flow” regime where convective constraint release (CCR) and chain stretch within the topologically constraining “tube” are important. Recently Teixeira et al. (Macromolecules, 2007) presented a fairly complete single molecule examination of DNA in the shear flow of an entangled solution including examining various aspects of the length fluctuations and length distribution as well as the mechanical properties all within the CCR regime. In order to understand the physical principles behind these measurements, a molecular scale simulation using the slip-link method (Masubuchi et. al., J. Chem. Phys. 2001, Schieber et. al. J. Rheol. 2006) has been implemented. The method includes examining nonlinear, worm-like chains for different levels of entanglement and Kuhn step numbers (i.e. polymer molecular weights). We demonstrate that, in parameter regimes comparable to the experiments mean field approximations are reasonably inadequate because of the broad molecular individualism in the chain dynamics. Furthermore, we examine tumbling dynamics via the power spectral density of length fluctuations in this regime and contrast these dynamics from the well-documented dilute shear behavior.

After revisiting the available work on shear flow, we present a single molecule study of semi-dilute and entangled lambda-DNA in extensional flow. It is now known that in both the semi-dilute and entangled regime of polymer solutions, flow type plays a key role in the dynamics. We examine these effects by investigating the behavior of lambda-DNA in a cross slot flow device under background concentrations of DNA as high as 35 c* (i.e. approximately 17 entanglements per chain). Measurements of the effect of increasing background concentration and varying flow strength on the molecular extension for a single stained DNA polymer chain in purely extensional flow will be presented.

Monday 3:10 San Carlos III HP15

Self-consistent modeling of constraint release in a single-chain mean-field slip-link model

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We present an improved way to incorporate constraint release in a slip-link model for entangled polymer dynamics. In contrast to previous models, Rouse dynamics of the entanglements is avoided; instead entanglements can be created and destroyed in the middle of the chain due to dynamics in the environment. The implementation, called `constraints dynamics', is fully consistent with primitive-path fluctuations. The new model shows a good agreement with the algorithm of Doi and Takimoto which manages constraint dynamics by coupling entanglements of different chains in a simulation ensemble. However, the proposed implementation requires no coupling to maintain self consistency. Moreover, the new algorithm can easily be generalized to describe multi-chain entanglements. The resulting model exhibits primitive path fluctuations and chain stretching so should also be applicable to branched polymers without modification.

Monday 3:30 San Carlos III HP16

Checking tube theory postulates with molecular dynamics

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Department of Mathematics, University of Reading, Reading RG6 6AH, UK

I will discuss the use of molecular dynamics simulations of entangled polymers in order to verify several assumptions of the tube and slip-link models. I will show that naïve definition of bonded stress results in major contribution from the non-bonded stress to the total relaxation modulus. However, one can define an effective bonded stress, which can be used in single chain models and has the same functional form as usual bonded stress. I will also examine coupling between different chains and show that in dense systems the coupling between bonds orientation is significant (of order of 40%). The implication to the tube theory will be discussed.

Monday 3:50 San Carlos III HP17

Probing the foundations of tube theory: Comparisons between model and experimental scalings for linear entangled polymers

Christian Bailly[1], Roland Keunings[2], and Chen-Yang Liu[3]
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Tube models have achieved spectacular success for predictions of the rheology of entangled polymers. Quantitative success has been achieved at the price of significant complexity increase as compared to the original de Gennes picture, but the models have retained their high internal coherence (only two fundamental scaling parameters, one for time and one for stress). However, not all is perfect in "tubeland" and very essential questions have yet to receive a fully satisfactory answer.

We summarize in this paper recent findings about three issues: 1. the molecular weight dependence of the plateau modulus, 2. the molecular weight dependence of the terminal relaxation time and 3. the experimental evidence of monomer redistribution in the tube.

1. By comparing a large number of reliable published data on narrow disperse polymers, we find that the dependence of the plateau modulus vs. the number of entanglements is negligible down to the lowest measurable values (somewhat above 10 entanglements). This questions some of the underlying physics in state of the art tube models, whether it is the quantitative description of constraint release or contour length fluctuations.

2. We explore the terminal relaxation time dependence vs. molecular weight with an approach we call "probe rheology", which consists in extracting the relaxation behavior of a small fraction of short entangled chains in a matrix of very long chains. If the relaxation times of the short and long chains are well separated, the short chains relax as if in a permanent network, hence constraint release events are effectively frozen. We observe that, in this case, the terminal relaxation of the short chains scales approximately according to pure reptation, which is inconsistent with the consensus idea that contour length fluctuations account for the bulk of the deviation from reptation scaling for moderately entangled polymers.

3. We have detected, for the first time, a small relaxation hidden under the high frequency "Rouse" regime, which can be ascribed to the monomer redistribution mechanism predicted by tube models. The location of the relaxation peak is close to the second crossover, as expected. However, the shape of the peak is more narrow than expected (Maxwellian instead of summation of Rouse modes). Interpretation about the shape is made difficult by the non universal experimental slope in the high frequency region (0.65 observed vs 0.5 predicted). Hence, detailed conclusions remain tentative.

These three examples show that there are still fundamental issues with the detailed physical picture of tube models. The description of constraint release is probably insufficiently accurate. Possibly, the description of contour length fluctuations requires further refinements as well (influence of the environment on early fluctuations). The issues with the tube description get even more serious when the experiments probe lengths (and corresponding relaxation time scales) smaller than the tube diameter.

Monday 4:10 San Carlos III HP18

Rheology of entangled polymeric liquids through simulations of the primitive chain network model with finite extensibility

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We here report on some modifications of the Primitive Chain Network (PCN) model, originally proposed in [Y. Masubuchi et al., J. Chem. Phys. 115, 4387 (2001)], which both refine the model and make it suitable for predicting nonlinear rheological response in fast flows. The equilibrium chain properties, such as square end-to-end distance and square radius of gyration, are shown to agree with those from Gaussian chain theory. From the simulations, the longest relaxation time and self-diffusion coefficient for a chain in the entangled network are calculated, and are shown to reproduce the experimentally found deviations from the molar mass scaling predictions of classical reptation theory. The simulation results are then compared with some existing viscoelastic data on monodisperse polystyrene melts [T. Schweizer, J. et al., J. Rheol. 48(6), 1345 (2004) and A. Bach et al, Macromolecules 36, 5174 (2003)], by using as single adjustable parameter (to be assigned once and for all) a basic relaxation time which relates to the coarse graining of the PCN model. Essentially quantitative prediction of zero-shear viscosity and linear viscoelasticity is achieved. Without further parameters, and accounting for finite extensibility of chains in the PCN model, the nonlinear behavior of the polystyrene melts in start-up of shear and uniaxial elongational flow is also reproduced by the simulations. Specifically, the viscosity and first normal stress coefficient growth functions are quantitatively predicted, whereas transient elongational viscosities are reasonably reproduced only up to extensional rates of the order of the reciprocal Rouse time. At higher rates, although the strain hardening effect is correctly captured by the simulations, steady state values are not. Notwithstanding this latter limitation, the simulation model appears adequate to portray the rheological behavior of entangled melts, both in the linear and the nonlinear range. Similar comparisons with experimental data on polymer solutions will also be presented.

Monday 4:30 San Carlos III 💿 HP19

Chain stretch and relaxations in transient entangled network probed by double-step strain flows

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Double-step strain flows on entangled polystyrene solutions were employed to characterize the properties of transient entangled network and, in particular, its impact on subsequent chain stretch and relaxations. Contrast was made between nonlinear stress relaxation data with specially designed protocols for imposing the first or the second strain. An analytical formulation based on an extension of the Doi-Edwards tube theory was then employed to retrieve the effective chain stretch following the second strain. Conclusions are made on the observed impact of flow-induced transient entangled network affecting the subsequent material deformation and chain relaxations.

Monday 4:50 San Carlos III 💿 HP20

Tube theory for entangled linear polymers: Influence of different molecular mechanisms in non-linear flows

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Classical tube theories (e.g., Marrucci and Ianniruberto [2003], Leygue et al. [2006]) are based on a combination of different molecular mechanisms, i.e., reptation, stretch dynamics, constraint release, finite extensibility, and contour length fluctuations. These theories, when compared with the recent data of Bach et al. [2003] for the elongational flow, show systematic discrepancies at high elongational rates (Marrucci and Ianniruberto [2004]). Recently, Marrucci and Ianniruberto [2004], by using scaling arguments, have shown that the concept of 'interchain tube pressure effect' removes these discrepancies. The concept of 'interchain tube pressure effect' considers the tube diameter dynamics. In the present work, a new "single segment" differential constitutive tube model has been developed describing the non-linear behaviour of entangled monodisperse linear polymers. The model accounts for reptation, stretch dynamics, convective constraint release, finite extensibility, and an interchain tube pressure effect. This simple model has the advantage of illustrating the new physical assumptions more explicitly. It also predicts "quantitative" features typically shown by elongational data in the non-linear range. Moreover, the influence of finite extensibility, convective constraint release (CCR) and stretch dynamics on an interchain tube pressure effect has been studied for moderately entangled linear polymer systems.

A. Bach, K. Almdal, H. K. Rasmussen, O. Hassager, Elongational viscosity of narrow molar mass distribution Polystyrene, Macromolecules 36 (2003) 5174-5179; A. Leygue, C. Bailly, R. Keunings, A tube based constitutive equation for polydisperse entangled linear polymers, J. Non-Newtonian Fluid Mech. 136 (2006) 1-16; G. Marrucci, G. Ianniruberto, Flow-induced orientation and stretching of entangled polymers, Phil. Trans. R. Soc. Lond. A 361 (2003) 677-688; G. Marrucci, G. Ianniruberto, Interchain pressure effect in extensional flows of entangled polymers, Macromolecules 36 (2004) 3934-3942.

Monday 5:10 San Carlos III 💿 HP21

Unified mathematical model for linear viscoelastic predictions of linear and branched polymers

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Application of the slip-link model to entangled star-branched polymers is considered. Relaxation of each arm occurs due to reptation, and destruction and creation of the entanglements, called 'constraints dynamics'. Rouse dynamics is completely avoided. In addition, the branch point can fluctuate around and even slide through the slip-links, all determined by the chain free energy. All the fitting parameters are determined from linear chain comparison. The proposed model is compared with the tube model, which contains certain limitations not found in the slip-link model. The proposed formulation can be applied to more complicated branches and to cross-linked networks as well.

HP-4. Applied and Industrial Rheology

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: David C. Venerus and Ole Hassager

Monday 2:30 San Carlos I 💿 HP22

Detection of low levels of long-chain branching in polyolefins

Teresa P. Karjala[1], Robert L. Sammler[2], Marc A. Mangnus[3], Lonnie G. Hazlitt[1], Mark S. Johnson[4], Charles M. Hagen[1], Joe W. Huang[5], and Kenneth N. Reichek[1]

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Shear creep experiments have been applied to probe the zero-shear viscosity of molten undiluted polyolefin chains directly and precisely in a constant-stress rheometer at 190 ºC. Such experiments, when combined with precise measurements of weight-average molecular weight Mw data calibrated relative to linear chains of high-density polyethylene, provide a very sensitive approach to detect low levels of long-chain branching. This detection limit is shown to be insensitive to whether the molecular weight distribution is mono- or multi- modal, and/or to whether the molecular weight distribution breadth rises to about ten. The approach is also shown to be insensitive to low levels of short-chain branching found in poly(ethylene-co-butene) up to 12 wt% butene and poly(ethylene-co-hexene) up to 14 wt% hexene. This proposed method, based on Mw and zero-shear viscosity, is concluded to be one of the most sensitive, robust, and fast approaches to detect low levels of long-chain branching in polyolefin materials.

Monday 2:50 San Carlos I 💿 HP23

On the use of indexes for quantifying long-chain branching in polyethylene: Can we describe the rheology of LCB PE and correlate it to processing performance by using a single number?

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Numerous analytical techniques and methods have been developed in the past decades in order to study macromolecular architecture, especially for the case of polyolefines. The goal was and still remains to detect, with an enhanced sensitivity, long-chain branching (LCB) in polyethylene and accurately quantify the branching degree. The previous studies resulted in a large number of different methods and LCB indexes (LCBI), derived from mainly rheological techniques, as well as size-exclusion chromatographic and spectroscopical measurements (GPC-MALLS, NMR). The majority of the existing indexes is applied to a series of model branched high-density polyethylenes with constistently varying molecular weight and LCB distribution as well as commercial materials. Several contradicting results are derived using LCB indexes and branching factors. This confirms once more the complexity of the problem and the lack of a single universally applicable LCBI. The most reliable procedure for assessing LCB is proven to be a combination of information for molecular weight distribution from GPC, the LCB distribution from GPC-MALLS,as well as the branch relaxation in the loss angle vs. complex shear modulus curve (so-called van Gurp-Palmen plot) along with elongational strain hardening as a function of elongational rate. These two rheological methods agreed with the GPC-MALLS results, added valuable information on the chain structure and connected it to processing performance of the studied material.

Monday 3:10 San Carlos I 💿 HP24

Temperature dependence of the elastic compliance of polyethylenes with different molecular structure

Julia A. Resch[1], Joachim Kaschta[1], Florian J. Stadler[2], and Helmut Münstedt[1]

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The elastic properties of polymer melts are a research topic with many open questions. This is due to the fact that the measurements are not easy to perform but also that various molecular and topographic parameters like molar mass distribution or long-chain branching have influence on the elasticity. In this research project the elastic properties of well characterized polyolefins are studied.

As a first step, the steady-state recoverable shear compliances Je_0 of commercial linear and long-chain branched LLDPE and LDPE were measured at several temperatures between 110°C and 190°C. For the linear materials and the LDPE no temperature dependence of Je_0 was found. For the long-chain branched LLDPE, however, a decrease in Je_0 with increasing temperature was observed.

To explain this behaviour relaxation spectra using combined data from creep-recovery and dynamic-mechanical tests were determined for all temperatures according to the method of Kaschta and Stadler [1]. The spectra of the LCB-LLDPE clearly reveal different temperature dependencies of various parts of the spectra. Thus, the contribution of the retardation strengths to the kernel function of recoverable compliance are different at different temperatures resulting in a temperature dependent steady-state recoverable shear compliance.

[1] Kaschta J, Stadler FJ, Avoiding Waviness of Relaxation Spectra, submitted to Rheologica Acta 2007.

Monday 3:30 San Carlos I 💿 HP25

Rheological properties of HyperMacs — long chain branched analogues of hyperbranched polymers

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We report on rheological results from HyperMacs, new long chain branched analogues of hyperbranched polymers. HyperMacs are polystyrene based branched systems synthesised via one-pot reaction involving the polycondensation of well defined AB2 macromonomers prepared by anionic polymerisation and differing from hyperbranched systems only in the fact that they have polymer chains, rather than monomers between branch points. The synthesis of HyperMacs in which the linear polymer chain between branch points can be varied by controlling the molecular weight of the macromonomer, enables a tuning of molecular parameters of the branched polymers and facilitate their use in structure-property correlation studies. The synthetic strategy although very efficient results in an increased polydispersity when compared to the macromonomer building blocks. For this reason and to get more precise information about the effect of branching on the rheological properties, the raw HyperMac was fractionated. Melt rheology showed HyperMacs fractions to be thermorheologically simple, obeying William-Landel-Ferry behaviour. Zero shear viscosities of the polymers were shown to increase with average molecular weight and the melts display shear thinning behaviour. HyperMacs fractions showed little evidence for relaxation by reptation and the rheological behaviour agreed well with the Cayley tree model for hierarchical relaxation in tube models of branched polymers. The dependence of G' and G" in the terminal region of each HyperMac fraction was modelled by a power-law type relationship and linear regressions were performed on each of the fractions master curves to determine the fitting parameters. The slopes determined from this simple linear regression were used to compare the experimental data with theoretically predicted terminal region behaviour. The G' terminal gradients show an average value for all the fractions being 1.5 ± 0.05 that is in good agreement with the value predicted by theory for the relaxation of entangled branched polymers (Cayley tree).

Monday 3:50 San Carlos I ◉ HP26

The influence of shear thinning on elongation hardening of long-chain branched polypropylene

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Long-chain branched polypropylene shows pronounced strain hardening in elongation. This property, important for various applications is strongly reduced by shear applied to the melt before elongation.

In this work the influence of shear history on the rheological properties of blends from a linear (L-PP) and a long-chain branched (LCB-PP) polypropylene was studied in detail. Shear thinning is produced in a cone-plate device and the annealing of it is recorded by the storage modulus, G´, immediately after applying the shear deformation. In the case of L-PP this recovery function is simple exponential, whereas additional relaxation processes are found with the presence of LCB-PP in the blend. Both the effect of shear thinning and the annealing time increase with the degree of long-chain branching (more details on shear thinning are intended to be presented in a poster).

In order to investigate the elongational behaviour after various shear histories the sheared sample is removed from the cone-plate system, compressed into a flat sheet and quenched very fast to ensure residual shear thinning. Constant elongation rate experiments have been performed using a uniaxial extensional rheometer, the SER universal testing platform where the tensile stress growth coefficient, $\eta_E^+(t)$, is recorded. Shear thinning reduces elongation hardening reversible. The annealing of this reduction depends on the shear history and the degree of long chain branching. The maximum of $\eta_E^+(t)$ is reduced tremendously by shear thinning even at low shear strains, e. g. for LCB-PP $\gamma = 5$ gives a reduction of ~ 40% and $\gamma = 90$ gives ~ 70% being about the maximum, but it is of interest that strains higher than $\gamma = 90$ influence the annealing remarkably. In addition larger shear strains shift the start of elongation hardening to higher elongation strains. These effects decrease with lower degree of long-chain branching. The annealing behaviour of the reduction of elongation hardening is very similar to that of shear thinning.

Monday 4:10 San Carlos I ◉ HP27

Strain hardening in uniaxial elongation vs. temperature for random copolymer melts with high comonomer content

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The extent of sparse long chain branching in metallocene-catalyzed random ethylene-alpha-olefin copolymers is known to go down with increasing comonomer content [Villar et al., 2001] and become progressively harder to detect. In general, even small levels of long chain branching lead to strain hardening in elongational flow; but this may be associated with a variety of other features such as a broad molecular weight distribution or a high molecular weight tail. Various characterization techniques have been proposed to detect small levels of long chain branching in copolymers with less than 20 wt% of comonomer- see e.g. Janzen and Colby (1999), Malmberg et al. (2002), Crosby et al. (2002) and van Ruymbeke et al. (2005, 2006).

The object of this paper is to present experimental results on the transient uniaxial elongational viscosity for a metallocene-catalyzed random ethylene-octene copolymer melt with much higher comonomer content – 38 wt% octene, for which the zero shear viscosity and the vanGurp-Palmen plot from dynamic moduli (cf. Trinkle et al., 2002) do not indicate long chain branching and also the molecular weight distribution is not broad. This material melts at 48°C and the flow tests were conducted in a Rheometrics Melt Elongational Rheometer (RME) at 120°C and 150°C up to Hencky strains of 3 over strain rates of 0.01 s^{-1} to 1 s^{-1}. Experimental procedures were verified with tests on a linear polypropylene known not to strain harden at 180°C. No strain hardening was observed for this polymer melt, which is consistent with published results of Spitael and Macosko (2004).

The random copolymer melt with 38 wt% comonomer showed distinct strain hardening at both 120°C and 150°C. The strain hardening ratio (with respect to $3\mathrm{eta}_0^+$) was greater at 120°C and also declined more gradually with strain rate at this temperature. The maximum value of strain hardening ratio was 3.7 at 120°C compared to 2.8 at 150°C. These values were greater than the strain hardening ratios observed at both temperatures for another random copolymer melt with (lower) 20 wt% comonomer; the presence of long chain branching in the latter case was evident from a vanGurp-Palmen plot- cf. Patham and Jayaraman (2005). The steady state creep compliance values were very close for these two copolymer melts, ruling out differences in high molecular weight components. The above results can be explained by applying a simple construction involving the relaxation spectrum $H(\lambda)$. A plot of lambda $H(\lambda)$ vs. $\log(\lambda)$ for the copolymer with 38 wt% octene showed two distinct peaks – one associated with the backbone and another associated with long chain branches which were not detected by zero shear viscosity or by vanGurp-Palmen plots.

Monday 4:30 San Carlos I HP28

Thermorheological behaviour of various polyolefins in the linear and non-linear viscoelastic regime

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From literature it is well known that polyethylenes can be thermorheologically simple or complex. A clear distinction is not made, however, between the viscoelastic properties in the linear and nonlinear regime. This paper deals with a systematical determination of activation energies of various polyethylenes in the linear and nonlinear range. The linear ethylene homopolymers (HDPE) are thermorheologically simple under all the conditions applied, the LDPE investigated were found to be thermorheologically simple in the linear range, but thermorheologically complex in the nonlinear regime. The activation energy decreases with increasing stresses and approaches the value of the HDPE. Long-chain branched polyethylenes polymerised with metallocene catalysts do exhibit a thermorheological complexity even in the linear range of deformation.

Various branching topographies i. e. the branch length, content and distribution lead to differences in the thermorheological behaviour and result in different dependencies of the flow activation energies on the relaxation times or strengths, respectively. Thus, it will be shown in which way the thermorheological behaviour of various polyethylenes can be used to get an insight into the branching architecture.

Monday 4:50 San Carlos I HP29

Melt rheology of polyvinilydene fluoride: Evidence of long chain branching and microgel formation

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Rheological measurements are used to study the influence of molecular weights and molecular weight distributions (MWD) on the melt polymer behavior of poly(vinylidene fluoride) (PVDF). These measurements are aimed at explaining the bimodal MWD displayed by PVDF when it is produced by continuous precipitation polymerization in supercritical CO_2 ($scCO_2$). The rheological behavior of polymer melts is strongly influenced by their molecular weight and especially by their architecture and MWD. Six commercial PVDF samples with weight-average molecular weight ranging from 139 to 263 kg/mol and polydispersity index ranging from 2.3 to 4 are investigated. The use of the Cole-Cole and van Gurp-Palmen (vGP) plots unequivocally reveals the presence of long-chain branching (LCB) in three of the samples. They furthermore allow for a qualitative classification of these samples by their LCB degree. The Mark-Houwink relationship between the intrinsic viscosity and weight-average molecular weight is determined and shows no dependence on a low degree of LCB. A similar effect is observed for the flow activation energy which increases linearly with increasing weight-average molecular weight with the exception of the flow activation energy for the highly branched PVDF sample. The power law relationship between low/zero shear viscosity and weight-average molecular weight holds for linear PVDFs while a strong deviation is exhibited by LCB PVDFs in agreement with the deviation to the Cox-Merz rule observed for these samples. The extent of this deviation, measured as the ratio between the low complex viscosity and the low/zero shear viscosity, increases with increasing degree of branching. In addition, samples known to contain microgels are also identifiable by extending the vGP analysis. The generality of this approach is substantiated by removal of the microgel fraction from these samples, which then exhibit conventional rheological characteristics.

Monday 5:10 San Carlos I HP30

Nonlinear viscoelastic and viscoplastic behavior of PET-based multi-layer polymeric films used in super-pressure balloon envelopes

Martin Hirsekorn[1], Frank Petitjean[2], and Arnaud Deramecourt[1]
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Super-pressure balloons provide a cheap, non-polluting, and quickly operable platform for in-situ measurements at altitudes up to about 25 km, and for remote-sensing of earth, atmosphere, and space from regions inaccessible to other means of transportation over similar observation periods. They are lifted by a helium filled, approximately spherical, closed envelope made of a PET based multi-layer polymeric film. The filling quantity of lifting gas is adjusted such that the envelope remains pressurized throughout the flight once float altitude is reached. The volume of the envelope is thus relatively insensitive to variations of internal and external pressure and gas leakage is limited to a minimum, permitting long term flights of up to several months. Nevertheless, the volume changes considerably due to deformation of the envelope material caused by the varying difference between internal and external pressure during day and night cycles. To control the balloon altitude (e.g., by means of varying the gas quantity or dropping ballast), it is essential to know precisely the evolution of the material deformation in time under constant and varying stress. We have carried out a series of creep and recovery tests at different stress levels using samples of the envelope film, which show that the response of the material is strongly time dependent, including viscoelastic and viscoplastic deformation, which both depend nonlinearly on stress. Moreover, the observed time dependence of strain during creep depends strongly on stress. Shifting along the logarithmic time and strain scales is not sufficient to superpose the strain curves at different stress levels. We present a model for the viscoelastic and viscoplastic behavior of the film that takes into account the dependence of the strain response on creep stress. For easy numerical implementation, the observed strain response is represented by a Prony series, whose coefficients form a continuous spectrum on the logarithmic retardation time scale. The spectrum is well approximated by an exponential power law distribution with exponent 3. The distribution is fully characterized by three stress dependent parameters: its center, width, and an intensity factor, corresponding to the maximum coefficient. The stress nonlinearities can be expressed in terms of simple analytic functions. The experiments show that both viscoelastic and viscoplastic strain are highly stress dependent over a limited stress range only and are approximately linear at low stresses and around the maximum stress reached during flight. A continuous threshold function is proposed that approximates well the observed stress dependence of the intensities. It is assumed that the other viscoelastic (viscoplastic) parameters change around the same threshold as the viscoelastic (viscoplastic) intensity and are approximately constant elsewhere. The model reproduces very well the experimentally observed strain response and provides a good prediction of the response at different stress levels.

MR-2. Passive and Active Microrheology

Organizers: Eric M. Furst and David A. Weitz
Session Chairs: Patrick T. Spicer and Matthew L. Lynch

Monday 2:30 Redwood MR7

Non-linear microviscosity of a colloidal suspension

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Measurements of the non-linear microviscosity of a suspension are affected by both direct probe-bath interactions, and bath-bath interactions. The latter can be correlated directly to macroscopic rheology, while the former is potentially an artifact that complicates the comparison between microrheological and bulk rheological characterization. Therefore, by studying these contributions, one can develop a more accurate comparison with macroscopic measurements, and develop non-linear microrheological methods. To explore these concepts further, we study the behavior of a colloidal suspension using active and oscillatory microrheology at large amplitudes. The experimental system is a suspension of index and density matched polymethyl methacrylate particles (PMMA), seeded with 3 μm melamine probes. The probe particles are trapped and oscillated using laser tweezers at frequencies that are typically less than 3 Hz and at amplitudes of 500 nm – 4 μm. The oscillation amplitude and phase of the probe are measured using a combination of video microscopy and a photo diode and lock-in amplifier system, and these values are used to compute the frequency and amplitude dependent microviscosity of the suspension. We determine the low frequency behavior of the suspension, and determine the transition from a linear to non-linear fluid response as a function of amplitude.

Monday 2:50 Redwood MR8

Linear and nonlinear microrheology of colloidal suspensions: Two distinct sources of stress

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Passive microrheology investigates the near-equilibrium, linear response properties of complex materials using the thermal motion of a probe particle. These same properties may be explored by gently but actively oscillating the probe. Stronger forcing more drastically drives the material out of its equilibrium state, potentially providing a window into the nonlinear rheological response of the material. The linear-response approach that underpins passive microrheology does not hold for nonlinear microrheology, necessitating a theoretical framework for its interpretation. Using a model system of a large colloidal probe immersed in a suspension of bath particles, we investigate the various sources of the stress on the (forced) probe. We discuss the two distinct classes of stress that arise: the direct interactions between the probe and the material, and the stresses due to microstructural deformation in the bulk. We treat two illustrative systems: (i) small-amplitude probe oscillations, wherein the rheological stresses from the bulk do indeed give rise to a Generalized Stokes-Einstein (Sutherland) Relation that is quantitatively consistent with the macroscopic linear viscoelastic properties, whereas the direct probe-material interactions give additional features to the GSESR that are not consistent with macro-rheology; (ii) steady probe motion through the material, which can give rise to a strongly non-equilibrium material microstructure. Again, we treat both direct and bulk stresses, and argue that the latter reflect the bulk rheology. Finally, we compare our results with experiments from Furst et al.

Monday 3:10 Redwood MR9

Bulk and DWS-based microrheology on vesicle depletion mixtures

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The addition of non-absorbing polymer to vesicle dispersions can result in extensive depletion-induced vesicle aggregation and phase separation or gelation. The time scale of phase separation and gel collapse is determined by a balance of gravitational, viscous and elastic forces. It is our desire to better anticipate the time-scale of the macroscopic changes by developing a measurement of the local viscoelastic properties, which should be related to relaxation processes associated with aging and macroscopic changes. The local viscoelastic properties are determined by diffusing wave spectroscopy (DWS)-based microrheology where moduli are computed from the motion of the vesicles. In this work, comparisons of frequency dependence and magnitude of the local and bulk elastic and viscous moduli are made on mixtures after polymer addition but before the appearance of macroscopic heterogeneities. In phase separating mixtures, the agreement between techniques is excellent. However, in gelling mixtures above the percolation threshold, there is a low-frequency crossover not present in the bulk rheology and magnitudes of the local moduli are two-orders of magnitude larger. In gelling mixtures below the percolation threshold, although the frequency dependence is similar, the magnitudes of the local moduli are also two-orders of magnitude larger than the bulk moduli. Fluorescent microscopy measurements indicate that differences are evident when the characteristic length scale of the mixture greatly exceeds l^*, the transport mean free path of the light. A combination of local and bulk viscoelastic properties (the latter typically used to parameterize the time-scale of changes) should offer unique insights into the role of different length-scales and processes on rate of macroscopic separation. An example will be presented with "cracking" gels.

Monday 3:30 Redwood MR10

Multiple particle tracking (MPT) measurements of heterogeneities in acrylic thickener solutions

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Synthetic acrylic polymers are frequently used as thickening agents in water-based coatings and adhesives or personal care products. Typically, these commercial alkali-swellable acrylates form inhomogeneous partly aggregated or cross-linked solutions. Inter- and/or intramolecular aggregation is due to hydrophobic groups randomly distributed along the chains and can be varied through the solvent quality. Crosslinking can be induced either thermally or by adding appropriate crosslinking agents during synthesis. Accordingly, such thickener solutions cover a wide range of rheological behavior, ranging from weakly elastic, almost Newtonian to highly elastic gel-like. Despite its high technical relevance, nothing is known so far about the contribution of the micro-scale inhomogeneities to the bulk viscoelastic properties.

Here we use the method of MPT, which was originally described by Apgar et al. [1], to quantify the degree of structural and mechanical micro-heterogeneity [2] of such acrylic thickener solutions. We use two commercial thickeners (Sterocoll FD and D, BASF AG) as model systems. The principle consists of monitoring the thermally driven motion of inert microspheres that are evenly distributed within the solutions and to statistically analyze the distribution of mean square displacements, from which information about the extent of heterogeneity can be extracted. We have used fluorescent polystyrene microspheres as tracer particles. The mixture containing the thickener solution including the tracers was deposited into a self build glass slide. Images of the beads were recorded via a progressive scan camera (AVT Pike, up to 60 fps) mounted on an inverted fluorescence microscope (Axiovert 200, Zeiss), equipped with a C-Apochromate 40x, 1.2 n.a, water-immersion lens combined with a 2.5x optovar. Movies of fluctuating microspheres were analyzed by the Image Processing System (Visiometrics iPS) sofware and the statistical analysis by Enthought Microrheology Lab sofware.

The ensemble-averaged MSD of Sterocoll FD solutions exhibited a power-law behavior scaling linearly with time, as expected for weakly elastic fluids and similar to that observed for a homogeneous aqueous glycerol solution, used as a reference system. However, the MSD distribution was wider and more asymmetric than for the glycerol solution. For the highly elastic Sterocoll D, the average MSD exhibits a subdiffusive behavior ($\Delta r^2(t) \sim t^\alpha$ with $\alpha < 1$), typical for highly elastic solutions. Moreover, the displacements of microspheres at different locations within the solution display a wide range of amplitudes and time dependences. The MSD-distribution is very broad / bimodal. A significant fraction of the particles is elastically trapped. The effect of solvent quality and crosslinking on the microscopic inhomogeneities is discussed.

[1] Apgar, Biophys. J. 2000, 79, 1095; [2] Weitz, D.A., Phys. Rev. E , 2001, 64, 061506

Monday 3:50 Redwood MR11

Microrheology of responsive hydrogel networks

Travis H. Larsen[1], Joel P. Schneider[2], and Eric M. Furst[1]

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Hydrogel networks offer exciting possibilities for the rational design of novel materials. Properties specific to tissue engineering, such as biocompatibility, biodegradability and remodeling characteristics, are dependent on the environmental responsiveness of the material. Thus, recent research has focused on using small peptide sequences that assemble or even self-assemble into materials. Peptides can be engineered such that the formation and final properties display responsive behavior. In this talk, we discuss the gelation kinetics of self-assembled hydrogels consisting of a beta-hairpin peptide. These materials are investigated using microrheology and far-UV circular dichroism (CD) spectroscopy. The intramolecular folding of this peptide is engineered to control its self-assembly into beta-sheet rich hydrogels. When the peptide is unfolded, it does not self-assemble, and aqueous solutions have the viscosity of water. Folding and consequent self-assembly are triggered by changes in pH, temperature or ionic strength. This folding and self-assembly mechanism allows temporal control of the material formation. CD spectroscopy shows that the kinetics of beta-sheet structure formation occurs in a concentration-dependent manner, but does not provide information on the kinetics of network assembly. Multiple particle tracking microrheology is used to define exact gelation times as a function of peptide concentration. The principles of time-cure superposition are used to rescale the mean-squared displacement of probe particles onto master curves before and after the gel point. A time shift factor accounts for divergence of the longest relaxation time as the gel point is approached, and a second shift factor characterizes the decrease in compliance as the gel network forms and becomes more elastic. By analyzing the shift factors based on scaling relationships near the liquid-solid transition, we are able to accurately determine both the gel time and critical exponents of the incipient gel. The gel point provides a key reference from which to define the kinetics of gelation, while the critical exponents provide insight into the gel connectivity. Overall, this enables an empirical relationship to be established between the rheologically-defined gelation time and the onset of beta-sheet formation as measured by CD.

Monday 4:10 Redwood MR12

Modeling aspects of two-bead microrheology

Christel Hohenegger[1] and M. Gregory Forest[2]

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We revisit the Mason and Weitz (Phys. Rev. Lett., 74, 1995) and Levine and Lubensky (Phys. Rev. Lett., 85, 2000) analysis for one- and two-bead microrheology. Our first motivation is the possibility of drawing inferences from experimental data about local diffusive properties of individual beads and nonlocal dynamic moduli of the medium separating the two beads. Our second motivation is the ability to perform direct numerical simulations of hydrodynamically coupled Brownian beads in soft matter. For both goals, we first must have a model for the coupling between these two transport properties. We reformulate the coupled generalized Langevin equations (GLE) following the scalar GLE analysis of Fricks et al. (J. Appl. Math., 2008), assuming an exponential series parametrization of both local and nonlocal memory kernels. We then show the two-bead GLE model can be represented as a vector Ornstein-Uhlenbeck process, which allows for a fast and statistically accurate numerical simulation of coupled bead paths (time series) and of ensemble-averaged statistics of the process. In this proceedings, we announce the framework to accomplish these two goals of inversion and direct simulation.

Monday 4:30 Redwood MR13

Material assembly and gelation kinetics of PEG-heparin hydrogels using multiple particle tracking microrheology

Kelly M. Schultz and Eric M. Furst

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Recently, heparin functionalized polymer scaffolds have been developed for tissue engineering applications. Such materials are designed to mimic the structural and mechanical properties of the extra-cellular matrix, while providing controlled sequestration and release of soluble factors, such as growth factors. We investigate the material properties of these chemically crosslinked, synthetic hydrogel systems. The experimental system is composed of the crosslinker, linear dithiolyated poly(ethylene glycol), and the network backbone, maleimide functionalized heparin. Multiple particle tracking is performed on material with one micron poly(styrene) probes embedded into it. Experiments capture the material response over short and long times. The short time data is taken to study the gelation kinetics of the material, while equilibrium measurements provide information about the final hydrogel properties. The hydrogel composition and the functionality of the heparin are systematically varied to establish regions of gelation. With this information, we are able to create a quantitative library of material assembly conditions as a function of crosslinker to backbone ratio, backbone functionality and total polymer concentration for applications in tissue engineering.

Monday 4:50 Redwood MR14

Effect of concentration on the microstructure of a yield-stress fluid

Felix K. Oppong and John R. de Bruyn
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Carbopol is a model yield-stress fluid used as a thickener in several products such as toothpaste and hairgel. Previous microrheological studies have shown that Carbopol is heterogeneous on micron length scales [1, 2]. In this work, we investigate the effect of Carbopol concentration c on the microstructure and microrheology of the fluid using the multiple particle tracking technique. We studied Carbopol samples with c ranging from 0.01 to 1.0 weight %. Over a range of times t, the squared displacement of the individual tracer particles grows as t^{α} where α is the diffusive exponent. At low concentrations all particles have essentially the same value of α. Above a critical concentration c* which corresponds to the appearance of a bulk yield stress, the distribution of α becomes bimodal, indicating the presence of a "fast" population of particles with α approximately equal to 0.8 ±0.1 and a "slow" population with α approximately equal to 0.4 ±0.2 Microrheology shows that the environment of the fast particles is predominantly viscous, while that of the slow particles is predominantly elastic. The fraction of particles in the slow population grows with increasing concentration as the bulk material become more elastic.

[1] F.K. Oppong, L. Rubatat, A.E. Bailey, B.J. Frisken, J.R. de Bruyn, Microrheology and structure of a polymer gel, Physical Review E **73** (2006) 041405; [2] F.K. Oppong and John R. de Bruyn, Diffusion of tracer particles in a yield-stress Fluid, Journal of Non-Newtonian Fluid Mechanics **142** (2007) 104.

Monday 5:10 Redwood MR15

Micro-rheology using multispeckle DWS with video camera: Application to film formation, drying and rheological stability

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We present in this work two applications of the microrheology technique: the monitoring of film formation and the rheological stability. Microrheology is based on the Diffusing Wave Spectroscopy (DWS) method [1,2] that relates the particle dynamics to the speckle field dynamics, and further to the visco-elastic moduli G' and G'' with respect to frequency [3]. Our technology uses the Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. For film formation and drying application, we present a new algorithm called "Adaptive Speckle Imaging Interferometry" (ASII) that extracts a simple kinetics from the speckle field dynamics [4][5]. Different film forming and drying have been investigated (water-based, solvent and solvent-free paints, inks, adhesives, varnishes, ...) on various types of substrates (metal, plastic, glass, PMMA, paper...) and at different thickness (few to hundreds microns). From the kinetics of film formation, a wide range of information can be extracted such as objective drying times (open time, touch-dry, dry-hard times, etc.), mechanism taking place (solvent evaporation, coalescence, cross-linking...), thereby offering new possibilities to investigate film formation and drying from complex colloidal systems. For rheological stability we show that the robust measurement of speckle correlation using the inter image distance [4] can bring useful information for industry on viscoelasticity variations over a wide range of frequency without additional parameter.

[1] PE Wolf and G. Maret, "Multiple Light Scattering from Disordered Media. The Effect of Brownian Motion of Scatterers" Z. Phy. B 65, 409, 1987; [2] D.J.Pine, D.A. Weitz, P.M. Chaikin and E. Herbolzeimer. "Diffusing Wave Spectroscopy". Phy Rev. Lett. 60, 1134, 1988; [3] T. G. Mason, K. Ganesan, J. H. van Zanten, D. Wirtz, and S. C. Kuo. "Particle Tracking Microrheology of Complex Fluids". Phy Rev. Lett. 79,17, 1997; [4] L. Brunel, A. Brun, P. Snabre, L. Cipelletti. "Adaptive Speckle Imaging Interferometry: a new technique for the analysis of microstructure dynamics, drying processes and coating formation" Optics Express, Vol. 15, Issue 23, pp. 15250-15259; [5] A. Brun, H.Dihang, L.Brunel 'Film formation of coatings studied by diffusing-wave spectroscopy", Process in Organic Coatings 2007.

MP-2. Coating and IT Applications

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: Kyung Hyun Ahn

Monday 2:30 Ferrante I-III MP7

Effects of process condition and material properties on replication and structural development in thermal nano-imprinting

Tadashi Matsumoto[1], Ken Miyata[1], Hiroshi Ito[1], Hiroshi Suzuki[2], and Tomonobu Furuta[2]
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Polymer film with nano-scale features surface of polycarbonate (PC) were produced by using thermal nano-imprinting process to analyze these effects of molding conditions and film properties on the replication of surface pattern, thermal shrinkage, and higher-order structure development of printed films. Replication ratio, which was defined as to feature height of film surface and depth of metal stamper, was increased at imprint temperature and its pressure. Residual strain of printed film was influenced by the imprint conditions, and it was increased with decreasing the cooling time. The optical retardation of film also was influenced by the imprint condition. In particular the retardation was decreased at higher imprint temperature and longer cooling time. Nano-features on the film also were unstable because large surface area and high residual strain. The surface thermal properties were investigated during heat treatment below the glass transition temperature.

Monday 2:50 Ferrante I-III MP8

Break-up of viscoelastic liquid curtain

Melisa Becerra and Marcio S. Carvalho
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Curtain coating is one the preferred methods for precision, multilayer coatings at high speeds. A thin liquid sheet, or curtain, falls freely over a considerable height before it impinges onto the substrate to be coated. Precision curtain coating was originally developed for multilayer photographic film but its use has expanded to many different applications such as optical films and specialty papers. Some advantages of this process include very high coating speeds, adaptability to a wide range of liquids and flexibility to apply thin liquid layer to irregular surfaces. The operability limits of the process are set by different flow instabilities in the coating bead, such as air entrainment, low speed heels and curtain pulling, and by curtain breakup. The conditions at which a Newtonian liquid curtain breaks can be derived based on simple balance between inertial and capillary forces. High speed visualization presented in this work shows in detail how a liquid curtain breaks. For a given liquid, there is a critical flow rate bellow which the curtain becomes unstable, creating a lower bound for the wet film thickness that can be coated. For viscoelastic liquids, the normal tensile stress related to the stretching of the polymer molecules as the liquid accelerates down the curtain changes the force balance. In this research, the critical condition at which a viscoelastic liquid curtain breaks is determined as a function of the rheological properties of the coating liquid. The results show that high extensional viscosity liquids create more stable coating. Liquid additives could be used in order to push the limits of curtain flow rates to smaller values.

Monday 3:10 Ferrante I-III 💿 MP9

Transient coating of the inner wall of a straight tube with a viscoelastic material

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We examine the transient coating of a straight tube with viscoelastic liquids. In particular, we investigate the case where a finite amount of viscoelastic material initially placed inside a tube is displaced by pressurized air so that it coats the inner surface of a very long tube. This involves the combined motion of the advancing front of the liquid, the formation and growth of an air bubble in its rear interface and the deposition of a thick film along the tube wall. The solid wall is assumed rough enough so that the no-slip condition can describe the wall-liquid interaction. This assumption results in a continuous collision of liquid parcels on the tube wall and the consequent motion of the advancing front. For the simulation of the processes the mixed finite element technique is combined with the Discontinuous Galerkin method for computing the extra stress tensor. A quasi-elliptic grid generation scheme is used for computing the highly deforming liquid domain and its boundaries. Global remeshing methodologies are also adopted in order to overcome difficulties arising from the collision of nodes on the advancing liquid front with the tube wall. The accuracy of the global solution is verified by selectively increasing the resolution of the mesh along areas where sharp boundary layers in polymeric stresses appear. A complete parametric analysis is performed in order to examine the effects of elasticity and inertia and of various rheological parameters. Results using the affine PTT constitutive model with a small value of the parameter in the exponent show that the thickness of the remaining film increases as the solvent viscosity decreases, because of the development of large the normal viscoelastic stresses along the bubble front and in the deposited film to the point that boundary layers in stress arise on the rear side of the film. On the contrary, increasing the extensional parameter decreases the film thickness. Inertia causes flattening of the advancing front, and non-uniform film distribution along the entire wall as well as acceleration of the process. Because of the transient nature of the calculations, viscoelastic stresses require longer time to become fully-developed as the Deborah number increases. Therefore, the effect of elasticity becomes less pronounced for higher values of . In all cases, the streamlines follow a 'fountain flow' pattern when viewed from a coordinate system located at the liquid tip, given that capillary forces are taken to be small. Two additional models are also examined; the FENE-CR and the Giesekus, and their predictions are compared to those of the PTT model.

Monday 3:30 Ferrante I-III 💿 MP10

Cracking in drying silica-polymer films: Morphology transitions

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Colloidal suspensions containing soluble organic binders are commonly used in paper coating applications to produce a porous particle-filled polymer matrix as the ink-absorption layer. During the drying process, the liquid meniscus between particles gives a negative capillary pressure, which draws in more particles toward the air-liquid interface and concentrates particles at the evaporating interface. The capillary action, as well as the constrained shrinkage of films binding to the substrate, can yield stresses in the coating. The film spontaneously cracks to release the stress when the magnitude of the stress exceeds a critical value. The cracking is detrimental to the coating products because liquid droplets penetrating into the crack can loose the final image quality. Despite the extensive studies for the stress development and subsequent cracking, the microscopic cracking behavior in particle-polymer coatings is far from complete understanding. Here we investigate the crack propagation in drying nano particle-polymer films cast on plane substrates. Silica-poly(vinyl alcohol) aqueous suspension coatings are dried on a transparent hot stage to acquire time-lapse microscope video images. The direct imaging reveals two distinct regimes: cracks nucleate, propagate and contact with each other to form a network pattern at high particle/polymer weight ratios, whereas the cracks stop propagating in a finite drying time and remain as isolated star-like patterns at lower particle contents. The morphology transition from the network- to star-like patterns was quantified from the crack surface density measurements. The density of crack nucleation points first increases and then decreases with increasing the particle contents, suggesting that the transition from star- to network-like cracks significantly release the stress to retard further crack nucleation. Drying regime maps demonstrate that the crack morphology can be regulated by tuning the initial suspension composition, film thickness, and drying conditions.

Monday 3:50 Ferrante I-III MP11

The effect of PVA adsorption on stress development during drying in PVA/silica suspension coating

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Liquid coating is necessarily followed by solidification through the drying process. During and after solidification, coating layer shrinks due to solvent evaporation. In the meanwhile, the stress develops because of volume shrinkage frustrated by adhesion of coating to a rigid substrate and causes defects such as peeling, cracking, curling and wrinkle. Many industrial coating materials are considered as a suspension which contains particles to give specific function like protection, conductivity, or optical purpose, for example. With the presence of the particles, it is challenging to control the microstructure of the suspension due to non-uniform distribution or aggregation of the particles. Previous researches demonstrated the importance of particle dispersion of starting aqueous suspension on the final properties of pigmented coatings. Although there exists experimental evidence that relates the initial condition of coating material to the final property, there is little understanding on the mechanism of microstructure or property evolution during drying in terms of process control. In this study, stress evolution during film formation of poly (vinyl alcohol)/silica suspension was measured with beam deflection method under the controlled environment. Rheological property of starting material was characterized with bulk rheometry, and the structural heterogeneity during drying was evaluated with particle tracking microrheology. Process variables chosen for this study were dispersion stability (pH) and the ratio of silica to PVA. Structural heterogeneity and stress development of suspension coating were found to depend on both pH and silica-PVA ratio. The reason is to be explained in terms of PVA/silica adsorption and dispersion stability.

Monday 4:10 Ferrante I-III MP12

Rheology and wetting properties of fluxes for flip chip packages

Jinlin Wang

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As the electronic industry is transitioning to lead free packages, this leads to significant challenges for solder, flux, and process developments. In flip chip packages, flux materials are used in several process steps, such as die attach, heat spreader attach, and solder ball attach. Depending on the flux process, such as screen print or dispense, the required flux viscosity can be very different. Flux materials with different chemistries are often needed for lead free packages with high peak temperature reflow profiles. Due to the flux chemistry and formulation difference, the rheological behavior of the fluxes can be quite different. It is critical to have a good understanding of the rheology properties of the flux and its correlation with the flux process in flip chip packages. This can help in optimizing the process conditions and reduce package defects. In the screen print process of a ball attach flux, the shear rate is relatively high. A relatively low viscosity is desirable for the printing process. After the print process, the shear rate is low and a high viscosity can help the flux stay in shape. A controlled stress rheometer was used to measure the viscosity of fluxes as a function of shear rate. The fluxes showed strong shear thinning behavior. Pot life test was conducted to study the stability of the flux. Some fluxes showed wall slippage in the viscosity test. A dynamic rheology test with small amplitude deformation was used for these fluxes. Yield stress and creep recovery tests were also conducted and the correlation of these rheological properties with the ball attach process was studied. Contact angle, surface tension, and tackiness are also important properties affecting flux process. The surface tension and contact angle of fluxes were measured for fluxes. The correlation between the wetting properties of the fluxes and flux performance in the process will be discussed.

Monday 4:30 Ferrante I-III MP13

Rapid convective deposition of microsphere monolayers for fabrication of microlens arrays

Pisist Kumnorkaew[1], Yik-Khoon Ee[2], Nelson Tansu[2], and James F. Gilchrist[1]

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Micron-sized microspheres were deposited into thin films via rapid convective deposition using a similar method to that studied by Prevo and Velev, Langmuir, 2003. By varying deposition rate and contact angle, the optimal operating ranges in which 2D closed-pack of silica existed were obtained. Using a confocal laser scanning microscope, dynamic self-assembly of colloidal particles under capillary force during solvent evaporation was revealed. The resulting microstructure is controlled by varying the macroscale parameters and interaction between substrate and colloidal particles played an important role in formation of ordered crystalline arrays. Using the same technique, stacked layers of 1 micron silica monolayer on top of 1.1 micron polystyrene monolayers and subsequent melting of the polystyrene to partially wet the silica microspheres were deposited on GaN layer. This process was implemented on the top p-GaN layer of InGaN quantum wells light emitting diode (LEDs) device structure, resulting in the formation of a microlens array for enhancing its light extraction efficiency. This approach led to ~230% increase of the LEDs output power.

Monday 4:50 Ferrante I-III MP14

Modeling of the stress distribution of the pressure sensitive adhesive in the multi-layered structures

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Pressure sensitive adhesive (PSA) has been widely used to bond various substrate materials in the multi-layered structures. Because of the dissimilar thermomechanical or hygromechanical behaviors of substrates, PSA experiences the large shear stress, which causes the delamination of substrate or the stress-induced birefringence in the multi-layered structures. Therefore, the control of the stress distribution in the PSA layer is very important in designing the multi-layered structures for the specific purposes. In this work, a mathematical model is developed for calculating the stress distribution of the PSA, which is induced by the dimensional change of substrates. The domain of the multi-layered structure is divided into sub-elements. The system of equations of the force balance for each sub-element is solved simultaneously for the calculation of the stress distribution. In this work we show two examples of the model prediction. In the first one, we calculate the stress distribution of PSA caused by the dimensional change due to the dissimilar coefficient of thermal expansion (CTE) of the substrates and compare the model predictions with the analytical solutions. In the second one, we show the prediction for the light leakage of the polarizer in the liquid crystal display

(LCD). The results of this work indicate that the developed model can be used for optimizing the stress distribution in the multi-layered structures. In addition, the model can predict well the pattern of the light leakage of the polarizer.

Monday 5:10 Ferrante I-III MP15

Extruded proton exchange membranes based on sulfonated polyaromatic polymers for fuel cell application

Yannick Molmeret[1], France Chabert[1], Cristina Iojoiu[2], Nadia El Kissi[1], Jean-Yves Sanchez[2], and Yves Piffard[3]
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A global approach of membranes elaboration in environmentally friendly conditions and at a moderate cost for applications in the fuel cells industry is proposed. Polyethersulfones (PSU) were chosen due to their solubility in organic solvents, useful for sulfonation, a necessary chemical modification to give them proton conductivity property. This could also be improved by filling the polymer with a solid inorganic proton conductor i.e. phosphatoantimonic (H3). Extrusion was chosen to process the membranes since it is a continuous process, adapted to large scale production of thin homogeneous films. However, it had to be adapted to PSU ionomers as, due to their high Tgs, their extrusion should be performed at high temperature and might induce a thermal degradation of the sulfonic functions. Two routes were explored for that: (i) extrusion of commercial PSU followed by membrane sulfonation; (ii) direct extrusion of sulfonated PSU. The best compromise between the sulfonation degree, i.e. the Ion Exchange Capacity (IEC), and the mechanical performance, was determined. It was shown through differential scanning calorimetry measurements (DSC) that ionomer's Tg increases linearly with the IEC, indicating an increase of the polymer stiffness with the incorporation of sulfonic functions. This was confirmed by rheometry, as the viscosity is higher for the ionomeric PSU. Increasing the IEC also leads to the degradation of the PSU at temperatures Td as low as 250°C. The difference between Tg and Td is thus too small to perform extrusion. The modified PSU blended with different weight% of adequate plasticizers was thus considered and it was finally possible to produce square meter films of the plasticized ionomer in a semi industrial production line. Conductivity of the extruded membranes was characterised after total removal of the plasticizer, the extruded membranes exhibiting promising conductivities. As sulfonated PSU have lower thermomechanical properties than the pristine PSU, H3 fillers were introduced to increase the conductivity, while keeping a moderate sulfonation degree. The filled PSU was characterized on a broad range of temperatures and shear rates using drag flow and capillary rheometers. PSU shear behavior is unmodified by the addition of the inorganic filler. This was ascribed to the polymer/filler compatibility. DSC and size exclusion chromatography were performed to evaluate the impact of the process on the polymer. Neither modification of the glass transition temperature, nor of the molecular weight distribution of the polymer was observed, indicating that, despite its strong acidity, H3 does not affect the chemical stability of the PSU matrix. Still again, extruded filled membranes showed good proton conductivity, without degrading the mechanical properties. This study shows that it is possible to produce, from ionomers based on high performance polymeric backbone as PSU, extruded membranes dedicated to PEM fuel cells, while avoiding any thermomechanical degradation.

IR-2. Interfacial Rheology and Thin Film Flow

Organizers: Jan Vermant and Kausik Sarkar
Session Chairs: Omar Matar and Jan Vermant

Monday 2:30 Bonsai I IR7

Advancing contact line dynamics induced by soluble surfactant deposition on a thin liquid film

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Recent experimental results have helped to elucidate the mechanisms of surfactant enhanced spreading and the subclass of superspreading. Unfortunately, the multiple scale nature of the problem has hindered a generalised theoretical treatment. Macroscopic models have not had the required resolution to capture the dynamics at the contact line where a thin precursor layer is seen in experiments and dynamic variations in wettability are expected to be important. We examine the dynamics in this region in the presence of surfactant above the critical micelle concentration. We couple a lubrication model to advection-diffusion equations for surfactant transport allowing for micelle formation and break-up in the bulk and adsorptive fluxes at both interfaces. Equations of state are supplied to model variations in surface tension and wettability. We exploit the structural disjoining pressure within out lubrication model, noting the importance of microscopic forces at this scale. Promisingly, the use of the disjoining pressure has recently yielded the formation of step like structures in nanoparticle laden fluids (Matar et al., under review).

Monday 2:50 Bonsai I IR8

Complex rheology of molecularly thin films and the role of surface and structure

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Confined films demonstrate a complex rheological behaviour in nano-scale, when the thickness becomes comparable to the size of individual atoms. Observed phenomena may include significantly enhanced viscosity and relaxation times. We report molecular dynamics simulation results of confined alkane (C_nH_{2n+2}) systems that reveal some important properties and explain the underlying physics of observed phenomena. These simulations show crucial importance of solid confining surfaces, and their characteristics on the rheological properties of these confined systems. Even small details, such as crystalline structure, surface roughness and relative orientation of the two confining surfaces change the rheological response in nano-scale. The film response to shear is highly correlated with its structure. When the thickness of the film reaches critical value dramatic changes in the film structure takes place leading to highly ordered stacks of extended molecules. The result is often a very high viscosity film. The formation of these stacked structures depends on the confining surfaces crystalline structure and roughness. The onset of structural changes due to confinement depends also on the size of the molecules. Under shear the boundary condition varies depending on the surface characteristics. The film under shear exhibits transitional shear viscosity changes with direct correlations to the structural changes. Depending on various scenarios, a film with the same molecular composition and thickness, may exhibit a viscosity several orders of magnitude larger than the bulk viscosity, or a viscosity same as the bulk viscosity or a viscosity even lower than the bulk viscosity. At such a length scales it is mainly the surface that dictates the rheology of the film.

Monday 3:10 Bonsai I IR9

Linear and nonlinear rheology of two dimensional polymers: A Brownian dynamics study

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Dynamics and rheology of two-dimensional polymer systems are studied by Brownian dynamics simulation. Two-dimensional polymers can be experimentally realized by, for example, polymer chains adsorbed on a lipid membrane or floating on a air-water interface. Understanding their dynamics will have technical and biological importance. In 2d, there is no entanglement among polymer chains, while the excluded volume interaction is believed to be much more important than in 3d. This suggests the dynamics of 2d polymers are quite different from that in 3d. In this paper, we will present our results of Brownian dynamics simulation for isolated and concentrated 2d polymers. Both equilibrium and steady shear behavior are studied. The results for dynamic linear viscoelasticity will also be presented.

In the case of an isolated polymer chain, its equilibrium size, for example root mean square of the end to end distance R, is proportional to $N^{3/4}$, where N is the degree of polymerization. The exponent 3/4 agrees well with the Frory exponent in 2d, which is believed to be exact. The longest relaxation time is proportional to $N^{2.5}$.

In the case of 2d polymer “melts”, the equilibrium size R is proportional to $N^{1/2}$ and the relaxation time is proportional to N^2. These results apparently agree with those of the Rouse model. The dynamic linear viscoelasticity (storage and loss moduli) are also similar to those of the Rouse mode. But the snapshots of the polymer conformation indicates that polymer chains are more or less segregated into a disk-like shape as suggested by de Gennes (and as observed by experiments and other simulations). If you look into the snapshots more closely, you will find there is a very large “shape fluctuations”. A Polymer chain usually takes a disk-like shape but occasionally takes an “elongated” shape. The zero-shear viscosity of 2d polymer melts is proportional to N, also in agreement with the Rouse model. At high shear rates, the viscosity is almost independent of N, and proportional to -0.44 power of the shear rate. This exponent, and independence on N, are similar to those observed in simulations of unentangled 3d polymers.

All the statics and linear rheology seem to agree with those of the Rouse model. But the segregation into the disk-like shape suggests that polymer chains are not Gaussian in 2d. Decomposition of the stress into intra- and inter-chain components indicates that most of the stress comes from inter-chain repulsion, while in the Rouse model all the stress comes from intra-chain contribution. These facts indicate that 2d polymers can not be interpreted, at least directly, as Rouse chains.

Monday 3:30 Bonsai I IR10

Dynamics of adhesion between the spherical PDMS rubber and the glass substrate

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The adhesion between rubbery particle and rigid substrate is important in various applications such as toners and micro-molding. To understand the process, we conducted a detailed study of the loading and the unloading process of very soft PDMS rubber (elastic modulus being of the order of 0.06 Mpa) on the glass substrate. We have taken the top view and the side view of the particle when it is deformed, and measured the contact area, the contact angle, and force as a function of the displacement normal to the substrate. We found that the deformation of the rubber in the cycle of the loading and the unloading process can be described by two typical processes, one is that the contact area changes while the contact angle remains constant, and the other is that the contact angle changes (between the advancing angle and the receding angle) while the contact area remains constant. We analyzed the experimental results using the JKR theory, and found that the results can be fitted well by the JKR theory provided that the surface energy of the JKR theory is replaced by the apparent surface energy (i.e., the energy dissipated in the system for the unit change of the contact area) as it has been assumed by previous researchers (Maugis, Schapery, Greenwood and Johnson). Deviation was found in the region where the contact angle changes significantly.

Monday 3:50 Bonsai I IR11

Direct and indirect polymer-polymer interfacial slip measurements in multilayered films

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Significant slip can occur during flow of two immiscible polymers due to reduced entanglements at their interface. The slip is of practical importance because of its effect on morphology and adhesion of these multi-phase materials, such as disordered two-phase blends and multilayer films. In this research, we investigate the amount of polymer-polymer slip over a range of shear stresses from rheological measurements (i.e., indirect method) and visualization measurements (i.e., direct method) on co-extruded multilayer films. Two types of polymer blends were chosen for our case study: polypropylene (PP)/ polystyrene (PS) and polyethylene (PE)/fluoropolymer (FP) blends. The multilayer samples of both PP/PS and PE/FP blends were prepared in a co-extrusion setup (Zhao and Macosko, *J. Rheol.* 2002) at 200 and 210 °C, respectively, in order to match viscosity and elasticity. The number of PP/PS layers of the sample ranged from 20 to 640 layers while that of PE/FP sample was fixed at 80. To determine the effect of alternately layered structure on the interfacial slip over a wide stress range, three types of rheometers were used: an in-line slit-die rheometer, a rotational parallel-plates rheometer, and a sliding-plates rheometer (SPR). It was observed that the apparent viscosity of a multilayer sample is lower than the average viscosity of two homopolymers for both PP/PS and PE/FP samples and decreases as the number of layers increases above a certain critical shear stress. These demonstrate the interfacial slip between two polymers indirectly. Furthermore, two visualization techniques were used to directly prove the interfacial slip. First, a bilayer sample with fine marking lines drawn at the interface was sheared in a SPR with a transparent top plate to measure the slip distance over a finite time. Second, a bilayer sample filled with tracer particles was sheared using a high-temperature shearing device (Linkam) and the in-situ velocity profiles of particles across the sample thickness were measured using a confocal microscope (Lam and coworkers, *J Rheol.* 2003). The slip velocity (i.e., the amount of macroscopic velocity discontinuity at the interface) with respect to shear stress was calculated from each rheological and visualization methods and compared.

Monday 4:10 Bonsai I IR12

Molecular dynamics simulation study of the glass transition temperature and the polymer chain dynamics near the substrate

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Glass transition temperature is one of the important properties of the polymeric materials. In the case of thin film, the boundary of the surface and the substrate wall is much effective to change the glass transition temperature of the film from the bulk value. Many studies have been done to clarify these natures. We conducted the molecular dynamics (MD) simulation to observe the glass transition temperature of the polymer surface, and the results were able to be compared with the experimental results qualitatively.

In this paper, we extend the previous method to obtain the glass transition temperature near the substrate wall, and observe the polymer chain dynamics near the substrate. We model the substrate wall in two ways; one is the flat potential wall and another is the LJ particle wall. Our result of the glass transition temperature corresponds to the experimental result by Tanaka and co-workers estimated by the lifetime of the fluorescence method. The analysis of the polymer chain is done by the mean square displacement (MSD) analysis. Using MSD analysis, the polymer chain dynamics in the reptation motion can be checked. Using this analysis, we can observe the typical motion of polymer chain near the substrate wall.

Monday 4:30 Bonsai I IR13

Numerical study of transient 3-D viscoelastic drop deformation under shear flow

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The study of the drop dynamics under different flow conditions is important in several flowing systems of industrial or biological relevance, e.g, emulsions, polymer blends, and blood, which can be described as a dispersion of drops. Flow-induced Newtonian drop deformation in a Newtonian media has been investigated extensively in the past; however, only few investigations considering non-Newtonian drops can be found in the literature. Due to the increasing complexity of the problem, considerably increase in computational resources, and improved numerical methods, numerical simulations are gaining in importance.

In this work, the transient 3-D viscoelastic drop deformation under a shear flow is studied. In free surface flow computations, the location of the interface is part of the solution. In order to obtain the correct location of the interface while preserving the volume of the drop, the isochoric domain deformation method is used in which the mesh is treated as an incompressible elastic pseudo-solid. All governing equations; the domain volume conservation, domain mapping, mass and momentum conservation, and constitutive equations; are solved coupled using the DEVSS-TG/SUPG finite element method. The transient flow is solved by using a fully implicit second-order predictor-corrector time integration scheme.

Monday 4:50 Bonsai I 💿 IR14

Interfacial elasticity of reactively compatibilized PP/PA6 blends

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The aim of the present work was to evaluate the interfacial properties of compatibilized PP/PA6 blend by means of measuring the melt elasticity of the samples in conjunction with the Palierne model. The PP/PA blend samples varying in blend ratio and compatibilizer concentration were prepared in an internal mixer. The relaxation time spectra of the blends were calculated from dynamic moduli obtained by the linear viscoelastic measurements. The analysis of the relaxation time spectra of the compatibilized blends showed two distinct peaks which could be related to the elastic response of the droplets, τ_s, and interface elasticity, τ_β. This was evidenced by decreasing the relaxation times with increasing the compatibilizer content. An attempt was also made to evaluate the Interfacial tension and interfacial shear modulus of the blend samples by utilizing the expanded version of the Palierne model in conjunction with the PA particle size obtained by the SEM micrographs. While the interfacial tension decreased with increasing compatibilizer concentration independent of PA content, the level of PP-gr-MA was found to play a different role in determining the interface shear modulus of the samples depending upon PA dispersed phase content. This could be explained in terms of changing the morphology of the samples from emulsion type to emulsion in emulsion morphology. It was shown that in the reactively compatibilized polymer blends; similar to physically compatibilized systems, the interfacial shear modulus is proportional to the interfacial coverage, indicating that the same mechanism governs the compatibilization for two systems. It was demonstrated that the results of linear viscoelastic measurements can provide a great insight into understanding the correlation between the interfacial elasticity and the morphology of immiscible polymer blends.

SC-2. Particle Level Simulation and Theory II

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Eric Shaqfeh and Roger T. Bonnecaze

Monday 2:30 De Anza III 💿 SC7

Electrokinetic boundary condition compatible with the Onsager reciprocal relation in the thin double layer approximation

Masao Doi and Masato Makino
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Electro kinetics is a classical subject of colloid science but has attracted a re-surging interest in recent years because of importance in various nano-bio applications. Electrokinetics is a complex phenomena as it involves coupled transport processes of ions and fluids(water). It has been shown that the equations can be simplifield enormously if the thickness of the electric double layer is negligibly small compared with the typical dimension of the problem. This approximation, called the thin double layer approximation, has been quite useful in understanding the electrophoresis of charged particle with complex shape and charge distribution.

However the boundary condition used in the conventional electrokinetic theory in the thin double layer has a flaw that it does not give the Onsager reciprocal relation for the sedimentation of charged particle. In this paper, we shall propose a new boundary condition which does not have this flaw.

The new boundary condition takes into account of the effect of surface slip and surface conductivity. When applied to the homogeneously charged spherical particle, the boundary condition gives a correction to the Stokes formula for the viscous drag, and the Smoluchowski formula for the electrophoretic mobility.

Monday 2:50 De Anza III SC8

Model analysis on dispersion characteristics of fine particles in Newtonian molten polymer

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A model analysis on time-dependency of cluster size distribution of fine particles in polymer has been performed. The present model for agglomerative suspension was developed based on Usui's thixotropy model, derived by taking the balance between shear breakup, shear coagulation and Brownian coagulation process. The analysis was applied to the experimental results taken by Kameyama et al. for silica/EMMA suspension. The time variation of cluster size distributions, of viscosities and of the mean number of particles in a cluster was calculated and the results were compared with experimental results. From this, the applicability of the present model was validated for the agglomerative silica particles slurry.

Monday 3:10 De Anza III SC9

A binary Yukawa mixture under shear: A computer simulation study of the transient dynamics

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Various experiments and computer simulations have demonstrated that shear strongly affects transport properties of glassforming liquids. If the shear rate exceeds the typical relaxation time of the system, an acceleration of the dynamics is observed which is reflected, e.g., in a decrease of the shear viscosity (shear thinning). The underlying mechanism of this change is still not well understood on a microscopic level. Recently, Fuchs and Cates [Phys. Rev. Lett. 89, 248304 (2002)] have developed a mode coupling theory (MCT) for glasses and liquids under shear where the steady state is derived through an integration over the transient dynamics. In order to check the latter MCT on a fundamental level we study the transient dynamics of a glassforming Yukawa liquid under shear by extensive molecular dynamics computer simulations. On the one hand, the dynamics from equilibrium to steady-state is considered, after a constant shear field has been switched on. On the other hand, we study the dynamics from the steady-state back to equilibrium. In both cases, the dynamics is analyzed by various quantities such as mean-squared displacements, time-dependent density correlation functions and the stress-strain relation. A rich phenomenology is observed. For the transition from steady-state to equilibrium, we demonstrate that, at least on a qualitative level, MCT is able to correctly reproduce the stress-strain relation as seen in the simulation.

Monday 3:30 De Anza III SC10

Anisotropic diffusion model for suspensions of short-fiber composite processes

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Fiber orientation kinematic models of non-dilute suspensions have relied on the Folgar and Tucker (1984) model for diffusion for over two decades. Recent research, however, has exposed the propensity of this fiber collision model to over-predict the rate of alignment. To promote the advancement of light-weight, high strength composites, a new fundamental approach is needed to more accurately capture fiber interactions within the melt flow. We present our initial work in the development of an objective directionally-dependant diffusion model for fiber collisions.

It has been observed that individual fibers within a suspension follow Jeffery's model (1922) for ellipsoidal motion for short time periods, then seemingly at random rotate to a different angle then continue to follow the Jeffery orbit. This paper modifies the Jeffery model to incorporate two new effects, (1) local directionally dependent effects assumed proportional to the probability of collision between two fibers, and (2) large scale volume averaged diffusion behavior analogous to shear rate dependant Brownian motion. The model is formulated at the discrete scale by assuming directional effects are proportional to the scalar triple product between two fibers directions. An extension of the model is made to the continuum scale for a distribution of fibers, and then recast in the orientation tensor form suggested by Advani and Tucker (1987) to allow for faster computations in large-scale simulations. Equations of motion for the second-order orientation tensor with the proposed collision model are demonstrated to be functions of orientation tensors up to and including tenth-order, thus requiring an additional computational burden over the previous models including closure approximations to represent the higher-order orientation tensors. Results in extensional flow demonstrate a significant scalable rate of alignment for the transient orientation state while retaining the desired steady state solution based on the appropriate selection of the two scalable parameters. The applicability of the model to shearing flows is discussed, and suggestions are given for extensions to incorporate shearing effects.

Monday 3:50 De Anza III 💿 SC11

Spherical harmonic solutions of fiber orientation probability distributions for composite processes

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This paper considers the computation of Partial Differential Equations (PDE) on the unit sphere such as the equations which involve probability distributions of orientations of fibers (see e.g., Jeffery's equation (1922) and modifications thereof). Our approach is to represent the fiber orientation probability distributions using a representation similar to that provided by a Fourier series, but written instead using the so-called spherical harmonics. We show that the resulting matrices in many cases turn out to be surprisingly sparse, in a very predictable manner, leading to fast and highly parallelizable computations. Spherical harmonics can be seen as a more systematic approach than current short fiber orientation analyses, which write the equation in terms of higher moments of the distribution. Furthermore the spherical harmonic approach removes the need for the tensor closures that are usually required.

We present software which automates the process of converting a PDE into its spherical harmonic representation, and produces a parallelized computer program. We also show results of computations with spherical harmonics of order 400. This is equivalent to computations with moments of order 400, or alternatively can be viewed as a finite element method with 80,000 elements.

Monday 4:10 De Anza III 💿 SC12

Direct numerical simulation of carbon nanofiber composites in simple shear flow

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The mechanical and transport properties of carbon nanofibres, CNF, in combination with their low production costs make them a promising material for use in polymer composites. However, the level of these properties is largely dependent on the fibres' dispersion state and aspect ratio, which, in turn, depend on the processing history of the composites. Due to strong Van der Waals interactions, CNFs tend to agglomerate, reducing their effectiveness in polymer composites. Applied shear during processing can break up the agglomerates and disperse the CNFs, but excessive shear can lead to fibre breakage, which negatively affects final properties. It is therefore crucial to 'tailor' the level of shear to obtain good dispersion, without fibre length reduction. The current work studies the effect of simple shear flows (dominant in typical polymer processes) on the dispersion state of CNF composites and consists in a direct simulation method based on the Particle Simulation Method developed by Yamamoto et al. to analyze fiber dispersed systems. In the present work fibers are modeled as a series of connected spheres, with stretching force, torsion and bending torques being considered. Also studied is the effect of van der Waals interactions on the state of aggregation of the nanofibres. The method is a very powerful one, currently allowing the semi-quantitative prediction of the dynamics of the fibre suspensions as well as the correct prediction of the kinematics, including some previously unexplained orientation effects observed experimentally.

Monday 4:30 De Anza III SC13

Simulations and rheology of particle filled polymer melts under shear and extension

Oliver G. Harlen[1], Ahamadi Malidi[1], Rosen Tenchev[2], Peter K. Jimack[2], Mark A. Walkley[2], P. Hine[3], and John Embery[3]
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In many processing applications filler particles such as glass beads and fibres are added to the polymer matrix. To study these multiphase systems we perform direct simulations of the motion of freely suspended particles when subjected to an external linear flow, such as simple shear or extensional flow. The simulations are conducted on a unit cell containing a small number of particles replicated on an evolving periodic lattice. The results of these simulations are compared with rheological experiments on suspensions of glass beads in polystyrene and polyethylene melts. For two dimensional simulations we have developed a technique that uses a fully Lagrangian finite element method on a quotient space representation of the periodic boundary conditions. However, as this method cannot easily be generalised to three dimensions we have also developed an Arbitrary Lagrangian-Eulerian (ALE) based simulation where the periodic boundary conditions are imposed weakly through side constraints. This latter technique allows us to compare fully three dimensional systems of suspended spheres against two dimensional systems of circular particles. Our simulations demonstrate that the behaviour of particles suspended in polymer melts modelled with tube based models such as the pompom and Roliepoly models is qualitatively different from that in dumbbell fluids such as Oldroyd or FENE models. In the latter case the addition of filler particles produces shear-thickening and an increase in first normal stress difference, whereas the polymer melt models predict a variation in shear viscosity that can be predicted by a simple shifting model and a decrease in N1. Furthermore by fitting the model parameters to rheology of the unfilled material we obtain good quantitative predictions of the shear viscosity. We also demonstrate that particle "chaining" is only found for tube based constitutive models in agreement with experimental observations that chaining occurs in suspensions of shear-thinning fluids but not Boger fluids.

Monday 4:50 De Anza III SC14

An O(N) Green's function method to calculate hydrodynamic interactions of particles in unbounded and confined geometries

Samartha G. Anekal[1], Juan P. Hernandez-Ortiz[2], Patrick T. Underhill[1], and Michael D. Graham[1]
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An extension of the Generalized Geometry Ewald-like Method (GGEM) (J.P. Hernandez-Ortiz et al., Physical Review Letters, 98, 140602, 2007), to include higher moments of the hydrodynamic force, and lubrication interactions, is presented. GGEM is an O(N) method to calculate hydrodynamic interactions between N particles. The hydrodynamic forces are split into a near-field and far-field part similar to the Accelerated Stokesian Dynamics (ASD) method (A. Sierou and J.F. Brady, Journal of Fluid Mechanics, 448, 115, 2001). The far-field contribution is split into a local part, calculated analytically, and a global part, which is calculated by numerically solving Stokes equations on a mesh. This replaces the FFT based sum in the ASD method. The resulting method is O(*N*) as opposed to O(*N*log*N*) in the ASD method. In confined systems, the new method has the added advantage that the confining walls do not have to be discretized into particles in order to capture the hydrodynamic effect of the walls.

GR-2. General Rheology

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Montgomery T. Shaw

Monday 2:30 Bonzai III GR7

Wall slip during the flow of carbopol solutions through a parallel plate channel

Paulo R. de Souza Mendes, Jonathan Pédron, and Renata A. Pereira
Department of Mechanical Engineering, Ponfifícia Universidade Católica-RJ, Rio de Janeiro, RJ 22453-900, Brazil

Experiments were performed to investigate the phenomenon of wall slip during the flow of aqueous solutions of carbopol through a parallel plate channel. The channel is 100mm wide and 150mm long, and the gap between plates is 1mm. The Reynolds number is low for all cases investigated, to ensure negligible development length. In the experiments, the pressure drop is measured for different flow rate values, and the results are presented in the form of curves of dimensionless average velocity versus dimensionless wall shear stress. Experiments with glycerol were also performed, and the results were shown to agree well with the analytical solution available in the literature, indicating that the flow is essentially one-dimensional as desired. Moreover, this agreement ensures the absence of wall slip for this Newtonian case. The carbopol solutions are characterized rheologically, and the viscosity function proposed by de Souza Mendes (J. Non-Newtonian Fluid Mech. 147, 2007, 109-116) is shown to fit well to the viscosity data obtained with a rotational rheometer. The momentum equation is integrated numerically for the velocity field in conjunction with the above mentioned viscosity function and assuming no wall slip. Comparisons between the experimental and numerical results show that wall slip (or apparent wall slip) occurs in the range of wall shear stresses below about twice the yield stress. Above this threshold, the numerical and experimental curves coincide. The wall slip observed is attributed to the presence of a thin layer of water at the wall.

Monday 2:50 Bonzai III GR8

Liquid-liquid displacement flows in an annular space including viscoplastic effects

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Visualization experiments were performed to investigate the displacement efficiency during the displacement by a Newtonian oil of aqueous solutions of carbopol flowing through an annular space. Applications include cementation processes of petroleum wells. The inner-tube outside diameter of the annulus is 16mm, while its gap is 9 mm. The tubes are made of transparent glass to allow flow visualization. The Reynolds number is kept low for all cases investigated, to ensure negligible inertia. The apparatus was built in such a way that the interface is always flat at the startup of the flow. The orientation of the axis with respect to gravity is varied from 0 to 90°. The main parameters that govern this flow are the orientation angle, the viscosity ratio, the density ratio, the flow rate, and the yield stress. In the experiments, the interface shape is recorded as it proceeds along the annulus for different sets of the governing parameters, and the displacement efficiency is determined.

Monday 3:10 Bonzai III GR9

Numerical investigation of the displacement of a viscous fluid by a viscoplastic material in a capillary tube

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A Galerkin finite element method is used to investigate the liquid-liquid displacement of two immiscible fluids in a tube. The displacing fluid is Papanastasious viscoplastic material. The length scale is small and. therefore the interfacial tension between these fluids plays an important role on the problem. The wetability and capillary conditions are such that there is a residual film of the displaced liquid attached to the wall. The fraction of mass of the displaced liquid that remains close to the wall (*m*) is an indicator of the eficiency of the displacement and, in this study, is computed as a function of the dimensionless numbers that frame the operating window of the process, namely capillary number (*Ca*), viscosity ratio (*N*) and Bingham number (*Bn*). Particular attention is given to the transition between the two well-defined regimes of this problem: by-pass flow and fully-recirculating flow. In this last case, there is a secondary recirculation in the displacing fluid that was well-captured by the mesh employed. Maps of flow regimes in the space defined by *N* x *Ca* are constructed for some values of *Bn*. The results have shown that, as the displacing fluid becomes more plastic, increasing the value of *Bn*, there is an increase of the value of *m*. The transition flow regimes indicate that increasing viscosity ratio and capillary number favors by-pass flow regimes. The increase of *Bn* anticipates the critical capillary number in which transition occurs.

Monday 3:30 Bonzai III GR10

On the nature of bubble velocity discontinuity in non-Newtonian fluids

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The motion of single air bubbles in non-Newtonian fluids was investigated. Depending on the rheological properties of the fluid (viscoelasticity, shear thinning), a discontinuity of the bubble velocity can be observed. This phenomenon was first discovered by Astarita & Apuzzo (1965) and has remained unexplained since then. An extensive experimental investigation was conducted to determine the conditions under which the velocity discontinuity occurs. The motion of air bubbles was studied for several classes of fluids (viscoelastic, shear thinning inelastic and constant viscosity elastic liquids). It was found that when the elastic forces overcome the surface tension forces, the shape of the bubble changes drastically, developing a concave shape and a cusped tail. For this new shape, the bubble drag coefficient is smaller, resulting in an increase of velocity. Moreover, if the fluid is shear thinning, the increase in velocity produces a reduction of the viscosity which, in turn, causes a further reduction of the drag and consequently a further increase of the velocity. It is also believed that a change of the bubble surface condition (slip to non-slip) is a result of the velocity increase. Elastic effects alone, may also contribute to the drag reduction. The combination of all these effects gives rise to the bubble velocity discontinuous behavior. We suggest that the onset of this phenomenon appears when a dimensionless number ?= $N_1 d/s$ representing the ratio of elastic forces to surface tension forces exceeds unity where N_1 is the mean first normal stress difference, d is the equivalent bubble diameter and s is the surface tension. A study of the magnitude of the different contributions leading to the bubble velocity discontinuity is also presented.

Monday 3:50 Bonzai III GR11

Hydrodynamics for nanofluidic flow

Billy D. Todd[1], Jesper S. Hansen[1], and Peter J. Daivis[2]
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A key problem in the prediction of the flow properties of highly confined (nano-scale) fluids is that the classical Navier-Stokes equations of hydrodynamics break down at this length scale. This has been demonstrated in a number of simulation studies in the past, in which the predicted classical velocity profiles for nonequilibrium fluids do not match the profiles generated via molecular dynamics simulation [1, 2]. The problem is more complicated than merely including explicit density dependence in the hydrodynamic equations, since it has also been demonstrated that the viscosity of such nonequilibrium fluids cannot be computed by a local approximation [2-5]. A non-local viscosity needs to be computed before accurate flow predictions can be made [6]. In this presentation we demonstrate how to compute a non-local viscosity kernel from either equilibrium or nonequilibrium molecular dynamics simulations of a homogeneous fluid at equivalent state points corresponding to those of an inhomogeneous fluid [7]. In order to use this viscosity kernel to predict the flow profiles, a new constitutive model needs to be invoked which explicitly considers the fluid non-locality, as well as the influence of the walls on the fluid shear stress. Such a model can be viewed as a generalisation of the classical Navier-Stokes equations for nanofluidic flows.

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Monday 4:10 Bonzai III 💿 GR12

Brownian dynamics of polymers at high strain rates

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We employ a version of the bead-spring model with hydrodynamic and excluded volume interactions in order to model the response of polymeric fluids to extensional flows with high strain rate. By comparing numerical computations with our laboratory experiments, we benchmark the quality of the theoretical predictions. We also discuss the predictions of the theoretical model for flows which are difficult to study experimentally.

Monday 4:30 Bonzai III 💿 GR13

A novel method of measuring the phase behavior and rheology of polyethylene solutions using a multi-pass rheometer

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The Advanced SCLAIRTECH(tm) Technology (AST) process is used to manufacture Linear Low Density Polyethylene using solution polymerization. In this process ethylene is polymerized in an inert solvent, which is subsequently evaporated and recycled. The reactor effluent in the process is a polymer solution containing the polyethylene product, which is separated from the solvent and unconverted ethylene/co-monomer before being extruded and pelletized. The design of unit operations in this process requires a detailed understanding of the thermophysical properties, phase behaviour and rheology of polymer containing streams at high temperature and pressure, and over a wide range of composition. This paper describes a device used to thermo-rheologically characterize polymer solutions under conditions prevailing in polymerization reactors, downstream heat exchangers and attendant phase separation vessels. The downstream processing of the AST reactor effluent occurs at temperatures and pressures near the critical point of the solvent and co-monomer mixture. In addition, the process trajectory encompasses regions of liquid-liquid and liquid-liquid-vapour co-existence, which are demarcated by a 'cloud point' curve. Knowing the location of this phase boundary is essential for the design of downstream devolatilization processes and for optimizing operating conditions in existing plants. In addition, accurate solution rheology data are required for reliable equipment sizing and design. At NOVA Chemicals, a robust high-temperature and high-pressure-capable version of the Multi-Pass Rheometer (MPR) is used to provide data on solution rheology and phase boundary location. This sophisticated piece of equipment is used to quantify the effects of solvent types, comonomer, and free ethylene concentration on the properties of the reactor effluent. An example of the experimental methodology to characterize a polyethylene solution with hexane solvent, and the ethylene dosing technique developed for the MPR will be described.(tm)Advanced SCLAIRTECH is a trademark of NOVA Chemicals

CF-3. Flow Instabilities II

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: R. Sureshkumar

Monday 2:30 Steinbeck CF13

The influence of monomer concentration on the flow-induced orientation and viscoelasticity in thermotropic copolyesters: In-situ X-ray scattering

Angel Romo-Uribe[1], Maraolina Domínguez-Díaz[1], Maria E. Romero-Guzmán[1], and Alan H. Windle[2]
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The influence of monomer composition on the flow-induced molecular orientation and viscoelastic properties of a series of thermotropic liquid crystalline polymers (LCPs) will be discussed. The flow behavior was investigated by in-situ X-ray scattering. The LCPs are based on the random copolymerization of 1,4-hydroxy-benzoic acid (B) and 2,6-hydroxy-naphthoic acid (N). Copolymers especially synthesized by the Celanese Co. with chemical composition in the ratio B:N of 25:75 and 75:25 mol% and weight-average molecular weight of ca. 5,500 g/mol were studied. The solid-to-nematic transition Tm and the decomposition temperature Tdec are not influenced by the monomer composition, Tm being about 280°C for both polymers and Tdec ~ 509°C. Polarized optical microscopy showed that the nematic phase of the materials consist of threaded texture, where the defect texture coarsens under thermal annealing but without eliminating completely these defects. The molecular orientation under flow was found to be quite different for these polymers. Applying steady shear to the B-N 75:25 mol% copolyester produced an orientation transition from log-rolling to flow-aligning regime. The log-rolling regime predominates at lower temperatures (T~ Tm). On the other hand, the application of steady shear to the B-N 25:75 mol% copolyester over a range of temperatures and shear rates only produced a flow-aligning regime. The B-N copolyesters are linearly viscoelastic, and the extent of the linear viscoelastic regime is restricted to 0.1% strain. Small-strain oscillatory shear showed that both copolyesters behaved predominantly elastic (G' > G") at lower temperatures, changing to predominantly viscous (G' < G") as the temperature increases. However, at constant temperature the B-N 25:75 mol% copolyester exhibited higher melt viscosity. The log-rolling and flow-aligning flow regimes appear to be associated to a smectic-like structure present only in the B-N 75:25 mol% copolyester as revealed by a 002 meridional reflection in the sheared polymer.

Monday 2:50 Steinbeck CF14

Numerical investigation of the flow field in confined impinging jets of non-Newtonian fluids

Adelio S. Cavadas[1], Fernando T. Pinho[2], and Joao M. Campos[1]
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High velocity impinging jets are frequently used in industry to cool metals and process food and pharmaceutical products because of the large increases in heat and mass transfer they promote near the impact surface. The jet may or may not be confined. In this work, we experimentally and numerically investigate the behaviour of impinging jets for various non-newtonian fluids. The approach flow is a symmetric fully developed flow in a rectangular channel of aspect-ratio of 13, that impacts onto a perpendicular wall. Then the flow splits in two and exits through two rectangular channels. Between the impact zone and the exits the fluid flows through confined channels having inclined plates at an angle of 12°.

The three-dimensional flow is isothermal and laminar and the fluids were aqueous solutions of xhantam gum and PAA. The experiments were carried out using laser Doppler velocimetry and flow visualization techniques. The Reynolds number in the inlet channel was varied between 10 and 800. The 3D numerical calculations were carried out using a finite volume code relying on at least second order differencing and interpolating schemes for accurate results. The PTT model was used for the viscoelastic simulations and to isolate shear-thinning from elastic effects the power law model was also used in some calculations.

The results of non-Newtonian simulations matched the measured data and consequently an extensive set of calculations was carried out for other flow conditions to investigate the influences of shear-thinning intensity and inlet Reynolds number on the steady flow within the cell, and in particular, on the pressure loss and the size and strength of the recirculation region formed along the sloping surfaces of the cell. The size and strength of this recirculation region increases with Reynolds number and three-dimensional effects due to the finite aspect ratio of the geometry are also reported.

The three-dimensional flow is characterized by a helical flow motion along the spanwise direction, from the centre of the cell towards the flat side walls. The end walls are shown to eliminate the recirculation inside the cell and a weak third component of velocity is seen to transport fluid particles from the symmetry plane towards the end walls. There is also a linear dependence between the pressure loss coefficient and the Reynolds number studied and that the recirculation length increases with shear-thinning intensity.

Monday 3:10 Steinbeck CF15

Oscillating hydrodynamical jets in steady shear of nano-rod dispersions

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The flow properties of nano-rods are strongly affected by the dynamical behavior of molecular alignment. A theoretical description can be made by an relaxation equation [1] of a tensorial order parameter as well as by a Fokker Planck equation [2] for a orientational probability distribution function (kinetic approach). For plane Couette flow geometry a rather complex orientational behavior occurs [3] even in the case where the alignment is spatially homogeneous and the flow profile is linear. In the last years the dynamics of the inhomogeneous alignment and the effect on the velocity profile was investigated intensively [4]. The dynamics of the orientation leads to strong derivations from the ordinary Couette flow profile. Depending on the model parameters and the boundary conditions various flow structures occur (like band bands [4,5]). In this contribution we model fluid-wall interactions by boundary conditions on the alignment tensor (strong anchoring condition). By a numerical analysis we found for different models (tensor model, Doi-Marucci-Greco model and kinetic model) flow oscillating local spurts of the velocity profile, referred to as hydrodynamical jets. The effect is even robust against 2-dimensional perturbations. Furthermore, we analyse the orientational dynamics and show the emergence of hydrodynamical jets is caused by the competition of elasticity and flow coupling.

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Monday 3:30 Steinbeck CF16

Fluid-fluid demixing in shear

Suzanne M. Fielding
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We study numerically phase separation in a binary fluid subject to an applied shear flow in two dimensions, with full hydrodynamics. For systems with inertia, we reproduce the nonequilibrium steady states reported previously by Stansell et al. The domain coarsening that would occur in zero shear is arrested by the applied shear flow, which restores a finite domain size set by the inverse shear rate. For inertialess systems, in contrast, we find no evidence of nonequilibrium steady states free of finite size effects: coarsening persists indefinitely until the typical domain size attains the system size, as in zero shear. We present an analytical argument that supports this observation, and that furthermore provides a possible explanation for a hitherto puzzling property of the nonequilibrium steady states with inertia.

Monday 3:50 Steinbeck 💿 CF17

Analysis of the normal stress differences of viscoelastic fluids under large amplitude oscillatory shear

Jung Gun Nam, Kyung H. Ahn, and Seung J. Lee
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The dynamic response of viscoelastic fluids under large amplitude oscillatory shear (LAOS) has been a subject of long history. In the LAOS flow, the analysis has been mostly focused on shear stress, possibly due to the lack of accurate measurement of normal stresses. However, as the instrumentation advances, it becomes possible to get more reliable data. The development of normal stresses under LAOS flow is a significant nonlinear effect that has been hardly obtainable in previous studies. Analyzing the normal stresses will be helpful in understanding and characterizing nonlinear viscoelastic behavior. In this work, we investigated the behavior of normal stress difference under LAOS flow using viscoelastic fluids including Boger fluid and polyethylene oxide aqueous solution. The first normal stress difference was measured and it was sinusoidal at a frequency twice that of the excitation frequency because of its dependence only on the magnitude of the strain, not on the direction of its operation. It showed a displacement that was equal to the elastic modulus multiplied by the square of the strain amplitude. It was also found that the shape of the first normal stress difference strongly depended on shear strain and frequency. At higher frequency, they showed asymmetric patterns in contrast to the shear stress, and the amplitude of the first normal stress difference became as large as the shear stress. And higher harmonics of the first normal stress difference which are the sum of even functions were compared with that of shear stress in terms of Fourier spectra, which was also performed with the help of constitutive equations.

Monday 4:10 Steinbeck 💿 CF18

Critical phenomenon analysis of shear-banding flow in polymer-like micellar solutions

Fernando Bautista[1], Juan H. Perez[2], Jorge E. Puig[2], and Octavio Manero[3]
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We examined the shear-banding flow phenomenon in polymer-like micellar solutions with the Bautista-Manero-Puig (BMP) model. Upon decreasing the shear banding intensity parameter of this model, which corresponds to increasing temperature, concentration or varying salt-to-surfactant concentration, a non-equilibrium critical line is reached. By using non-equilibrium critical theory, which concerns with scaling theory, we obtain a set of anti-symmetrical curves that are the Legendre transform of the normalized stress versus normalized shear rate flow curves, similar to magnetic transitions around the critical point. In addition, we derived the non-equilibrium critical exponents and show that these critical exponents obey the Widow and Griffiths relationship for equilibrium critical exponents. Those exponents have non classic values.

Monday 4:30 Steinbeck 💿 CF19

Experimentally assessed three dimensionality of polymer melt flows through abrupt contraction dies

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Abrupt contraction geometries are rarely intentionally used in industrial processing of polymer melts since they pose the potential of polymer stagnation, degradation as well as the effects of processing inhomogeneities. However, such geometries provide challenging complex flows for testing of, in general two-dimensional, numerical simulations, the testing of rheological parameters and validation of modelling of the flow response of melts with tailored architecture. The majority of previous experimental work has been conducted to provide measurements in only the streamwise-normal (x-y) plane and much conjecture has taken place as to the true quantitative nature of the three-dimensionality. Through the manufacture of new windowed dies we have been able to access the stress and velocity fields in the two orthogonal planes (x-y and x-z) using the techniques of full field stress birefringence and particle tracking velocimetry for a range of dies of different contraction and aspect ratios. Complementing these techniques with particle image velocimetry has allowed new insights into the nature of the corner vortex growth for long chain branched materials. These results, as well as those for a well-characterised linear material, will be presented.

Monday 4:50 Steinbeck CF20

Purely-elastic flow instabilities in a 3D six arms cross slot geometry

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The appearance of purely-elastic instabilities in some canonic viscoelastic flows is now an established fact. Examples are the opposed-jet flow of viscoelastic fluids observed by Chow et al (1988), or more recently the three-dimensional cross-slot microchannel flow by Arratia et al (2006).

Poole et al (2007a) simulated the two-dimensional cross-slot flow of an Upper-Convected Maxwell (UCM) model under creeping-flow conditions, and were able to capture qualitatively the onset of a bistable steady asymmetric flow above a first critical Deborah number followed by a later transition to a time dependent flow. These numerical results were in qualitative agreement with the experimental findings of Arratia et al (2006). Poole at al (2007b) extended the study of Poole et al (2007a) by considering the three-dimensional nature of a real microfluidic cross slot flow and investigated in detail the effect of the aspect ratio of the geometry, by varying the depth of the cross slot from low values (quasi-Hele Shaw flow) up to very large values (quasi-two dimensional flow).

In this work we further extend the previous investigations by considering inlets and outlets in all three-directions. Using a 3D finite-volume numerical method, the viscoelastic flow inside a 3D six arms cross geometry is studied and we report the presence of flow asymmetries under perfectly symmetric flow conditions for viscoelastic fluids. Using the UCM model under creeping flow conditions, the effects of the ratio of inlet to outlet flow rates (I_o) and Deborah and Reynolds numbers on the onset of the flow instability are investigated in depth, thus demonstrating its purely elastic nature.

Using two different inlet flow rate configurations (I_o=4:2 and 2:4), we were able to assess the importance of different types of extensional flow near the stagnation point. Uniaxial extension is observed in the 4:2 flow rate configuration, whereas biaxial extension is experienced by fluid elements near the stagnation point for the 2:4 configuration. We found that the uniaxial extension flow configuration is prone to the onset of steady flow asymmetries, at a rather small Deborah number (De_{crit}=0.21). On the other hand, for the biaxial extension flow configuration a perfectly symmetric flow is observed, even at De=0.3, illustrating its stable character as compared with the uniaxial extensional flow case. These results provide new insight into the viscoelastic flow instability mechanisms in cross-slot flows.

Arratia PE, Thomas CC, Diorio JD & Gollub JP. *Physical Review Letters*, **96**, (2006) 144502; Poole RJ, Alves MA & Oliveira PJ. *Physical Review Letters*, **99**, (2007a) 164503; Poole RJ, Alves MA, Afonso A, Pinho FT & Oliveira PJ. AIChE 2007 Annual Meeting, Salt Lake City, Paper 94827 (2007b); Chow A, Keller A, Müller AJ & Odell A. *Macromolecules*, **21** (1988) 250-256.

Monday 5:10 Steinbeck CF21

Modes of aero-breakup with visco-elastic liquids

Chee-Loon Ng and Theo G. Theofanous

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This work is about the breakup of millimeter-scale visco-elastic drops that are suddenly exposed to supersonic gas flows. The breakup is characterized by both the rheological properties of the liquids and by the aerodynamics force of the gas flows, with the principal scaling parameter being the Weber (We) number. We present data on deformations, liquids velocities, modes of breakup, and particle sizes after the breakup. These data are critical to the understanding of the competition between different (acceleration, deformation, instability) timescales and the breakup outcomes of different liquid rheologies, especially at high strain rates. The liquids tested were polystyrene-butyl methacrylate dissolved in tributyl phosphate solution and polystyrene oxide dissolved in water. The former was particularly suitable for these experiments as it has a low vapor pressure. The experiments were carried out in a pulsed supersonic wind tunnel and separately in a shock tube facility with over 4 meters of optically-accessible expansion section. Laser induced fluorescence and shadowgraphy diagnostics involved a copper-vapor laser (511 nm wavelength, 15 ns pulse duration, 50 kHz repetition frequency, 0.2 MW/pulse) and a Nd:YAG laser (532 nm wavelength, 5 ns pulse duration, 20 MW/pulse). The instrumentation employed were: (1) 2-camera laser strobe illumination high-speed video imaging system setup in different views (straight and/or oblique), and (2) 8-camera 11 Mp shadowgraphy still imaging system. The latter has a field of view of over 2 inch that is capable of observing droplets down to 50 microns. Dynamic pressures employed covered the range 104 to 106 MPa. These results, along with the experimental capability developed, constitute to the key building blocks for our overall, long-term aim towards predicting the atmospheric dissemination of large quantities liquids at different atmospheric conditions for different spatial dimensions, fluid and rheological properties. In addition, the data are of resolution and quality needed to test direct numerical simulations of high-speed interfacial flows.

MF-2. Microfluidics: Non-Newtonian Flows

Organizers: Todd M. Squires and Annie Colin
Session Chairs: Jonathan Rothstein and Justin J. Cooper-White

Monday 2:30 Portola MF7

Elastic instabilities in entry flows: A consequence of upstream stretch or downstream relaxation?

Lucy Rodd[1], Daewoong Lee[2], Kyung H. Ahn[2], and Justin J. Cooper-White[1]

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The flow of dilute to semi-dilute solutions of polyethylene oxide through planar abrupt 16:1 microfabricated contraction geometries is investigated. This study extends previous work on micron-scale entry flows, in which strong viscoelastic effects could be generated in weakly elastic fluids, merely by reducing the lengthscale of the device. As with the previous study, the flow behaviour upstream of the contraction plane is characterized according to a number of flow regimes including Newtonian-like flow, steady viscoelastic flow, inertio-elastic instabilities, and vortex growth, which occur over a range of Reynolds numbers, $0.2 < Re < 40$ and Weissenberg numbers, $0 < Wi < 140$. In the present work, we specifically explore the effect of the contraction length on the upstream kinematics, which are quantified using micron-particle image velocimetry. Velocity field data is accompanied by pressure drop measurements over the contraction, which provide further insight into the importance of contraction length and the resulting viscoelastic response of the fluid. It was found that the overall effect of an increase in contraction length is to stabilize the flow upstream of the contraction (for the same Reynolds and Weissenberg numbers) thereby suppressing so-called "inertio-elastic" effects upstream of the contraction. Such "inertia-like" time-dependent flow structures were previously attributed to the interplay of fluid elasticity and inertia, however the present work suggests that these elastic phenomena are more function of the flow configuration both upstream and downstream of the contraction, and not inertia related. These findings are highly relevant to the performance of microfluidic devices, agricultural spray nozzles and inkjet printing devices, all of which involve the transport of weakly elastic fluids through micron-scale confined flow geometries.

Monday 2:50 Portola 💿 MF8

Effect of viscoelasticity on drop deformation in 5:1:5 contraction/expansion micro-channel flow

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A numerical algorithm was developed based on finite element method to investigate drop deformation in 5:1:5 planar contraction/expansion micro-channel flow. Creeping flow was assumed since Re ~ 10-4. The Oldroyd-B model was adopted as a constitutive equation for the viscoelastic fluid. As stabilizing schemes for elastic instability, the discrete elastic viscous stress splitting (DEVSS-G), streamline upwind Petrov Galerkin (SUPG) and matrix logarithm techniques were applied to the governing equations. Front tracking method was used to track the interface of the drop. The position of the interface was calculated using the Runge-Kutta 2nd order method for time discretization. Immersed boundary method was implemented to deal with surface tension, and adaptive time step method was used for efficient calculation since the drop moves faster in the narrow channel. For Newtonian drop in Newtonian matrix (NN), we could obtain various results by controlling drop size, Ca (capillary number ~ viscous force / surface tension) and viscosity ratio between drop and matrix. Manifold patterns of the drop were observed at the exit region of the narrow channel, while no significant difference was observed as an 'oblong shape' at the entrance region of the narrow channel because of the confinement effect by walls. We also investigated 're-entrant cavity' in the narrow channel and 'drop swell' at the exit region of the narrow channel. Corner vortex enhancement was reported depending on the position of the drop. When the drop was positioned at the entrance or exit region, corner vortices were enhanced due to high pressure difference between drop and wall. Newtonian drop in viscoelastic matrix (NV) shows relatively large deformation ('ellipse shape') in the narrow channel, while viscoelastic drop in Newtonian matrix (VN) shows a similar result with the Newtonian case (NN) leading to a 'bullet shape'. In the NV case, unusual behaviors were reported. i.e. 'rear bulge' phenomenon was observed in the narrow channel since viscous force was weakened inside the drop. As De (Deborah number ~ polymer relaxation time / characteristic process time) of the matrix increases, unsymmetric corner vortices tended to develope. Also, reduced pressure drop between inlet and outlet was observed compared to NN and VN cases.

Monday 3:10 Portola MF9

Microfluidic characterization of the flow of wormlike micelles: Shear-banding, interfacial instability and tracers migration

Philippe Nghe[1], Guillaume Degre[1], Patrick Tabeling[1], and Armand Ajdari[2]

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We characerize by Particle Image Velocimetry the Poiseuille flow a semi-dilute solution of wormlike micelles (a CTAB and sodium nitrate aqueous solution) in pressure resistant microchannels. Thanks to the high aspect ratio of our channels, we can measure the local rheology of the solution, independantly from the slippage at the wall, according to a method already validated on non-newtonian polymer solutions. As the pressure driving the flow is increased, the velocity profiles reveal first a newtonian phase, then apparition of a dramatically lower viscosity second phase at the walls, which is the so called shear banding regime. First we deduce the local rheology of the solution from these velocity profiles, in agreement with the macroscopic rheology obtained in Couette rheometers. Then we study the development of an instability at the interface between the two phases, with a wavevector in the vorticity direction and a wavelength corresponding to smallest dimension of the channel. Finally we discuss the hypothesis of passive tracers : depending on their size, we observe a tracer depletion in the high-shear phase, which may be to high normal forces.

Monday 3:30 Portola 💿 MF10

Flow and stability of wormlike micellar and polymeric solutions in converging and T-shaped microchannels

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The flow and stability of wormlike micellar and polymeric solutions is investigated in two prototypical converging and elongational geometries; (i) microfabricated hyperbolic contractions and (ii) flow along T-shaped microchannels. Understanding the flow behavior of such fluids at the microscale is important to the design and optimization of microfluidic devices for lab on a chip processes and fluidic computing applications as well as to industrial applications such as extensional flow through porous media. The controlled flow rates and very well-defined geometries achievable in microfluidics enable us to gain insight into the extensional rheology of complex fluids at high extension rates and to investigate the onset of elastically-driven flow asymmetries. In the present study, cetyltrimethylammonium bromide wormlike micelles in aqueous solutions of sodium salicylate as well as dilute polyethylene oxide (PEO) solutions are selected as test fluids. Using the micellar fluids, it is possible to quantify the two-dimensional distribution of both the velocity and stress fields in hyperbolic-shaped micro-contractions using a new microscope-based flow-induced birefringence technique in conjunction with microparticle imaging velocimetry (μPIV). The knowledge of both the stress and velocity data allows us to better understand the behavior of shear-banding fluids in inhomogeneous extensional flows. In the case of dilute PEO solutions flowing through perfectly symmetric T-shaped microchannels, a local extensional flow develops where the two streams meet. The resulting birefringent strand of highly-oriented material can lead to symmetry-breaking bifurcations in the flow at high Deborah number which can be quantified using microparticle imaging velocimetry. The spatio-temporal characteristics of these purely elastic flow asymmetries can also be compared to predictions of numerical simulation.

Monday 3:50 Portola MF11

Reversible and irreversible flow-induced phase transitions in micellar solutions

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It is well known that certain surfactant solutions (e.g. CTAB, CTAT) can undergo a phase transition from a solution phase to a gel-like phase upon increasing the shear rate above a critical value [Wunderlich et al. (1987), Liu and Pine (1996), Hartmann and Cressely (1997,2000), and Bandyopadhyay and Sood (2001), Vasudevan et al. (2007)]. The phase transition occurs because of the formation of shear induced structures (SIS), and manifests as an increase in the apparent viscosity of the solution (i.e. the solution shear-thickens). The critical shear rate for the onset of shear-thickening, and the extent of viscosity enhancement in such systems are very sensitive to salt concentration. Several studies on SIS formation indicate that these structures are large micellar networks that exhibit gel-like behavior with a chaotic nature and elastic characteristics. However, upon cessation of the applied strain, the network structure disintegrates almost instantaneously, highlighting the shear sensitivity of the SIS. In this work, we initially study the effect of salt concentration on SIS formation in shear-thickening surfactant-salt solutions of CTAB/NaSal in a conventional cone-and-plate rheometer. Specifically, we identify the critical parameters for SIS formation, and study the shear-sensitivity of these structures. Further, we present a novel method to produce stable and irreversible SIS by rapid straining in microfluidic devices. Using this process, we observe that the micelles can be quenched in a meta-stable (shear-induced) gel-like state, because of which the gels can be independently collected and characterized. These gels have a stable interface with the surrounding fluid. AFM results clearly indicate highly aligned micelles with a short range order. This could serve as an ideal mesoporous scaffold for various nano-manufacturing applications to produce active materials. Moreover, since this sol-gel transition is accomplished without the addition of alcohols, the process is completely bio-compatible. Several surfactant systems have been tested to ensure that the process is robust.

[1] Wunderlich I., Hoffmann H., Rehage H., Flow birefringence and rheological measurements on shear induced micellar structures, Rheo. Acta., 26: 532-542 (1987); [2] Liu C., Pine D.J., Shear Induced Gelation and Fracture in Micellar Solutions., PRL 77, 10, 2121-2124 (1996); [3] Hartmann V., Cressely R., Influence of sodium salicylate on the rheological behaviour of an aqueous CTAB solution, Coll. Surf. A: Physicochemical and Engineering Aspects 121 151-162(1997), and Cappelaere E., Cressely R., Influence of NaClO3 on the rheological behavior of a micellar solution of CPCl, Rheo. Acta 39: 346-353 (2000); [4] Bandyopadhyay R., Sood A., Chaotic dynamics in shear-thickening surfactant solutions, Europhys.Lett.,56 (3), 447-453 (2001); [5] Vasudevan. M., Shen A., Khomami B., Sureshkumar R., Self-similar shear-thickening behavior in CTAB/NaSal surfactant solutions. arXiv:0706.3063 (2007).

Monday 4:10 Portola MF12

Morphology development of immiscible polymer blends in extensional flows developed within a microfluidic device

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A microfluidic device was used to create precisely controlled drops of a polydimethylsiloxane oil in polybutadiene oil and then study the morphological development of the drops in extensional flows under a series of different flow conditions. Nearly monodisperse drops were generated using a microfluidic hydrodynamic flow-focusing device. Once formed, the drops were driven through a contraction which stretched and, depending on the capillary number of the flow and the viscosity ratio of the two fluids, broke-up the drops. Two different types of contractions were employed; a hyperbolic contraction which resulted in a homogeneous extensional flow and a linear contraction which resulted in a flow whose extension rate increases as the drop passes through the contraction. The former is directly related to the flow field a drop experiences in a filament stretching rheometer (FiSER). The latter corresponds to extensional flow experienced by a Newtonian fluid in a capillary break-up rheometer (CaBER). The microfluidics results are compared directly to the results of both FiSER and CaBER measurements where direct observation of the drop morphology cannot be made, but must be inferred by the stress evolution and the predictions of numerical simulations. We will demonstrate that the combined use of both microfluidics devices and bulk measurement techniques, like FiSER and CaBER, provides a great deal of insight into the dynamics and morphological evolution of immiscible polymer blends. A number of different parameter spaces were investigated including, but not limited to the effect of extension rate, viscosity ratio and drop size on the morphological evolution and extensional rheology of the polymer blends. Additionally, we will demonstrate through both microfluidics and CaBER measurements that modifying the fluid-fluid interface by populating it with colloidal particles or surfactants can have a large effect on both the extensional rheology as well as the morphological development of an isolated drop. Finally, we will demonstrate that the extensional flow produced within the microfluidics device can have a significant effect on the crystallinity and order of the particles populating the interface of the drop.

Monday 4:30 Portola MF13

Extensional effects in viscoleastic fluid flow through a micro-scale double cross-slot

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The flow of fluids with viscoelastic properties through a microfluidic flow-focusing device was studied numerically using a finite volume code [1]. The conceived device is shaped as a double cross-slot with three entrances and three exits, in a symmetric configuration, aiming to achieve a constant extensional rate at the centreline. The effect of the Reynolds and Deborah numbers on the flow patterns is analysed. Several constitutive differential equations are studied, such as the upper-convected Maxwell, Oldroyd-B and Phan-Thien-Tanner models. As a consequence of the small length scales and high deformation rates associated with the micro-channel flow, strong viscoelastic effects are observed, even for dilute polymeric solutions.

This geometry enables the generation of a region of converging flow with a nearly hyperbolic shape, with the added advantage of keeping the flow region of interest away from walls, thus minimizing shear effects. The imposed Hencky strain can be controlled by varying the ratio of the flow rates in the inflowing branches. The shape of the streamlines defining the converging region is strongly influenced by the flow rate ratio and by the geometric parameters of the device (e.g. the relative size of the entrance branches). By tuning these parameters, we show that we are able to generate a region of nearly constant extensional rate at the centreline. As such, this study demonstrates the potential of this device to be used as an extensional micro-rheometer suitable for measurements of extensional properties of dilute polymeric solutions.

[1] Alves MA, Pinho FT, Oliveira PJ (2000) Effect of a high-resolution differencing scheme on finite-volume predictions of viscoelastic flows. Journal of Non-Newtonian Fluid Mechanics 93:287-314.

Monday 4:50 Portola MF14

Electro-wetting: A microliter drop rheometer and interfacial tensiometer

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We use strength of electrowetting on dielectric (EWOD) for the rapid characterization of the rheological properties and the interfacial tensions (σ_{LV} or σ_{LL}) of liquid droplets. This characterization essentially requires 2-3 micro-liter of volume. An alternating electric potential was applied between conductive drop and the electrode underneath a hydrophobic dielectric layer. Subsequently the resulting change in the sessile drop shape and contact angle was measured as a function of both continuous voltage amplitude ramps as well as sudden steps. Having calibrated the device using the EWOD response of water, interfacial tensions were calculated using Lippmann-Young model for the macroscopic contact angle. Various liquids including surfactant laden drops as well as protein solutions and cell growth media were investigated with interfacial tensions ranging from 5-73 mN/m, which were found in excellent agreement to the values obtained on commercial tensiometer with Du Noüy method. The viscoelastic properties of gelatin solutions were characterized based on their time-dependent response, showing a distinct onset of elastic behavior below a critical temperature, in agreement with the macroscopic gelation temperature. We also demonstrated possibility of performing the measurements without any loss of accuracy using coplanar patterned electrodes on the substrate, therefore avoiding any direct electrical contact with the drop.

Monday 5:10 Portola MF15

Electrowetting-controlled drop generation in microfluidic flow-focusing devices

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Physics of Complex Fluids, Univ. Twente, Enschede, The Netherlands

Recent upsurge in droplet-based microfluidic research is fuelled by the potential application of drops for biochemical analysis, protein crystallization and novel material synthesis. Two competing microfluidic platforms exist for drop manipulation in such applications. In the first, pressure-driven flows are used to create droplets continuously in a flow-focusing device (FFD) and electric fields are used to manipulate droplets (sorting and coalescence) downstream. In the second, electrowetting-on-dieletric (EWOD) is used to digitally manipulate drops in a sandwich geometry that is devoid of channels. While the hydrodynamic approach provides high-throughput capability, it is neither amenable to drop-on-demand control nor dynamic modulation of surface wettability - a governing parameter for the dynamics of two-phase flows. Alternatively, EWOD provides exquisite control over surface wettability, but current implementations of EWOD incorporate a channel-free architecture and therefore lose the ability to integrate already existing channel-based technologies (e.g. membrane valves). Here, we adopt a unified approach to create a soft microfluidic platform that harvests the power of the two methods and offers the capability to address their limitations. We achieve this integration by incorporating EWOD into a flow-focusing device and demonstrate electrowetting-induced drop-on-demand generation. Depending on the applied voltage, different drop generation regimes are identified, ranging from a dripping regime at low voltage to regime involving an instability mechanism of the three phase contact line that is closely related to electrospraying. The latter regime yields a particularly high production rate (O(10kHz)) of micrometer-sized drops. Our results demonstrate that electrowetting in a channel-based architecture combined with flow-focusing is a powerful means to generate and control drops digitally for lab-on-chip applications.

EM-2. Extensional Rheometry

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: Malcolm Mackley

Monday 2:30 De Anza I EM7

Measuring the elongational properties of polymer melts: A simple task?

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Elongational properties of polymer melts are of great interest from the fundamental and application point of view. The development of long-chain branched polymers, for example, has increased the interest in elongational flow measurements as the so-called strain-hardening behaviour is often taken as a proof for branching and an indication of good processability. Therefore, in the last years much effort was made to simplify elongational flow measurements on polymer melts. One result are add-on tools for shear rheometers. When they appeared to the market the attitude came up that the measurement of elongational properties of polymer melts would become an easy task.

For an assessment of the capabilities and the limitations of different tensile rheometers measurements with the Münstedt-type oil bath rheometer (MTR) and the TA Instruments extensional viscosity fixture (EVF) on materials of various molar masses and molecular topography (linear and long-chain branched), were performed. The effect of the experimental procedure on the results will be documented. The temperature distribution as well as the influence of the sample homogeneity on the elongational viscosities measured are addressed. Furthermore, the extended capabilities of the oil bath rheometer (e. g. measurements in creep, determination of elastic properties) are demonstrated and discussed in comparison of the EVF.

Monday 2:50 De Anza I EM8

Measurement of reversed extension flow using the filament stretch rheometer

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Reversed extension flow is an especially challenging task for any constitutive modeling approach. In the reversed part of the flow the work performed by the polymer is mounted and it is theoretical related to the entropic state of the polymeric material. No technique to measure a well defined reversed extension flow has been published in the scientific literature until now, according to our knowledge, whereas an immense variety of experimental and theoretical scientific studies on reversed shear flow, such as large oscillative shear flow (LAOS), has been presented. Although one has to keep in mind that in the early developments in elongational rheometry as Meissner (Meissner (1971) Rheologica Acta 10, 230 - 242) presented methods to measure the elastic recovery. The elastic recovery is the maximal recoverable Hencky strain in the reversed flow following uniaxial elongation, usually measured without externally applied forces on the sample during the reversed flow. In this type of measurements the actual deformation during the reversed flow is not known. The advantage of the Filament Stretching Rheometer compared to conventional techniques for elongation rheometry is the ability to predict the location of the mid filament plane (the necking) of the extended sample. Subsequently this critical region can be monitored, and the distance between the end plates adjusted obtaining a predefined (but not necessarily constant) stretch rate at the neck. The measurement of reversed material functions in extension is demonstrated using the Filament Stretching Rheometer. This includes startup of uniaxial elongational flow (potentially until steady state) followed by biaxial squeezing, and large amplitude oscillatory elongation (LAOE). The latter is demonstrated on highly extensible elastomers, whereas in LAOE measurements on liquids the LAOE flow need to be imposed upon a constant strain rate uniaxial elongation. The used Filament Stretching Rheometer (Bach , Rasmussen , Hassager (2003) Journal of Rheology 47, 429 - 441) allows measurements on polymeric fluids, including polymeric melts, from room temperatures until 200°C.

Monday 3:10 De Anza I EM9

A new dual controlled stress/rate extensional rheometer for high viscosity systems

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Over the last 30 years Extensional Rheometry has been continually at the forefront of research in Rheometry for two main reasons; its relevance to real-world flow situations and the difficulty in performing well-controlled, physically relevant experiments. In fact, the rheological properties of polymer melts in uniaxial extensional flow are recognised to have a great relevance for polymer processing. The behavior of this class of materials when subjected to extension-dominated flows, as in the case of fiber-spinning, blow molding, thermoforming or film blowing processing sequences, is dependent on their response to extensional deformations. Also, the study of this type of flow allows an insight into the molecular structure of the materials to be obtained, since extensional behavior is very dependent on the particular structure (molecular weight, molecular weight distribution, degree of branching, etc.) being deformed. In addition, it is recognized that the response to extensional deformations is much more dependent on the internal structure of the materials than for the case of shear deformations, due to elongation being considered a stronger flow. Therefore, although shear flow is the most common flow situation encountered in real processing sequences, the elongational component of the flow is very relevant even when present to a low extent. Our group has been working in this area since the late 1990's, having developed its own experimental capability in the form of a controlled-rate extensional rheometer that adapts onto a rotational TA Instruments Weissenberg rheogoniometer. The main aim of this presentation is to introduce a new generation dual controlled-stress/rate extensional rheometer for high viscosity systems that allows samples to be tested up to physical rupture. The instrument designated the Extensional Flow Cell, EFC, is again an adaptation to a rotational rheometer, in the present case Paar Physica MCR 300, the extensional stress or rate being controlled in via a real time feed-back loop.

Monday 3:30 De Anza I EM10

Determination of extensional rheological properties by contraction flow

Mats Stading

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Extensional rheological properties are important for diverse applications e.g. processing of viscoelastic fluids, mouthfeel of semi-solid foods, cell mitosis, baking e.t.c. and also a useful tool for testing the applicability of constitutive equations. Despite the documented influence of extensional rheological properties, it is seldom measured due to experimental difficulties. There are only commercial equipments available for low-viscosity fluids by capillary breakup and for polymer melts by Meissner-type winding of ribbons around cylinders. Both methods have limited applicability for medium-viscosity fluids such as foods and other biological systems. Contraction flows are extensively studied and a new test method has been developed based on contraction flow through a hyperbolic nozzle. The method is suitable for medium-viscosity fluids and has been validated by comparison to results from filament stretching and capillary breakup. The contraction flow method has been used to characterize food and medical systems, distinguish between different food products having equal shear behaviour, quantify ropy mouth feel and to predict foaming behaviour of biopolymers.

Monday 3:50 De Anza I EM11

The effect of step-stretch parameters on capillary breakup extensional rheology (CaBER) measurements

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Extensional rheometry has only recently been developed into a commercially available tool with the introduction of the capillary breakup extensional rheometer (CaBER). CaBER is currently being used to measure the transient extensional viscosity evolution of mid to low-viscosity viscoelastic fluids. The elegance of capillary breakup extensional experiments lies in the simplicity of the procedure. An initial step-strain is applied to generate a fluid filament. What follows is a self-driven uniaxial extensional flow in which surface tension is balanced by the extensional stresses resulting from the capillary thinning of the liquid bridge. In this talk, we will present a series of experiments in which the step-strain parameters of final length and the extension rate of the stretch were varied and their effects on the measured extensional viscosity and extensional relaxation time were recorded. To focus on the parameter effects, well-characterized surfactant wormlike micelle solutions, polymer solutions and immiscible polymer blends were used to include a range of characteristic relaxation times and morphologies. Our experimental results demonstrate a strong dependence of extensional rheology on step-stretch conditions. In addition, numerical simulations were performed using the appropriate constitutive models to assist in both the interpretation of the CaBER results and the optimization of the experimental protocol. From our results, it is clear that any rheological results obtained using the CaBER technique must be properly considered in the context of the stretch parameters and the effects that pre-conditioning has on viscoelastic fluids.

Monday 4:10 De Anza I EM12

Break-up in capillary thinning experiments: Using the CaBER to determine maximum tensile strength at low stressing rates

Alex S. Lubansky[1], Rhodri Brad[1], Rhodri P. Williams[1], Davide Deganello[2], Tim C. Claypole[2], and David T. Gethin[2]
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The maximum tensile strength of fluids is an important guide to the onset of cavitation. Being able to predict the onset of cavitation is important in formulation for industries as diverse as printing and automotive industries. A technique has been developed to use break-up at the end of a capillary thinning experiment to determine the maximum tensile strength of the test fluid. The technique has been applied to a range of concentrations and molecular weights of polyethylene glycol. The results have been validated by comparison with the values and behaviours observed from the bullet piston apparatus. Some discussion regarding the advantages, differences and applicability of using the CaBER is also provided. Some discussion is also provided regarding break-up in capillary thinning experiments.

SE-1. Rheology of Foams

Organizers: Denis Weaire and Lynn M. Walker
Session Chairs: Andrew M. Kraynik and Denis Weaire

Monday 2:30 De Anza II SE1

Critical review of foam rheology with application to oil and gas recovery

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Foam found many applications in the realm of earth sciences and especially in the fields of and gas recovery and subsoil environmental remediation. Bulk foams are used for boring subterranean formations reaching depths of several thousands of meters. They are mainly used to ensure that hydrostatic pressure in the bored well does not exceed that of the fluids in the bored earth layers; this improves considerably the inflow of hydrocarbons from the formation into the well. Foam also serves as lubricant and cooling of the drill pipe. Foams generate by pushing gas or steam through a porous matrix together with water containing a surface active agent have proved to be an excellent way to squeeze hydrocarbons out of earth strata. It is well known that such foams have much higher apparent viscosities than their liquid and gas constituents. This effect is also applied to block earth strata or otherwise redirect flow from one stratum to another, for example during steaming of polluted soils to clean-up their dense non-aqueous pollutants (DANPL). Describing the rheology of foam in such a complex dynamic conditions has remained a challenge however because the rapid and change in the rearrangement of foam bubbles. Furthermore earth processes are imminently rich in interfacial effects. Engineers have relied on semi-empirical approaches to model foam rheology but that approach is often unsatisfactory. The aim of the paper is to provide a critical survey of the existing rheological models for foam. The available experiments will be used to dispute or validate the models. Gaps and challenges will be highlighted to frame areas where further research developments are needed.

Monday 2:50 De Anza II SE2

Rheological characterization of foamy oils under pressure

Patrice Abivin[1], Isabelle Henaut[1], Michel Moan[2], and Jean-Francois Argillier[1]
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Heavy oils are a strategic source of hydrocarbons due to the large amount of reserves located mainly in Venezuela and Canada. They distinguish from conventional oils by their higher density and viscosity. When a reservoir is depleted, the lightest components (methane, ethane, etc.) can exsolve from the crude oil and create a gaseous phase. In conventional oils, bubbles grow and coalesce quickly. On the contrary, in heavy oils, bubbles are small and remain dispersed within the oil for a long time. This "foamy oil" phenomenon changes drastically the flow properties of the crude oil. This article is devoted to the characterization of the heavy oil foamy behavior through a rheological study. Our objectives are to study the kinetics of bubble evolution in heavy oil and to measure their influence on viscosity. A new experimental method was developed, based upon rheological measurements under pressure. Several heavy oils containing dissolved gas have been depleted inside the pressure cells of controlled stress rheometers to create foamy oils. Viscosity and elastic properties have been continuously measured using oscillatory and continuous tests from the nucleation up to the disengagement of bubbles from oil. The occurrence of bubbles was visualized using X-ray scanning experiments. Results demonstrate that foamy oil kinetics is mostly related to the oil viscosity. They also reveal that under low shear rates, the presence of bubbles leads to an increase in heavy oil viscosity, as predicted by the Hard Sphere Model or by Taylor. A theoretical model describing the viscosity of foamy oil was then established. It takes into account both first-order kinetics of appearance and release of bubbles in oil and a basic suspension model. Good agreement was obtained between experimental data and model predictions. Finally, several tests reveal the strong influence of the shear rate on the foamy oil behavior and point out the major role of bubble deformation on the viscosity of foamy oils, as shown previously in other viscous materials such as magmas and polymers. Under high shear rates, we suggest that the stabilization of the elongated bubbles in oil leads to the establishment of an anisotropic material, which can be seen as a sandwich-like structure. As a result, the viscosity appears lower in the direction of the deformed bubbles.

Monday 3:10 De Anza II SE3

Coupling between interfacial and macroscopic foam rheology

Sylvie Cohen-Addad[1], Reinhard Hohler[1], Georges Debrégeas[2], and Sebastien Besson[2]
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Aqueous foam is constituted of gas bubbles densely packed in a surfactant solution. Even though it is made only of fluids, it behaves like a solid viscoelastic material for small applied stress. Quasi-static foam elasticity, due to the surface tension of the gas-liquid interfaces, is now well understood, but the dynamical response and in particular the origin of dissipation raise complex questions that are still open. Moreover the frequency dependence of the complex shear modulus resembles that of other disordered soft solids such as concentrated emulsions, pastes, onion lamellar phases, etc. This raises the question whether the similarity originates in common generic mechanisms.

In coarsening foams, a slow relaxation mechanism has been identified. It is directly coupled to the ageing process via coarsening-induced bubble rearrangements leading to Maxwell liquid behaviour [1, 2]. At high frequency, foams and other soft solids present a characteristic increase of the complex shear modulus with the square root of frequency. To explain it, a dissipation mechanism involving mesoscopic weak regions, due to "defects" in the bubble packing, has been proposed [3]. Recently an alternative relaxation mechanism has been proposed, predicting the same kind of rheological behaviour on the basis of surfactant diffusion [4]. At intermediate frequencies, an additional mechanism has been proposed. It involves a structural relaxation governed by the surface tension and the surface viscosity of the gas-liquid interfaces [1].

To clarify the origins and the interplay of the linear viscoelastic dissipation mechanisms in foams, we investigate the relaxation processes over 6 decades in frequency, using oscillatory measurements of the complex modulus at high frequency (up to 100 Hz) and creep measurements to probe the low frequency response. We study how foam rheology depends on the interfacial elasticity and rigidity and on the foam structure to discriminate between dissipation due to weak regions and surfactant diffusion.

[1] Cohen-Addad S, Höhler R, Khidas Y (2004) Phys. Rev. Lett. 93, 028302-4; [2] Vincent-Bonnieu S, Höhler R, Cohen-Addad S (2006) Europhys. Lett. 74, 533-539; [3] Liu A J, Ramaswamy S, Mason T G, Gang H, Weitz D A (1996) Phys. Rev. Lett. 76, 3017-3020; [4] Besson S, Debrégeas G (2007) Eur. Phys. J. E.

Monday 3:30 De Anza II SE4

Foam structure and rheology in thin gaps

Douglas A. Reinelt[1] and Andrew Kraynik[2]
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The cell-level structure and rheology of gas-liquid foam confined between parallel flat plates are strongly dependent on the ratio R/H, where R is bubble radius and H is plate spacing. We consider various three-dimensional foam structures that consist of N layers of bubbles and explore the range of R/H over which each structure is stable. In the "dry" limit, where the gas fraction is unity, one confined layer is composed of hexagonal cylinders; two layers contain Fejes-Toth cells, which are a hybrid between hexagonal cylinders and Kelvin cells; and more than two layers are modeled as Kelvin cells sandwiched between Fejes-Toth cells. We also consider wet foams where all of the liquid is assumed to be located in traditional Plateau borders in the bulk and wall Plateau borders adjacent to the plates. Brakke's Surface Evolver is used to calculate the foam structure and stress as a function of R/H, which enables us to evaluate elastic behavior for a wide range of parameters. The results also provide a relationship between the two-dimensional structure at the wall and bubble radius, which has application to foam characterization.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Monday 3:50 De Anza II SE5

Structure and rheology of random wet foam

Andrew Kraynik[1] and Douglas A. Reinelt[2]
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The cell-level structure and rheology of wet foams under quasi-static conditions is calculated with Brakke's Surface Evolver for spatially periodic systems ranging in complexity from ordered (Kelvin, FCC, and Weaire-Phelan) to random. All of the liquid is assumed to be located in Plateau borders, which form a continuous network of channels along the cell edges. These features significantly increase the size and complexity of the simulations. Plateau's laws are no longer valid in the wet regime. In particular, as the liquid volume fraction increases, the films that separate bubbles shrink in area until bubbles lose contact. The connectivity of the Plateau borders can exceed four, which is strictly enforced in the dry limit. This presentation will focus on elastic behavior and emphasize the qualitative and quantitative differences between the rheology of ordered and random foams.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Monday 4:10 De Anza II SE6

Foam rheology in two dimensions

Denis Weaire
School of Physics, Trinity College, Dublin, Ireland

The rheology of foams is a research problem of long standing and great current interest. In part this has been generated by the 2D experiment of Debregeas et al, which showed strong shear localisation in a 2D Couette rheometer. This was originally interpteted in terms of quasistatic simulations, and subsequently in terms of an elementary continuum model in which localisation is attributed to wall drag (entirely absent in the other approach). An ongoing debate seeks to reconcile these two contrasting viewpoints. The type of (soft disk/sphere)model previously developed by Durian has been used to shed further light on the relationship between microscopic and macroscopic (continuum) descriptions. This theme was continued in 3D simulations of more conventional foam rheology. In both cases the object is, in part, to identify the source of the Herschel-Bulkley power-law dissipation, a common feature of experimental analysis. We comment further on more realistic dynamic representations of a foam at the cellular level. While all of this serves to tie together hitherto unrelatable findings, and put foam rheology on a clearer theoretical basis, it inevitably raises fresh questions.

Monday 4:30 De Anza II SE7

Shear banding in bubble rafts

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There exists a broad range of phenomena that leads to the coexistence of non-flowing and flowing regimes in materials. Depending on the material of interest and the geometry of the flow, various behaviors are observed. In this talk, we will focus on the situation in which one observes a discontinuity in the rate of strain at the transition from flow to non-flow. This situation has been observed in a wide-range of complex fluids, including pastes, emulsion, slurries, and foam. We discuss experimental studies of a quasi-two dimensional system: bubbles floating on the surface of water (bubble rafts). We will present results on both the average behavior of the transition, including dependence on system size, and the short-time behavior that is dominated by individual bubble dynamics and strong fluctuations. A key feature of the average behavior is a discontinuity in the rate of strain at the transition from flow to no-flow. As with similar situations in three-dimensional flow, this requires new constitutive equations for the material that capture the discontinuity. We will also discuss the nature of the fluctuations in the location of the transition region, and how averages over these fluctuations converge.

Monday 4:50 De Anza II SE8

Localization of topological changes in Couette and Poiseuille flows of two-dimensional foams

Simon Cox, Aled Wyn, and Ioan Tudur Davies

Institute of Mathematical and Physical Sciences, Aberystwyth University, Aberystwyth, Ceredigion SY23 3BZ, UK

Foams are elasto-visco-plastic materials that are widely used in enhanced oil recovery and ore separation. To make progress in predicting their dynamic response, we consider two-dimensional (2D) foams, such as can be formed between closely-spaced parallel glass plates. These have the added advantage that while their properties are closely related to the 3D foams found in industry, each bubble can be seen and its position and shape tracked over time. They therefore provide a model system for study.

The local structure of a foam determines, to a certain extent, its elastic properties such as shear modulus. We will present simulations that describe the dependence of shear modulus on topological and volumetric disorder in 2D. At high strain, or strain-rate, the bubbles in a flowing foam are increasingly deformed until they switch neighbours in a T1 topological change. This marks the transition from the elastic to a plastic regime.

Our work shows that under flow, for example simple shearing between parallel plates, the presence and position of localized regions of T1s in the foam is related to the disorder. Under gravity, the descent of objects embedded in the foam depends upon the relative contributions of pressure and network forces to their mutual repulsion or attraction.

During a T1 there is a period of time in which the foam is out of equilibrium. The rate of return to equilibrium depends upon such factors as the surfactant used and the presence of external friction. We will present experiments and simulations that probe this viscous relaxation process.

Tueday Morning – 5 August 2008

KL-3. Keynote Lecture 3

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Christoph Schmidt

Tuesday 8:30 Serra I KL3

Nonlinear elasticity of elastomers and gels as revealed by multiaxial deformations

Kenji Urayama
Kyoto University, Kyoto, Japan

Nonlinear elasticity of elastomers and gels has been investigated by many researchers, but most of the studies rely on only uniaxial deformation. The characterization of the stress-strain behaviors under many types of deformations is undoubtedly needed for the full understanding of the nonlinear elasticity, because uniaxial deformation is only a particular one among all physically accessible deformations. General biaxial strains with varying independently the two principal strains cover all types of deformation for incompressible materials. In this talk, I introduce our recent studies using biaxial stretching for several elastomeric materials: (i) end-linked polydimethylsiloxane networks, (ii) crosslinked rubbers with various degrees of swelling, (iii) carbon-black filled rubbers exhibiting a considerable viscoelastic relaxation, (iv) slide-ring (polyrotaxane-based) gels whose cross-links are movable along the network chains in response to imposed deformation (collaborative work with the Prof. Ito's group at the University of Tokyo).

KL-4. Keynote Lecture 4

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Jim Harden

Tuesday 8:30 Steinbeck KL4

Biopolymer, protein and protein-biopolymer interfaces and gels: Structure-property-function relationships and relevance to tissue generation

Justin J. Cooper-White
Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland 4072, Australia

Tissue engineering is a multidisciplinary field aimed at recapitulating the normal process of healing and organogenesis through the use of artificial scaffolds, engineered surfaces and cells. Depending on the chosen method of use, these scaffolds may be cultured with the chosen cell type/s in vitro prior to implantation, or alternatively, they may be immediately implanted in vivo without preculture, again, without or with cells. Obviously, with all of these options available to the tissue engineer, the exact nature of the surfaces to which cells will interact and adhere, and the three dimensional nature of the artificial environment provided by these scaffolds must not only be known, but also well controlled. This talk will provide an overview of our recent work which has focussed on understanding how the constitution of the surface presented to the cells determines not only the biochemical properties of the interface, but also its physical (rheological) properties. More importantly, what properties of the surface and the 3D porous space dominate observed cell behaviour and therefore, what is the 'functionality' that needs to be included into three dimensional formats of these 'surfaces' to encourage appropriate cell growth and tissue development. In particular, I will describe the methods that are being utilised to manipulate polymeric (biopolymer through to protein-based) materials to present desired surfaces to a multitude of cell types and the controlled presentation of these surfaces throughout porous three dimensional polymeric scaffolds. Results of in vitro and in vivo assessments of these new materials will be discussed throughout the talk, showing their successful utilisation in various (targeted) tissue applications.

HS-3. Immiscible Polymer Blends

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chair: Kiyohito Koyama

Tuesday 9:45 San Carlos IV HS16

Melt rheology of nanoparticle-polymer blends

Jonathan E. Seppala and Michael E. Mackay
Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA

Previously we found that nanoparticles reduce the viscosity of polymer melts above a certain concentration. This concentration corresponds to the average gap between the nanoparticles being smaller than the polymer size (denoted as confined). It was also shown that at nanoparticle concentrations below this "confined" condition the viscosity of polymer melts increases well beyond what is predicted by Einstein. We investigated this region and hypothesize this effect is a slight phase separation of the nanoparticles and polymer molecules which produces a suspension of super particles with an increased effective volume fraction. Furthermore, the transition from unconfined to confined systems was explored where it is believed that contour length or density fluctuations contribute to the viscosity decrease.

Tuesday 10:05 San Carlos IV 💿 HS17

Behaviour of dispersed particles in PS/PE blends during and after elongation

Zdenek Starý and Helmut Münstedt

Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nuremberg, Erlangen 91058, Germany

Morphology development in PS/PE blends at various stages of uniaxial deformation and after cessation of the flow was studied. Under given deformation conditions the dispersed PE particles stretch and form highly elongated fibrils in agreement with a modified capillary number model. The morphology development after deformation was investigated for two different modes – relaxation and recovery. It was found that the stress in the sample is the crucial parameter determining the morphology development. During the first part of relaxation the stress in the sample is sufficient to hold the particles in the highly elongated state and, therefore, Rayleigh breakup takes place according to the Tomotika theory. It results in considerably finer phase structure. Contrary to this, in the absence of the stress in the sample, i.e. in the recovery mode, the fibrils start to shrink immediately after the deformation and after a certain time the spherical morphology is restored. The presence of the compatibilizer at the interface markedly affects the deformation behaviour of dispersed droplets and their breakup by lowering the interfacial tension and by suppression of the coalescence. Therefore, the rheological behaviour of the PS/PE blends compatibilized with styrene-butadiene-styrene block copolymers with well defined supramolecular structures was also studied. Modified capillary number model was used for qualitative prediction of the fibril formation under elongational deformation in uncompatibilized and compatibilized blends. The phase structure of the elongated samples quenched in liquid nitrogen was analysed by scanning electron microscopy and small-angle X-ray scattering.

Tuesday 10:25 San Carlos IV HS18

Chemorheological study of blends undergoing polymerization induced phase separation (PIPS)

Patrick T. Mather and Xiaofan Luo

Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244, USA

Epoxy/poly(e-caprolactone) (PCL) blends belong to a class of materials that can undergo polymerization reduced phase separation (PIPS). This occurs in the epoxy/PCL system when the epoxy is crosslinked with 4,4'-diaminodiphenylsulfone (DDS), due to the evolution in inter- versus intra-molecular hydrogen-bonding with conversion. As polymerization and crosslinking proceeds, a series of events can take place including phase separation, chemical gelation, physical gelation, and vitrification leading to a complex rheological response. A variety of final morphologies can be created depending on the cure temperature and PCL weight fraction. In this work, we will present our recent chemorheological studies of this material system coupled with cure kinetics monitored by differential scanning calorimetry (DSC) and morphology monitored using microscopy. Our major focus will be the impact of phase separation mechanisms on the rheological behavior of the system.

Tuesday 10:45 San Carlos IV 💿 HS19

Rheological properties of PET/PC immiscible polymer blends: Effect of catalysts and stabilizers

Souad Mbarek[1], Christian Carrot[1], Mohamed Jaziri[2], and Yvan Chalamet[1]

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The extensive use of poly(ethylene terephthalate) (PET) in packaging, mainly as bottles, drives the research on recycling. Mechanical recycling by melt blending is an interesting method but it gives rise to the problem of incompatibility of PET with other polymers such as polycarbonate (PC). The reactive compatibilization of PET/PC blends has been investigated [1,2]. Compatibilizing copolymers are formed in situ by exchange reactions promoted by added catalysts and lead to interesting morphologies and improved adhesion at the interface. Rheological properties of PET/PC immiscible polymer blends are mostly determined by the morphology of the phase domains generated during the blending process. Factors governing the development of the morphology of polymer blends include the composition, the rheological properties of the neat components, the processing conditions, and the interfacial properties. In turn, the addition of catalysis in PET/PC blends leads to large changes in the blend rheology [2]. In this work, the rheology of PET/PC blends was measured in the melt at 260 °C in dynamic oscillatory shear flow using parallel plate geometry in the linear viscoelastic domain and for frequencies ranging from 100 to 0,1 rad s^{-1}. Reactive blending of PET/PC system with and without transesterification catalyst was performed in a co-rotating intermeshing twin-screw extruder. The thermal stability in the melt of PET/PC/catalysts is a key limitation of the measurement time and in turn of the frequency window despite the use of nitrogen atmosphere. For longer residence time, a noticeable decrease of the viscosity was observed. This decrease was attributed to thermal degradation of the blend induced by the transesterification exchange reactions. To avoid this problem, measurements have been carried out for PET/PC/catalyst and PET/PC/catalyst/stabilizer compounds. Phenolic antioxidants have been evaluated, alone or in combination with phosphites, especially concerning their ability to reduce transesterification exchange reactions after the extrusion process. The results show that the effectiveness of phenols is more important than that of phosphite. It was also demonstrated that phenol type antioxidants freshly added to PET/PC extruded blends are more efficient to inhibit transesterification than the same stabilizer extruded with PET/PC/catalyst. The addition of Irganox 1010 can delay the beginning of the decrease in rheological properties for PET/PC/catalyst blends by 10 min. This time is sufficient to transform PET/PC blends without decreasing their final properties.

[1] S. Mbarek, M. Jaziri, C. Carrot, Polym. Eng. Sci. 2006, 46, 1378; [2] C. Carrot, S. Mbarek, M. Jaziri, Y. Chalamet, C. Raveyre, Macromol. Mater. Eng. 2007, 292, 693-706.

Tuesday 11:05 San Carlos IV 💿 HS20

Numerical investigation of the influence of viscoelasticity on drop deformation in shear

Kristof Verhulst[1], Ruth Cardinaels[1], Paula Moldenaers[1], Yuriko Renardy[2], and Shahriar Afkhami[2]

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This talk follows on the presentations of Verhulst, Moldenaers and Cardinaels, who address experimental results for the influence of viscoelasticity on drop deformation in shear. A viscoelastic drop suspended in a Newtonian liquid, or a Newtonian drop suspended in a viscoelastic liquid, is sheared and investigated for transients, relaxation after cessation of shear flow, and step-up in shear rate. The numerical simulations are conducted at parameters chosen to model the experiments. We use the volume of fluid (VOF) continuum surface force (CSF) algorithm for situations dominated by shear and the paraboloid representation of the interface in the surface tension force (PROST) algorithm in the absence of shear. The Oldroyd-B and Giesekus constitutive models are implemented. An interesting result is that by stepping up in the capillary number gradually, the Oldroyd-B model can simulate stationary states at higher capillary numbers than without the graduated steps. This sensitivity to the initial condition does not occur for the Newtonian counterpart in Stokes flow because of the governing partial differential equations are of elliptic type. At sufficiently high Deborah number and capillary number, the PDE is no longer elliptic, and this is also reflected in the experimental data on step-ups, which achieve stationary states at capillary numbers above the 'critical' value.

SG-3. Effect of Nanoconfinement on Dynamics

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Didier Long

Tuesday 9:45 San Carlos II SG16

Interfacial and confinement effects can modify T_g in thin polymer films by over 100 K and over length scales of several hundred nanometers

John M. Torkelson[1], Connie B. Roth[2], Rodney C. Priestley[2], Soyoung Kim[2], Perla Rittigstein[2], and Manish K. Mundra[3]
[1]Chemical and Biological Eng. & Materials Sci and Eng., Northwestern University, Evanston, IL 60208-3120, USA; [2]Chemical and Biological Eng., Northwestern University, Evanston, IL 60208-3120, USA; [3]Materials Sci. and Eng., Northwestern University, Evanston, IL 60208-3120, USA

Over the past decade, there has been significant study indicating that the glass transition temperature, Tg, of polymers and low molecular weight glass formers can be strongly modified by as much as 70 K via the presence of free surfaces (polymer-air interfaces) and interfaces. However, in almost all cases, modifications of Tg have been observed when the relevant confinement length scale is several tens of nanometers or less. Here using a multilayer film / fluorescence technique, we demonstrate that a single layer in a multilayer film containing only one polymer species can have its Tg modified by an interface that is several hundreds of nanometers away. Furthermore, in experiments involving films with a 14-nm-thick free-surface layer of polystyrene sitting atop an underlayer film consisting of a different polymer, it is possible to adjust the Tg of the polystyrene layer from ~318 K to ~448 K simply by choice of the thickness and type of polymer making up the underlayer. In certain cases, the polystyrene free-surface layer has its Tg dynamics "slaved" to the dynamics of the underlayer. This work demonstrates that the glass transition behavior at a particular location can be strongly impacted by the amount and type of neighboring material over length scales and extents far greater than has previously been appreicated. We shall also discuss several polymer systems that exhibit no measurable perturbation to their glass transition behavior by the presence of a free surface and circumstances in which we can employ a novel multilayer film / dielectric spectroscopy method to study directly the alpha-relaxation dynamics at interfacial layers within polymer films.

Tuesday 10:05 San Carlos II SG17

New thoughts on glass transitions in polymer thin films

Jane E. Lipson[1] and Scott T. Milner[2]
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Polymeric materials formulated as thin films can exhibit glass transition temperatures which are significantly shifted relative to bulk values. Depending on whether the film is supported (on a substrate) or freely-standing the temperature shift can go in different directions relative to the bulk. For all films the magnitude of the shift depends on film thickness. For supported films the shift appears to depend on substrate-polymer interactions, while for free-standing films there is a striking dependence on molecular weight. Experimental data published over the last five years have included some elegant and intriguing results which provide a significant challenge for those wishing to understand these phenomena. In this talk a model that predicts glass transitions in both free-standing and supported films will be presented and tested against extant data. Ideas for future experiments will also be discussed.

Tuesday 10:25 San Carlos II SG18

Time-temperature and time-thickness superposition in ultrathin polymer films

Paul A. O'Connell and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, USA

There is significant information in the literature in which the glass transition temperature Tg is seen to decrease with decreasing film thickness for ultrathin polymer films, i.e., in the nanometer thickness regime. There is little reported information that allows one to determine if the observed reduction in Tg is accompanied by "traditional" shifts in the viscoelastic behavior through both time-temperature and time-thickness superposition concepts. Here we report on the viscoelastic response of ultrathin polymer films in the vicinity of their Tgs using a novel bubble inflation method and show that time-temperature superposition holds for each thickness. We also find that time-thickness superposition appears valid in the segmental relaxation regime, if one uses both a vertical shift and a horizontal shift, indicating both a stiffening of the glassy compliance and a shifting of the glass transition temperature. However, at long times, there is an extra stiffening mechanism that leads to a breakdown of time-thickness superposition as one leaves the segmental regime towards the "rubbery" but stiffened plateau regime. The implications of the results are discussed.

Tuesday 10:45 San Carlos II SG19

Glass transition temperature of polystyrene at interfaces with inorganic substrates by time- and space-resolved fluorescence spectroscopy

Keiji Tanaka[1], Yohei Tateishi[1], Toshihiko Nagamura[1], Hiroshi Morita[2], and Masao Doi[2]
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Glass transition temperature (T_g) of a typical amorphous polymer, polystyrene (PS), at the interfaces with various inorganic substrates was non-invasively examined as a function of the depth by fluorescence lifetime measurement using evanescent wave excitation [1]. T_g was discernibly higher at the interface than in the bulk, and there was T_g gradient near the interface. The T_g value extrapolated to the outermost region, namely,

the center of the interface, was strongly dependent on the interfacial free energy. The experimental result was good accordance with the prediction based on the coarse-grained molecular dynamics simulation.

1) K. Tanaka, Y. Tsuchimura, K. Akabori, F. Ito, T. Nagamura, Appl. Phys. Lett. 2006, 89, 061919-1-2.

Tuesday 11:05 San Carlos II SG20

Molecular dynamics of ultra-thin supported polysulfone films

Diana Labahn and Andreas Schoenhals

Federal Institute of Materials Research and Testing, Berlin, D-12205, Germany

Broadband dielectric spectroscopy (10 mHz to 10 MHz) was employed to study the glassy dynamics of ultra thin supported polysulfone layers. The ultra thin films were prepared between two aluminum electrodes. Glass slides, cleaned in an ultrasound alkaline bath, rinsed in pure chloroform, and dried under nitrogen flow, were used as supporting substrates. Thin polymer films were spin-coated from a chloroform solution at 3000 rpm. The film thickness from microns down to below 10 nm was adjusted by changing the concentration of the polymer in solution. After spin-coating, the samples were annealed at a temperature well above the bulk glass transition (Tann = Tg,Bulk + 35K). To investigate the influence of the annealing conditions for a constant film thickness of 14 nm the annealing temperatures was varied from close to the glass transition up to Tg,Bulk + 35K. As a main result, for carefully annealed samples no change of the glass transition temperature with the decreasing film thickness is observed in contradiction to literature results (Torkelson et al. Polymeric Materials: Science & Engineering 2007, 97, 783). A more detailed analysis using a derivative technique shows that the Vogel temperature increases und the fragility parameter decreases with decreasing film thickness. The annealing experiments at constant film thickness show that the glass transition of the layers decreases with decreasing annealing temperatures. So the difference between literature and our results can be understood on the base of the different annealing conditions. The intensity of the dielectric glass transition decreases strongly with decreasing film thickness. This is modelled by an immobilized surface layer strongly adsorbed onto the Al-electrodes. A thickness of 5nm was estimated for the thickness of this surface layer.

Tuesday 11:25 San Carlos II SG21

Glassy dynamics in polymer thin films by inelastic neutron scattering

Toshiji Kanaya

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Dynamics of glass-forming materials in thin films is one of the current topics in condensed matter physics. We studied polystyrene (PS) thin films by neutron and X-ray reflectivity and found interesting but anomalous properties from the thickness measurements: glass transition temperature Tg decreases with film thickness below about 40 nm, there exists ultra-slow relaxation process in thin films, and thermal expansivity in glassy states decreases with film thickness. In order to understand the interesting findings, we started to study dynamics of PS thin films (20-100 nm) in glass and near glass transition by inelastic neutron scattering (INS) in meV and ueV region. In meV region we found that mean square displacement <u2> decreased with the film thickness below about 100 nm. Corresponding to the decrease in the mean square displacement, the density of phonon states G(w) as well as the so-called picosecond fast process depressed with decreasing the film thickness in meV region. We also studied dynamic heterogeneity of the glassy thin films in terms of non-Gaussian parameter to find the heterogeneity increased with decreasing the film thickness. These findings suggest that potential hardening occurs in the thin films due to a hard layer at the interface. In ueV region the temperature dependence of <u2> changed at the glass transition temperature Tg for the bulk sample. As the film thickness decreased, the glass transition temperature evaluated from the temperature dependence of <u2> increased. This observation completely contradicts the results by neutron and X-ray reflectivity measurements, where Tg decreases with film thickness. In the meeting we will discuss the difference in Tg between the INS and the XR results.

HP-5. Entangled Polymers I

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Ole Hassager and David C. Venerus

Tuesday 9:45 San Carlos III HP31

Rheo-dielectric studies of concentrated polyisoprene solutions

Jai A. Pathak[1], Riccardo Casalini[1], C. M. Roland[1], Simone Capaccioli[2], and Nikos Hadjichristidis[3]

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We have performed dielectric spectroscopy on concentrated and well-entangled Cis-1,4-Polyisoprene solutions in n-tetradecane while they undergo steady step shear. The volume fraction of polymer is ~ 0.2, and the number of entanglements per chain varies between 20 and 30. Cis-1,4-Polyisoprene is a Stockmayer Type-A dipole, with one dipole moment component along the chain backbone. Hence dielectric spectroscopy on it reveals the global chain relaxation (normal mode/end-to-end vector relaxation), in addition to its segmental mode relaxation. We critically examine the normal mode in strongly non-linear (shear thinning) flows in the cone (22.8 mm diameter)-platen (25 mm) geometry, into which the dielectric setup has been integrated. While Watanabe and co-workers have recently reported results of their elegant rheo-dielectric experiments on Polyisoprene solutions in oligomeric butadiene in both the linear and non-linear regimes, we are able to access larger Weissenberg numbers (and hence more strongly non-linear flows), as we work with a sea of fluid surrounding the cone, and the edge remains intact deeper into the shear thinning regime. In addition to visual inspection of the sample edge, we also check for validity of the Cox-Merz rule, by plotting shear viscosity data in the steady state of step strain experiments along with the complex viscosity, finding good agreement between the two. The normal mode dielectric loss peak is well resolved: DC conductivity effects at low frequencies (arising from ionic impurities) do not mask the normal mode peak in the dielectric loss. Preliminary results indicate that the dielectric strength continually decreases well into the non-linear regime, perhaps a consequence of the orthogonal directions of the dielectric measurement (velocity gradient direction) and the chain stretching (flow direction). Current efforts are focusing on quantifying the change in dielectric strength in concert with the measured rheological material functions (shear viscosity, first normal stress difference, shear stress), interpreting the results and reconciling them with predictions of tube model based molecular theories in the non-linear regime proposed by various different groups.

Tuesday 10:05 San Carlos III 💿 HP32

Effects of supercritical fluids, pressure, temperature, and molecular structure on the rheological properties of molten polymers

Hee Eon Park and John M. Dealy

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Since high pressures are involved in most plastics forming processes, reliable high-pressure rheological data are required for the simulation of the foaming process. The effect of pressure is in some ways the reverse of that of temperature; for example increasing T decreases the viscosity, while increasing P increases it. Supercritical fluids (SCFs) such as carbon dioxide and nitrogen can act as physical blowing agents in the manufacture of foams and as plasticizers to reduce melt viscosity during processing. The effects of dissolved SCF, pressure, and temperature on the rheological properties of a melt must be known to achieve optimum processing conditions. We used a high-pressure sliding plate rheometer, in which the shear strain, temperature, pressure, and SCF concentration are all uniform. A shear stress transducer senses the stress in the center of the sample to avoid edge effects. It was possible to use shift factors for temperature, pressure and SCF concentration to obtain a master curve. The effect of temperature could be described by the Arrhenius equation, and the effect of pressure was described by the Barus equation. The effect of SCF concentration could be described by the Fujita-Kishimoto equation. The relative effects of concentration, pressure, and temperature were quantified. To study the effects of short and long chain branching and a phenyl side group, three polymers were used: polyethylene, polypropylene, and polystyrene. We quantified the effects of pressure, temperature and dissolved gases on the rheological properties of these three polymers by use of shift factors.

Tuesday 10:25 San Carlos III HP33

Universal scaling characteristics of stress overshoot in startup flow of entangled polymer solutions and melts

Sham Ravindranath and Shi-Qing Wang

Polymer Science, University of Akron, Akron, OH 44325, USA

We have carried out conventional rheological measurements to explore the well-known stress overshoot behavior in startup flow of entangled polybutadiene (PBD) solutions and styrene-butadiene rubber (SBR) melts. In the elastic deformation regime where the product of flow rate and terminal relaxation time is higher than the number of entanglements per chain, Z, we observed universal scaling features associated with the stress maximum ?y for samples of different levels of entanglements per chain ranging from 27, 40 to 160. Specifically, both startup shear and extension produce a force maximum at a strain that increases with the applied rate to its 1/3 power. Moreover, the force maximum is proportional to the elapsed strain. Remarkably, these scaling laws form master curves when the peak stress, strain rate and peak time are all normalized with the cross-over modulus Gc, reciprocal Rouse time, and Rouse time ?R respectively. Equally noteworthy is the emergence of a super-master curve for the normalized stress ?(t)/?y as a function of the normalized strain at various applied rates.

Tuesday 10:45 San Carlos III 💿 HP34

Establishing a new nonlinear Q parameter from FT-rheology first investigation on monodisperse polymer melts

Kyu Hyun and Manfred Wilhelm

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Nonlinear response of monodisperse polymers has been investigated under oscillatory shear with Fourier-Transform rheology (FT-rheology). The relative third intensity ($I_{3/1}$), which is quantification of nonlinearity, was found to show a extended power-law relationship with strain amplitude at low and medium strain amplitudes. On a log-log plot, the $I_{3/1}$ were investigated at different excitation frequencies, temperature and molecular weight. Simulation results with different constitutive equations [Giesekus, exponential Phan-Thien Tanner (E-PTT)] were also compared with experimental result. From experimental results, the $I_{3/1}$ was affected by the excitation frequency and temperature, and the slope for linear polymer remained constant (γ_0^2), regardless of molecular weight, molecular weight distribution, and excitation frequency. This is in accordance with the predictions of constitutive equations (Giesekus and E-PTT). From these results, we proposed new nonlinear parameter, which is defined as $Q = I_{3/1}/\gamma_0^2$. This new nonlinear parameter from FT-rheology is investigated as a function of molecular weight and polymer topology.

Tuesday 11:05 San Carlos III HP35

Polydispersity in the tube model

Bart Vorselaars and Alexei E. Likhtman

Department of Mathematics, University of Reading, Reading, Berkshire RG6 6AX, UK

Sufficiently long polymer chains in an equilibrium melt are entangled. These entanglements give rise to a slower stress relaxation. For monodisperse melts this process is well described by the current tube models. Next to the dominant reptation mechanism these models include subdominant mechanisms such as chain contour length fluctuations and constraint release. In the polydisperse case the mechanism of constraint release becomes much more important. The relaxation of short chains not only causes the plateau modulus of long chains to decrease (due to the dilution in the number of entanglements and hence an effective increase in the tube diameter), but it is experimentally observed that it also leads to a decrease in the disengagement time. In particular this last observation is not well described by the current tube theories such as double reptation. As commercially available polymer melts are generally of a polydisperse nature, any practical application of the theory should describe the polydispersity rather well. In this study we aim at improving the tube model for polydisperse melts. We modify the double reptation algorithm by renormalizing the elementary Rouse time and the number of entanglements of each molecular weight, taking into account all other molecular weights in the melt. In the particular case of binary blends our theory covers the well known regimes of tube dilution and constraint release Rouse relaxation. An extensive comparison with industrial polydisperse melts is presented.

Tuesday 11:25 San Carlos III HP36

Extensional rheology of polypropylene melts: Experiments and modeling

Antonios K. Doufas

Research & Technology, Sunoco, Inc., Pittsburgh, PA 15206, USA

Extensional rheology of polypropylene melts is investigated both from an experimental and modeling point of view. Among others, one way of approaching extensional rheology of polypropylene is the rheotens device that appears to most closely simulate deformation under fabrication conditions such as fiber spinning, non-woven spunbonding, film casting and film blowing. The rheotens model of Doufas (2006) [Doufas, A.K., “Analysis of the rheotens experiment with viscoelastic constitutive equations”, J. Rheol. 50, 749-769 (2006)] coupling the transport equations with constitutive equations based on polymer kinetic theory, is expanded and applied to the simulation of polypropylene melt rheology data. Comparisons of model predictions with experimental data from the literature as well as newly developed data will be discussed. A variety of polypropylene materials and test processing conditions will be demonstrated. Correlation of extensional rheology as measured by rheotens, die swell and shear rheology will be investigated.

HP-6. Cross-linked Polymers and Gels

Organizers: Lynden A. Archer and Alexei E. Likhtman

Session Chairs: Claude Cohen and Julia A. Kornfield

Tuesday 9:45 San Carlos I 💿 HP37

Analysis of rubber elasticity in terms of crosslinks and entanglement contributions

Seong Hyun Yoo and Claude Cohen

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End-linked poly(dimethylsiloxane) (PDMS) networks synthesized from telechelic precursor chains of different molar mass were prepared with varying volume fractions of non-reactive chains acting as solvent. Uni-axial extension and compression measurements were performed on these networks to investigate their stress-strain behavior and examine the role of cross-links and entanglements on their properties. The measurements were carried out for both the swollen networks (as prepared) and the dried networks (after extraction of the non-reactive solvent chains). Deviations from ideal rubber elasticity increased with both molar mass of the precursor chains and the reactive polymer concentration of the networks. Analysis of the data in terms of the two moduli (Gc and Ge) of the non-affine slip tube model will be presented.

Tuesday 10:05 San Carlos I 💿 HP38

Primitive chain network simulations for particle dispersed polymers

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Polymeric materials with dispersed solid particles are often used as functional materials. Hence their dynamics is worth being investigated. However, effective simulation methods of particle suspensions in polymeric matrices do not seem available, since coarse-grained molecular dynamics is still unable to deal with the long relaxation times of such systems. Continuum-mechanics calculations are also difficult due to the simultaneous occurrence of memory effects and hydrodynamic interactions. In this study a novel simulation method is proposed, which extends the primitive chain network simulation model for entangled polymers. The model represents the liquid system as a 3-dimensional sliplink network, and the solid particles floating in the liquid as cross-linked domains with elastic and viscous contrast from the matrix. Initial conditions were generated by simulating phase separation of blends, by stopping coarsening at some length scale, and finally by crosslinking the dispersed phase. Interaction between the liquid and the solid is given by a repulsive potential similarly to incompatible polymer blends, while a no-slip boundary condition at the solid surface is controlled by hooking and unhooking dynamics of the polymer chain ends with the crosslinked network of the solid. Shear flow simulations were performed with shear rates smaller than the inverse longest relaxation time of the matrix. It was confirmed that the steady shear viscosities obtained at several particle concentrations are consistent with Einstein relationship.

Tuesday 10:25 San Carlos I HP39

Nonlinear mechanical behavior of scarcely crosslinked poly (dimethyl siloxane) gel: Effect of strand length polydispersity

Hiroshi Watanabe[1], Hideaki Takahashi[2], and Yoshitake Ishimuro[2]

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Nonlinear mechanical behavior was examined for a scarcely crosslinked poly(dimethyl siloxane) gel (referred to as Gel-1/1) under constant-rate elongation and large step shear strains. The average molecular weight of the gel strands evaluated from the equilibrium modulus in the linear viscoelastic regime was Mc = 160K, and the strands had a significantly broad molecular weight distribution, Mw/Mn = 500 as estimated by fitting the linear viscoelastic moduli with a Rouse network model. In the elongational test at constant elongational rates $d\varepsilon/dt$ (= $d\{\ln \lambda\}dt$; λ = elongational ratio), the Gel-1/1 sample exhibited rate-insensitive strain hardening followed by rupture at λmax = 4.5. This λmax was significantly smaller than the λmax° nominally expected for a gel composed of monodisperse strands having Mc = 160K; λmax° = 49 and λmax/λmax° = 0.09 for those strands. In contrast, a reference experiment made for a Gel-U sample composed of monodisperse strands (Mc = 84K) indicated that λmax of this gel was not significantly different from λmax°; λmax = 14, λmax° = 36, and λmax/λmax° = 0.4 for Gel-U. These results suggested that the low-M fractions of the strands in the Gel-1/1 sample were highly stretched and broken at λ much smaller than λmax° being defined for the average Mc, thereby governing the nonlinear elongational behavior/rupture of Gel-1/1. Under large step shear strains γ (> 2), Gel-1/1 exhibited nonlinear decay of the shear stress with time. Analysis of the linear viscoelastic moduli of Gel-1/1 after imposition of large strains indicated that the stress decay under large strains reflected scission of the low-M fractions of the gel strands as well as the motion of scission-formed long strands occurring with time. This behavior was qualitatively similar to the nonlinear elongational behavior, although a delicate difference related to a time-dependent strand cessation and the motion of scission-formed long strands remained between the nonlinearities under the large shear and elongation.

Tuesday 10:45 San Carlos I HP40

Anisotropic thermal conductivity measurements on cross-linked polybutadienes in uniaxial elongation

David C. Venerus and Dimitre Kolev
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Cross-linked elastomers have numerous applications including automobiles, sporting goods, and biomedical devices. During both their processing and application, these materials experience large mechanical stresses and thermal gradients. In this study, we investigate the mechanical, optical and thermal transport behavior of cross-linked polybutadienes. These materials have been prepared by lcightly cross linking well-entangled polybutadienes using an organic peroxide cross-linking agent at low concentration. One of the polybutadienes has a narrow molecular weight distribution. We report linear viscoelastic measurements of this system at various stages of cross-linking. Samples obtained after nearly complete conversion of the cross-linking agent, which can be characterized as lightly cross-linked (i.e., more than 10 entanglements per cross-link), were subjected to a series of large strain, uniaxial deformations. Measurements of the tensile stress and two components of the thermal conductivity tensor will be reported as a function of elongation. These data are also used to examine the stress-thermal rule in which the stress and thermal conductivity tensors are linearly related.

Tuesday 11:05 San Carlos I HP41

Interfacial friction of PDMS network films

Lucas J. Landherr, Lynden A. Archer, and Claude Cohen
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This study focuses on developing a surface-attached lubricant for use in nanoscale applications that would significantly decrease friction and wear. Vinyl-terminated polydimethylsiloxane chains are spincoated with a crosslinking agent and platinum catalyst onto silicon wafers covered with a self-assembling monolayer. Atomic force microscopy is used to analyze the coefficient of friction (COF) of the PDMS-SAM surface tethered network. The combined polymer network and SAM layer are found to decrease the COF by up to 96 percent. Friction is found to be lowest for nanoscale thick networks; these polymer networks are poorly crosslinked and resemble hyperbranched polymers, but still have COFs almost 30 percent lower than a solitary SAM layer. Model networks with microscale thicknesses have COFs approximately three times larger than the thinner networks. Research conducted into the addition of pendant chains into the thicker networks shows the COF decreases to a minimum before increasing as the polymer network deteriorates. We also discuss the effect of free chains in these surface-tethered networks on friction and adhesion characteristics of surfaces.

Tuesday 11:25 San Carlos I HP42

Rheological models for molecular design of adhesives

Gérard R. Marin[1] and Christophe Derail[2]
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Pressure Sensitive Adhesives (PSAs) are polymer-based adhesives which present stickiness (“tack”) at room temperatures. Hot Melt (HM) adhesives are processed at high temperatures (usually above 80°C) and present stickiness at high temperature and a usual polymer solidlike behavior at room temperature. Both families of adhesives usually contain polymer(s) and tackifying resin(s) which are usually made of small compatible organic molecules which bring "tack" and softness to the adhesive, by lowering the elastic modulus value (topological effect) and shifting the glass transition temperature (thermodynamic effect). The adherence properties of adhesives strongly depend on their rheological properties, as viscous losses are predominant in the breaking of an adhesive joint, such as tape peeling. Rheological properties control also in a large extent the process properties of adhesives and may be linked to process characteristics such as the “open time” (in the case of HM) or “setting time”. The tremendous progress made on the understanding of the viscoelastic properties of linear and model branched polymers allows now to predict their rheological properties from structural parameters. Inversion of these models allows designing molecules to fit expected viscoelastic and properties. This concept may be applied to adhesives, as the respective effects of polymer(s) and resin(s) on the viscoelastic and adherence properties are now much better understood. Examples will be given of such a "molecular design" concept for adhesives, in the cases of PSAs based on block copolymers, Hot-Melt adhesives and model adhesives which exhibit the main features of these structure-properties relationships.

BR-1. Rheology of the Cytoskeleton

Organizers: James L. Harden and Christoph F. Schmidt
Session Chair: Claudia Mierke

Tuesday 9:45 Redwood BR1

Local deformations and nonlinear elasticity in semiflexible biopolymer matrices

Qi Wen[1], Anindita Basu[1], Jessamine P. Winer[2], Arjun Yodh[1], and Paul A. Janmey[2]
[1]Physics, University of Pennsylvania, Philadelphia, PA, USA; [2]Institute for Medicine and Engineeering, University of Pennsylvania, Philadelphia, PA, USA

Networks formed by filamentous biopolymers like collagen and fibrin have viscoelastic properties that are very different from those of rubber-like elastomers or hydrogels formed by flexible polymers. Compared to flexible polymer gels, filamentous biopolymer networks generally have much higher shear moduli, they often exhibit a striking increase in elastic modulus with increasing strain, and they show a pronounced negative normal stress when deformed in simple shear. Several different theories have been proposed to explain these unusual features. One approach extends concepts of entropic elasticity to a regime where the polymer chains are already significantly extended in the absence of external forces because of their finite bending stiffness. Others consider the balance between bending and stretching of filaments. The theories that relate microscopic structural parameters such as persistence length and mesh size of biopolymer gels to their macroscopic rheology make different predictions about whether the deformation of these materials is affine: that is, whether the macroscopic strain of the bulk material is equal to the local strain within the material at each point. The validity of this assumption for the dilute open meshworks biopolymer gels is experimentally tested by embedding micron diameter fluorescent beads within networks and quantifying their displacements as the macroscopic samples are deformed in a rheometer. In some cases individual polymer chains can be imaged within the strained network to relate molecular deformation to macroscopic material properties. For homogenous networks of thin fibers such as fibrin protofilaments, nonaffinity measures are low and do not change as the material stiffens. As fiber diameter and mesh size increase, non-affinity also increases and becomes strain dependent. Correlation of nonaffine deformation and strain stiffening can help differentiate between different theoretical models.

Tuesday 10:05 Redwood BR2

Nonlinear elasticity of composite networks of stiff biopolymers with flexible linkers

Chase P. Broedersz[1], Cornelis Storm[2], and Fred MacKintosh[1]
[1]Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands; [2]Instituut Lorentz, Leiden University, Leiden, The Netherlands

Recent in vitro experiments on F-actin networks with the physiological cross-linker filamin have shown very striking non-linear elastic behavior, including 1000-fold stiffening under strain. This behavior appears to result from the highly flexible nature of filamin, although the basic physics of such a network is not understood. We present an effective medium theory of flexibly cross-linked stiff polymer networks. We model such composite networks as a collection of randomly oriented rods, each of which is mechanically connected by flexible connectors to a surrounding elastic continuum, which self-consistently represents the behavior of the rest of the network. This model yields a cross-over at a characteristic strain from a linear elastic regime to a highly nonlinear elastic regime that stiffens in a way quantitatively consistent with experiment. The characteristic strain is determined by the ratio of the cross-linker and rod lengths.

Tuesday 10:25 Redwood BR3

Microrheology of microtubule and actin-microtubule networks

Maria L. Kilfoil, Vincent Pelletier, Antony Orth, and Daniel Foreman-Mackey
Physics, McGill University, Montreal, QC H3A 2T8, Canada

We have investigated the viscoelastic properties of microtubule networks and actin-microtubule composite networks using multiparticle tracking passive microrheology. The 1 point (autocorrelation) and 2 point (cross-correlation between probe pairs) are used to characterize the local and bulk material, respectively. We find striking agreement between the microtubule network's viscoelastic moduli and the prediction from the Doi-Edwards model for semi-dilute rigid rod solutions, and compare the microrheology to bulk rheology measurements. Furthermore, we have found that the viscoelastic properties of composite actin-microtubule networks are completely different from those of actin networks and microtubule networks alone, despite evidence from the autocorrelation data that the local microenvironment is dominated by the actin. The Poisson ratio of the networks, calculated from the 2 point analysis, indicates that the presence of microtubules in an otherwise incompressible actin network causes the material to be compressible.

Tuesday 10:45 Redwood BR4

Buckling and force propagation along intracellular microtubules

Moumita Das[1], Alex J. Levine[2], and Fred MacKintosh[1]
[1]Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands; [2]Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, CA, USA

The mechanics of most eukaryotic cells is governed by their cytoskeleton, a composite polymeric scaffold made of a variety of semiflexible protein filaments and crosslinkers. The *nonlinear elasticity* arising due to the *semiflexibility* of these biopolymers, together with the *composite* nature of the network leads to new physics not observed for flexible or one-component polymer networks. Of all the cytoskeletal filaments, microtubules are the stiffest and play a crucial role in cell mechanics and intracellular transport. Recent experiments [1] have shown that the mechanical reinforcement due to the surrounding cytoskeleton allows microtubules (MTs) to bear very large compressive loads (up to 100pN), and can greatly affect force transmission along MTs. Motivated by this, we study theoretically the mechanical response of and force propagation along elastic filaments embedded in the non-linearly elastic cytoskeletal matrix. We find that, although embedded microtubules buckle when their compressive load exceeds a critical load found earlier, the resulting deformation is restricted to a penetration depth that depends on both the non-linear material properties of the surrounding cytoskeleton, as well as the direct coupling of the microtubule to the cytoskeleton possibly through MT-associating proteins (MAPS). This gives rise to a finite, monotonic force-extension behavior. This work shows how the range of compressive force transmission by microtubules can be as large as tens of microns and is governed by the direct coupling to the surrounding cytoskeleton.

[1] CP Brangwynne et al., J. Cell Biology, 173, 733 (2006).

Tuesday 11:05 Redwood BR5

Rheology of reconstituted networks of biopolymers

Yi-Chia Lin, Karen E. Kasza, Norman Y. Yao, Sabine Volkmer, and David A. Weitz
School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

This talk will review recent progress on the measurement of the rheology of reconstituted networks of biopolymers. Data will be presented on actin networks cross-linked with different cross-liking molecules, and on networks of intermediate filaments.

MP-3. Injection Molding

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: Wesley R. Burghardt

Tuesday 9:45 Ferrante I-III 💿 MP16

High strain rate rheometry of polymer melts using an instrumented injection molding machine

Adrian L. Kelly, Tim D. Gough, and Phil D. Coates
IRC in Polymer Engineering, University of Bradford, Bradford BD7 1DP, UK

With the increased use of micro-scale and thin-walled injection moulding processes, wall shear strain rates experienced by polymer melts flowing through the gate region can be greater than 1e6 s-1. This is outside the region of conventional flow characterisation and therefore there is a need to characterise polymers at extremely high processing rates. A modified high-force all-electric moulding machine has been used in air-shot mode with capillary dies fitted at the nozzle to examine the rheology of a number of commercial polymers at uncorrected strain rates of up to 6e6 s-1. Shear and extensional flow properties were obtained through the use of long and orifice (close to zero land length) dies of the same diameter. A range of polyethylene, polypropylene and polystyrene melts have been characterised to examine the effect of molecular weight and chain branching. Wall slip behaviour of two grades of HDPE has been examined at high strain rates, and the effect of hyperbranching on PMMA has been studied.

Tuesday 10:05 Ferrante I-III 💿 MP17

In situ x-ray scattering measurements and polydomain simulations of molecular orientation development during injection molding of liquid crystalline polymers

Jun Fang and Wesley R. Burghardt
Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, USA

The properties of liquid crystalline polymers (LCPs) are profoundly affected by the molecular orientation state generated by flow fields encountered during processing. In this talk we report on a coordinated experimental/computational study of injection molding of commercial thermotropic LCPs. In situ synchrotron x-ray scattering, combined with a customized injection molding apparatus, is used to track development of molecular orientation during the mold filling process for several different LCP materials in two simple plaque mold geometries: square and T-shaped. While geometrically simple, these flows are characterized by complex inhomogenous mixtures of shear and extension, which influence orientation development. Use of high brilliance undulator radiation at the Advanced Photon Source, coupled with a high speed CCD detector provides sufficient time resolution (~ 12 frames per second) to resolve the transient orientation dynamics during and following mold filling. The experiments are complemented by process simulations performed using commercial mold filling software. A very close analogy between the Folgar-Tucker fiber orientation model and the Larson-Doi polydomain model for textured liquid crystalline polymers is exploited to allow for the first tests of Larson-Doi model predictions in injection molding processing.

Tuesday 10:25 Ferrante I-III MP18

Rheology-structure relationships for wet powder-suspension transformation in extrusion processing

Tim O. Althaus[1] and Erich J. Windhab[2]
[1]Laboratory of Food Process Engineering, ETH Zurich, Zurich, Kanton Zurich 8092, Switzerland; [2]Institute of Food Science and Nutrition, ETH Zurich, Zurich 8044, Switzerland

A paste can be described as a dense suspension of rigid fillers in a viscous fluid phase. Extrusion is a process commonly used to achieve a desired shape, and finds application in the production of a range of materials including catalyst supports, ceramics and foods. In several technological areas the solid concentration required in the final products (such as paints, food pastes, pharmaceutical) comes close to the critical concentration above which a homogeneous paste cannot be produced with the standard mixing processes. In this concentration range the viscosity increases consistently, high mixing homogeneity is difficult to achieve, and air is incorporated in the system during mixing. Such systems may appear as a wet powder in which the fluid phase, the solid fillers and the gas phase coexist. In the presented work a new concept has been developed in order to describe the fluid- and powder mechanics related structure-rheology relationships of model systems, which experience transition from a 3-phase wet powder (3P) to a 3-phase aerated concentrated suspension (3S) to a 2 -phase suspension (2S). Experimental work has been carried out applying the 3P2S dynamic structure transition to velocity and stress fields acting in extrusion entrance / die flows.

Tuesday 10:45 Ferrante I-III 💿 MP19

Simulation of orientation in injection molding of high aspect ratio particle thermoplastic composites

Gregorio M. Vélez-García[1], Aaron P. Eberle[2], Kevin C. Ortman[2], Donald G. Baird[2], and Peter Wapperom[3]
[1]Macromolecular Science and Engineering, Virginia Tech, Blacksburg, VA 24061, USA; [2]Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, USA; [3]Mathematics, Virginia Tech, Blacksburg, VA 24061, USA

High aspect ratio particle composites such as nanocomposites or fiber composites are a promising technology to manufacture lightweight materials. The properties of these materials highly depend on the orientation of the particles in the matrix. At present, the available simulations of injection molded parts of fiber composites ignore the viscoelastic behavior of the polymeric matrix and were typically performed using Hele-Shaw flow approximations. Therefore the predictions of these simulations were highly limited. In this study, the flow through a center gated disk and end-gated plaque geometry is simulated numerically for a highly concentrated short glass fiber in a PBT (Newtonian) or PP (viscoelastic) matrix. For this, a 2D Finite Element Method (FEM) analysis was performed using the traditional Galerkin method for the balance equations and discontinuous Galerkin for the constitutive equations. The fibers and viscoelastic matrix are modeled using the Doi and a Phan Thien-Tanner model, respectively. The impact of Hele-Shaw flow approximation, initial fiber orientation and a viscoelastic matrix was investigated. The predictions were evaluated with experimental data obtained using Laser Confocal Microscopy.

Tuesday 11:05 Ferrante I-III MP20

Numerical study on the impact of additives on shrinkage of injection molded polypropylene

Rong Zheng, Chitiur Hadinata, and Peter K. Kennedy
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Crystalline microstructure established during injection molding of semi-crystalline polymers can affect rheological and solidification behavior of the processed polymer, and cause differential and anisotropic shrinkage of the solidifying polymer. The variation in shrinkage will lead to warpage of the final product, which is generally undesirable. Certain colorants added in the material can further enhance the product distortion because of changes in the crystallization behavior of the material resulting from the nucleating effects of the pigments. In this work we present a numerical study on the flow-induced crystallization in injection molding and investigate the influence of colorants. The mathematical model used to describe the crystallization kinetics is based on Hoffman-Lauritzen theory to predict the growth rate as a function of both temperature and pressure. The model links nucleation rate of the crystalline entities to the change in dumbbell free energy induced by the flow. Parameters in the model were determined from experiments, mainly utilizing the Linkam shearing hot stage and Differential Scanning Calorimetry (DSC). A commercially available isotactic polypropylene was used as the base material. Two types of blue colorants, Cu-Phthalocyanine and Sodium Alumino Sulpho Silicate –which we denote by P and U, respectively – were used as additives. For each P and U colorant with different concentrations, twenty-eight moldings were produced. Cavity pressure and molding shrinkage were measured for comparison with numerical solutions. Results showed that the predicted pressure-time profiles are in agreements with experiments. We found that the crystallization kinetics were accelerated by flow effects for both U-colored and P-colored materials. However, sensitivity of the P-colored material to shear rate was higher than the U-colored material. It is also found that, while the influence of U-type colorant on the shrinkage appeared to be practically negligible, the P-type colorant reduced the shrinkage in the flow direction but increased the transverse shrinkage significantly. We surmise that warpage problems will be more likely with this colorant than the uncolored or U-colored materials.

IR-3. Interfacial Rheology and Thin Film Flow

Organizers: Jan Vermant and Kausik Sarkar
Session Chairs: Kausik Sarkar and Siegfried Steltenkamp

Tuesday 9:45 Bonsai I IR16

Cholesterol effects on the surface viscosity of lung surfactant monolayers

Siegfried Steltenkamp, C Alonso, Todd M. Squires, Si Young Choi, and Joseph A. Zasadzinski
Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, USA

Lung surfactant (LS), a complex mixture of lipids and proteins that line the alveolar epithelial surfaces of humans and other mammals, has to achieve several seemingly contradictory results for proper lung function to occur. First, LS must form a stable interfacial film with sufficient integrity to sustain high surface pressures (low surface tensions) on compression of the interface during exhalation. At the same time, LS must spread quickly to re-cover the interface during inspiration. This requires a subtle balance of lipids and proteins in the interfacial films, and may require different interfacial compositions and a wide variation in surface viscosity and elasiticity during lung expansion and compression. An lack of LS in premature infants leads to neonatal respiratory distress syndrome (nRDS), which is treated by replacing the native LS with surfactants derived from animals. An important question in developing replacement surfactants is whether or not cholesterol belongs in a replacement lung surfactant. We present detailed measurements of the macroscopic and microscopic surface viscosity of LS and phospholipid monolayers that show the two to three order of magnitude reduction in surface viscosity on addition of 1 – 3 mole% cholesterol. This dramatic change in the ordering of the film is also seen in the monolayer compressibility and at slightly higher mole fractions, in the collapse pressure of the monolayers.

Tuesday 10:05 Bonsai I IR17

From molecular pressure sensors to surface frictions

Hui Xu[1], Frank Sun[1], David Shirvanyants[1], Michael Rubinstein[1], Sergei Sheiko[1], Krzysztof Matyjaszewski[2], and Kathryn Beers[2]
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Flow properties of molecularly thin films are at the foundation of many practical applications such as lithography, microfluidics, coatings, and lubrication. Further advances in these fields depend on understanding the mechanisms that control the kinetics of flow. However, one of the problems in flowing monolayers is the independent characterization of the driving and frictional forces that are intimately coupled through the molecular interactions between the fluid and the substrate. In this regard, the visualization of compressible macromolecules during flow provides an exceptional opportunity to study these forces. Here we report on the monitoring of comb-like macromolecules as they change their shape in response to variations in the film pressure during flow. After appropriate calibration, these molecular sensors can be used to gauge both the pressure gradient and the friction coefficient at the substrate. We further characterized the surface frictions of such comb-like macromolecules under various humidity conditions.

Tuesday 10:25 Bonsai I IR18

Viscoelasticity of semifluorinated alkanes at the air-water interface

Christina Christopoulou[1], Dimitris Vlassopoulos[1], George Fytas[1], and Chris Clark[2]
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We studied the viscoelastic properties of semifluorinated alkanes F(CF2)n(CH2)mH (referred as FnHm) spread on the air-water interface. These specially synthesized model ‘doubly-hydrophobic’ macromolecules of varying architecture reside at the air-water interface in the form of well-defined disk-like surface micelles that minimize the free energy. Small angle x-ray scattering over studies indicated a typical ‘disc’ diameter about of 30 nm in diameter. Pressure area isotherms performed on Langmuir monolayers of the micelles exhibit two transitions: one at ~ 4 mN/m and a second at ~ 7 mN/m. In both regimes the film exhibited a solid like viscoelastic response. As the surface pressure increased in each regime values of the storage and the loss surface moduli increased as well. These findings are discussed in view of recent theoretical developments and provide opportunities for manipulating surface structure and rheology of such types of macromolecules. Last the effect of architecture on this surface structure - rheology interplay is also addressed.

Tuesday 10:45 Bonsai I IR19

Rheology measurements of spider-silk proteins adsorption at surfaces

Cyrille Vézy, Kevin D. Hermanson, Markus Harasim, and Andreas R. Bausch
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New release systems are required in many technical and industrial applications such as flavor encapsulation or drug delivery. Encapsulation of flavors and drugs in micron-sized capsules can be achieved by emulsion or flow focusing techniques. Here, we use recombinantly produced spider-silk proteins as a shell material for microcapsules. For a full tuning and controlling of the release mechanism, interfacial properties of the microcapsules have to be understood.

In order to investigate the adsorption kinetic and mechanism of spider-silk proteins at an interface, we perform interfacial rheological measurements. We compare the adsorption kinetic and mechanism of β-lactoglobulin and spider-silk proteins at liquid/liquid or air/liquid interfaces. By measuring the time evolution of the shear and loss modulus of the film formation, we show that already at 4 μg/ml concentrations of spider silk proteins mechanical stable films are formed. In comparison, β-lactoglobulin films form only at two order of magnitude higher concentrations with a lower mechanical stability as observed for spider silk films. Moreover, the mechanical properties of such formed spider-silk membranes can be sensitively tuned by adding phosphate. This demonstrates the excellent efficacy of spider-silk proteins to form thin membrane films, required in many encapsulation application.

Tuesday 11:05 Bonsai I ⊛ IR20

Modeling and characterization of encapsulated microbubbles for ultrasound imaging and drug delivery

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Intravenously injected encapsulated microbubbles improve the contrast of an ultrasound image. Their destruction is used in measuring blood flow, stimulating arteriogenesis, and drug delivery. We measure attenuation and scattering of ultrasound through solution of commercial contrast agents such as Optison (GE Health Care, Princeton, NJ) and Definity (Bristol Meyer-Squibb Imaging, North Ballerina, MA). We have developed an interfacial rheology model for the encapsulation of such microbubbles. By matching with experimental data, we obtain the characteristic rheological parameters. We compare model predictions with other experiments. We also investigate microbubble destruction under acoustic excitation by measuring time-varying attenuation data. Three regions of acoustic pressure amplitudes are found: at low pressure, there is no destruction; at slightly higher pressure bubbles are destroyed, and the rate of destruction depends on a combination of PRF and amplitude. At a still higher pressure amplitude, the attenuation decreases catastrophically. The last two regimes correspond respectively to 1) slow destruction of bubbles due to increased gas diffusion and 2) complete bubble destruction leading to release of free bubbles. An analytical model for the bubble growth and dissolution will be presented. The effects of membrane permeability and elasticity on the stability of microbubbles are investigated. (Supported by DOD, NSF and University of Delaware Research Foundation)

SC-3. Yielding and Thixotropy I

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chair: Philippe Coussot

Tuesday 9:45 De Anza III ⊛ SC16

Theory of thermodynamic stresses in colloidal dispersions at the glass transition

David Hajnal[1], Oliver Henrich[2], Jérôme J. Crassous[3], Miriam Siebenbürger[3], Markus Drechsler[4], Matthias Ballauff[3], and Matthias Fuchs[5]
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We consider a model dense colloidal dispersion at the glass transition, and investigate the connection between equilibrium stress fluctuations, seen in linear shear moduli, and the shear stresses under strong flow conditions far from equilibrium, viz. flow curves for finite shear rates. To this purpose thermosensitive core-shell particles consisting of a polystyrene core and a crosslinked poly(Nisopropylacrylamide)(PNIPAM) shell were synthesized. Data over an extended range in shear rates and frequencies are compared to theoretical results from integrations through transients and mode coupling approaches. The connection between non-linear rheology and glass transition is clarified. While the theoretical models semi-quantitatively fit the data taken in fluid states and the predominant elastic response of glass, a yet unaccounted dissipative mechanism is identified in glassy states.

Tuesday 10:05 De Anza III ⊛ SC17

Rheology and extrusion of cement-fly ashes pastes

Francesca Micaelli[1], Christophe Lanos[1], and Giovanni Levita[2]
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The aim of the work is to verify the possible use of fly ashes in cement pastes to optimize the forming of cement based material by extrusion. Two types of fly ashes were examinated: native fly ash (regular morphology, mean particle diameter 45 μm) and micronized ashes (diameter 4 μm) obtained by grinding the native ashes. In a first phase of the work the rheology of concentrated suspensions of ashes (solid volume fraction F=0.35-0.4) in water is studied by a parallel plates rheometer Physica Rheo-logic (Rheolab MC20) (smooth surfaces, 2.5 cm diameter). Flow curve provided by shear rate control tests (in the range 0 to 700 s-1) reveal the typical non-newtonian complex behaviour of the concentrated suspensions (viscoplastic fluid with shear thinning phenomena and time influence). In stationary flow state, tested suspensions viscosities versus

F were satisfactorily described by the Krieger-Dougherty model. Shear test performed on bimodal concentrated suspensions obtained by mixing native and modified fly ashes in water in variable ratio content evidenced a minimum value of the suspensions viscosity when the volume fraction of smaller particles is equal to 30 – 35% (uninfluenced by shear rate value). An optimal composition of fly ashes mixes is so identified. Appling the coated grain concept (each grain is associated to a coated fluid layer with appropriated mean thickness) viscosity of structural units suspension is reconsidered. An "overlapped grain" suspensions model able to describe the bimodal suspensions behaviour is proposed. Same types of testes are performed with rough plates on two or three component systems (Portland cement and fly ashes or optimal mixture of fly ashes) with higher values of solid volume fraction. Bingham viscoplastic behaviour is identified. Results showed that the plastic viscosity and plastic yield values present minimal values for the same optimal formulation of bimodal mixes. Rheology of three component systems appears quite independent from the optimal ashes mix-cement ratio in the range of composition 0 – 60% vol. but logically influenced by F. The rheological study is extended to more concentrated systems (F = 0.45 –0.55) using an extruder rheometer. Tests with dies of 10 mm diameter and different lengths (3, 5 and 10 cm) at different ram displacement velocity were performed on simple pastes of fly ashes and cement and on bimodal systems of fly ashes and cement-fly ash mixtures. The experimental data are analysed by the Benbow model determining the rheological parameter so (initial bulk yield stress) and to (initial wall shear stress) characterizing the material. Both type of fly ash showed a so value lower than those of cement while the to value of micronized ashes is higher, causing the more irregular morphology of particles. Fly ash bimodal systems showed a minimum value of so for the same micronized ash content found in more diluted suspensions. Finally it is observed that the addition of 30% vol. of ashes mix determined a significant reduction of required extrusion load.

Tuesday 10:25 De Anza III 💿 SC18

Multi-scales analysis to study the rheological behavior of natural mud suspensions

Yannick Melinge[1], Patrice Estelle[1], Arnaud Perrot[2], and Christophe Lanos[1]
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In this article, we study the rheological properties of evolved, polydispersed and fine suspensions. The case of muds is used as illustration. These families of liquid-solid mixtures constitute suspensions whose rheological behavior is complex and of various particle interaction origins (colloidal, hydrodynamic, frictional, ...). This behavior is affected by the chemical evolutions of the mixtures as well. Such mixtures can come within industrial applications, such as the case of water treatment station muds or muds of rivers, estuaries or seas. In order to study the properties of transport of such suspensions, we undertook a large experimental study on materials coming from Bay of Quiberon (southern of Brittany - France). These materials are mainly clays, silts, sands, but also salts, crystals and diatoms. These elements form the fine fraction of the mud, which is mainly studied in this work. In a general way, the rheological behavior of such mixtures evolves and so time dependant. The main behavior is viscous, viscoplastic even elasto-visco-plastic. However, in this article, the elastic part of the behavior is not studied. In isothermal condition and liquid phase, the suspension rheological properties are studied by means of a multi-scales approach. The structure build up under shear and the influence of the solid volume fraction are analysed. The identification of the granular interactions is also studied by an approach of Structural Units type. This work is completed starting from mixtures for which the chemical activity is not significant. This state of the matter constitutes a reference in the research of the chemical role part on the structure evolution of these fluids. In this work, the plastic limit is systematically identified and the suspension stability properties are particularly studied.

Tuesday 10:45 De Anza III 💿 SC19

Suspensions of noncolloidal particles in yield stress fluids: Experimental and micromechanical approaches

Fabien Mahaut, Xavier Chateau, Kien Luu Trung, Philippe Coussot, and Guillaume Ovarlez
LMSGC, Institut Navier, Champs sur Marne, France

We study experimentally and theoretically the behavior of suspensions of noncolloidal particles in yield stress fluids. Our goal is to link the paste properties to the yield stress fluid properties as a function of the particle volume fraction independently of the physicochemical properties of the yield stress fluid and particles, i.e. we focus on the purely mechanical contribution of the particles to the paste behavior.

In this aim, monodisperse suspensions with solid concentration ranging from 0 % to 50 % are prepared with various yield stress fluids (with different yield stress physical origins) and with particles of various sizes and with different surface properties. We also manage to develop procedures that allow studying homogeneous and isotropic suspensions. The results on all materials are consistent the one with the others, consistently with our goal. We obtain the universal laws linking the elastic modulus and the yield stress of the suspensions to the suspending paste properties (independently of their physical origin) and to the particle volume fraction (independently of their size and surface properties).

A nonlinear homogenization method is used to estimate the overall properties of the suspension with overall isotropy. When the particles are isotropically distributed within the suspending fluid and when the heterogeneities of the rate of strain field can be neglected over the domain occupied by the suspending fluid, it is shown that the elastic modulus/concentration relationship is linked to the yield stress/concentration relationship by means of a very simple law. We show that our experimental results are in very good agreement with this theoretical law.

We also present preliminary results concerning the flow properties of the same suspensions. We perform the experimental study with the help of a MRI device that allows measuring the local shear rate and local concentration of the suspensions, so that shear-induced migration is properly accounted for. The behavior of all suspensions is well fitted to a Herschel-Bulkley law. We show how the Herschel-Bulkley parameters depend on the particle volume fraction, and compare our results to the results obtained with the nonlinear homogenization method.

Tuesday 11:05 De Anza III SC20

Yield stress

David V. Boger[1], Ken Walters[2], Mike F. Webster[3], and Rhodri P. Williams[4]
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In this presentation, we shall show for the first time the fifth Institute of Non-Newtonian Fluid Mechanics (Wales) film entitled “Yield Stress”. The film is divided into the following sections: 1. Introduction. 2. The history of the yield stress concept. 3. Examples of materials exhibiting a yield stress, including videos of the slump test and other techniques for evaluating the yield stress. 4. The “yield stress controversy”. 5. Things agreed by all concerning the yield stress concept. 6. Conclusion.

GR-3. General Rheology

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Andrew M. Kraynik

Tuesday 9:45 Bonzai III GR16

Environmental rheology

David V. Boger
Dept of Chemical & Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

The minerals and energy industries worldwide are currently experiencing an unprecedented boom. Many of these companies are upbeat about sustainable development but most of their effort in sustainable practice is directed towards the social and stakeholder interaction in the community; very little effort is being made to apply sustainable practices to the management of the huge amount of liquid waste tailings produced by these industries as a suspension. Even though the technology exists now to move from wet to dry disposal methods, the industry still insists on building traditional dams that defer the costs associated with dealing with waste until some time in the future when the company often is able to escape the liability. The paper summarises how basic knowledge in rheology has been and can be exploited to minimise the waste associated with these important industries; we call this ‘environmental rheology’.

Tuesday 10:05 Bonzai III GR17

Sharing the World's advanced rheology through Rheo-Hub

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Several of the world's leading rheologists share their expert software codes with the wider community of materials researchers and practitioners through “Rheo-Hub”, a central computer platform from which the user interrogates rheological expert codes (“engines”) and rheological data by comparing, merging, and funneling these into further interrogations and explorations. Results are returned as visuals so that the visual intelligence of the user gets involved in the cognition process. Explorations may be repeated in different ways (using different expert codes for answering the same research question) and viewed from different graphical viewpoints. This creates the multi-scale and multi-expertise workspace that is needed to support quantitative rheological explorations and to prepare for discovery. The hub technology will be presented and examples will be shown. Rheo-Hub’s strengths are data analysis, integration of experimental results with theoretically predicted rheology, visuals for communicating results, and introduction of a rheological data standard.

Tuesday 10:25 Bonzai III GR18

Virtual psychorheometry: Concept and Application

Hiroshi Mizunuma[1], Kazuyoshi Nishizawa[1], Shingo Hirose[2], and Takehiko Segawa[2]
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A virtual reality technique was used to merge a rheometry and a sensory test. In this study, the liquid application with our fingers was investigated as an example. We developed a virtual experience device, which displayed a select menu of rheological models and the slide bars to fix the model constants for panelists. Then, the panelists put their fingers on a small slider on the virtual experience device, and had virtual experiences as if the panelists had applied liquid with their fingers. Since the rheological characteristics are easily changed through an operation of a mouse or a keyboard, the panelists can investigate how the changes in the rheological characteristics influence the sensation. The rheological characteristics can be optimized psychologically for the application. We named this method a virtual psychorheometry. The virtual psychorheometry is composed of two processes. The first process is to analyze the liquid flow in the application and to make a virtual experience device. We measured the horizontal and the vertical reaction force to our fingers and the thickness of the applied liquid. Then, we defined a response function to our finger motion based on the measurements. This response function was used to control a reaction force actuator in the virtual experience device. The second process is the virtual experience through the device. The panelists investigate a good feel adjusting the rheological characteristics on the virtual experience device. The sensory evaluation obtained is direct linked to the rheological characteristics given to the device. In addition, since the sensory evaluation is decided by our finger motion and the response function, it is possible to analyze the sensory evaluation logically. The results for standard viscosity liquids and cosmetic base oils were discussed including the effects of shear thinning viscosity and a contact angle on the surface.

Tuesday 10:45 Bonzai III GR19

Development of branched polycarbonate by an ultrasound-assisted melt mixing process with multifunctional agents

Tae Yong Hwang[1], Hee Jung Kim[1], Hyungsu Kim[2], and Jae Wook Lee[1]
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The chain structure of polymer molecules is an important characteristic of polymers. In the polymer industry, in-situ processing during polymerization or a post-processing is applied to alter the chain structure as an attempt to produce polymers with tailored properties. Among various methods to control the chain structure, ultrasound-induced polymer chain scission is a useful route which can either be used as a post-processing step or can be used during ultrasound-induced polymerization. In our previous studies, we intended to induce degradation of polymer melts in a sonicated intensive mixer and extruder. By combining high intensity ultrasound which causes chain scission of polymer molecules and a multifunctional agent (MFA) having double bonds at its ends, we were able to modify the molecular structure of polycarbonate (PC) from linear to branched structure during melt processing. The three double bonds in chain ends of MFA were expected to act as sites for trapping macroradi-

cals of PC during the course of ultrasound-assisted mixing process. The transformation of molecular structure of PC was confirmed by the measurements of rheological properties of the modified PC.

Tuesday 11:05 Bonzai III 💿 GR20

Couette rheometry from differential approach: Comparative study and experimental application

Patrice Estelle[1], Christophe Lanos[1], Yannick Melinge[1], and Arnaud Perrot[2]
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The Searle-Couette system or rotational coaxial cylinder viscometer is widely used for rheological measurements. It consists of two coaxial cylinders with a fluid being placed in the annulus between them. The torque and rotational velocity of the inner cylinder are measured to determine shear stress and shear rate. The shear stress can be directly calculated from the measured torque. The approximation techniques in shear rate calculation are generally dictated by the radius ratio between coaxial cylinders and the rheological behaviour of tested fluid, which requires an a priori assumption of a constitutive equation. So, numerous methods, solutions, and procedures have been proposed for the determination of shear rate value. This paper presents also an approach to deriving the shear flow curve in Couette rheometer from torque-rotational velocity data. Here, the approach consists in the step-by-step computation of an average shear rate, when the cylindrical gap is partially and fully sheared, from a differential method using a linear relationship between the shear stress and the shear rate. We focus in particular on the applicability of this approximation in shear rate calculation. First, the approach is assessed by examining synthetic data generated with Newtonian, non-Newtonian and yield stress materials with known properties, varying the gap radius ratio. The performance of our approach, compared to approximations stemmed from literature, is estimated by computing the percentage deviation of the calculated shear rate from the true shear rate at the bob which was taken from the assumed fluid model. The results prove the relevance of the proposed approach. Then, its efficiency is examined by applying it to process Couette data of yield stress fluids taken from published works. It is finally used to derive the Couette experimental shear flow curves of Newtonian and yield stress materials. Results, which are favourably compared with torsional flow curves, show that the proposed approach correctly predicts the rheological behaviour of the investigated materials.

Tuesday 11:25 Bonzai III 💿 GR21

Estimation of the molecular weight between crosslinks of crosslinked semicrystalline polyolefins

Marc A. Mangnus[1], Teresa P. Karjala[2], and Mikhail M. Gelfer[3]
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The molecular weight between crosslinks (MXL) of crosslinked semicrystalline polyolefins, polyethylene in particular, has been estimated from uniaxial tensile tests in the melt state with the Sentmanat Extensional Rheometer (SER). Applying the Mooney-Rivlin equation to these stress-strain data resulted in the determination of an apparent molecular weight between crosslinks. This fast and convenient technique correlates well with the conventional approaches where MXL is obtained via Flory-Rehner calculations on analytical swell measurements and the plateau modulus obtained via shear viscosity.

CF-4. Shear Banding I

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Sandra Lerouge

Tuesday 9:45 Steinbeck CF22

Shear banding: Complex dynamics, 3D flows, and boundary conditions

Suzanne M. Fielding
School of Mathematics, University of Manchester, Manchester, Greater Manchester M13 9PL, UK

After a brief introduction to the phenomenon of shear banding in complex fluids, I will give an overview of some recent progress in modelling it theoretically. This will include a discussion of bulk and interfacial instabilities leading to complex dynamics of the bands; vorticity banding and 3D roll-like flows; and the role of the boundary conditions at the wall of the rheometer.

Tuesday 10:05 Steinbeck CF23

Simulations of the dynamics and rheology of wormlike micelles

Johannes T. Padding[1], Edo S. Boek[2], and Wim J. Briels[1]
[1]Computational Biophysics, University of Twente, Twente, The Netherlands; [2]Schlumberger Cambridge Research, Cambridge, UK

We perform coarse grained computer simulations of solutions of semidilute wormlike micelles and study their dynamic and rheological properties, both in equilibrium and under shear flow. The simulation model is tailored to the study of relatively large time and length scales (micrometers and several milliseconds), while it still retains the specific mechanical properties of the individual wormlike micelles. The majority of the mechanical properties (persistence length, diameter and elastic modulus of a single worm) are determined from more detailed atomistic molecular dynamics simulations, providing the link with the chemistry of the surfactants. The method is applied to the case of a solution containing 8% (by weight) erucyl bis (hydroxymethyl)methylammonium (EHAC). Different scission energies ranging from 15.5 to 19.1 kT are studied, leading to both unentangled and entangled wormlike micelles. We find a decrease of the average contour length and an increase of the average breaking rate with increasing shear rate. In equilibrium, the decay of the shear relaxation modulus of the unentangled samples agrees with predictions based on a theory of breakable Rouse chains. Under shear flow, transient over- and undershoots are measured in the stress tensor components. At high shear rates we observe a steady-state shear stress proportional to gamma^(1/3), where gamma is the shear rate. This is confirmed by our high shear rate experiments of real EHAC in a tapered plug geometry.

Tuesday 10:25 Steinbeck CF24

Rheology of wormlike micelles in a microchannel: Evidence of non local effects

Chloe Masselon, Jean-Baptiste Salmon, and Annie Colin

L.O.F., unité mixte CNRS-Rhodia-Bordeaux 1, Pessac Cedex 33608, France

Complex fluids show non linear properties under simple shear flows since they have various microstructures leading to flow induced phase transitions and instabilities. Such a coupling has widely been studied for wormlike micelles. Their flow curve exhibits a stress plateau separating high and low viscosity branches, leading to shear-banding flow. To account for those shear-banding observations, a first theoretical model was proposed by Spenley et al [1]. Yet the selection of the value of the stress plateau at which the shear-banding occurs was only recently ensured by introducing a diffusive non local term in the constitutive equations [2]. That diffusion term takes into account the stress propagation across the interface between the low and highly sheared bands. At this stage, experimental evidence of these non local terms is still missing. We present here an original experimental study of the rheology of wormlike micelles in a microchannel. We managed to evidence non local effects in such a confined geometry, and we accurately determine the diffusive non local term involved in the constitutive equation describing the behaviour of these systems. More precisely, we study the flow of semidilute wormlike micellar systems in a straight glass microchannel (200 µm wide, 1 mm high, 6 cm long). Contrary to Couette and cone-and-plate cells or even large pipes, such a confined planar Poiseuille flow dramatically enhances the effect of non local terms. We present results on two different wormlike micellar systems and at different concentrations. For a CPCl-Sal system (a mixture of cethylpyridinium chloride and sodium salycilate in NaCl salted water) we vary the surfactant concentration, and for a CTAB-NaNO3 (cethyltrimethylammonium bromide in NaNO3 salted water) we investigate different salt concentrations. We characterize the local rheology of those wormlike micelles thanks to particle image velocimetry [3]. We show that the flow curves deduced from the velocity profiles at different pressure drops do not collapse and cannot be described by a simple constitutive equation linking the local shear stress to the local shear rate. We demonstrate the existence of non local effects in the flow of wormlike micellar systems, and make use of a theoretical framework allowing the measurement of a diffusion coefficient [2] and therefore of correlation lengths. In addition to such phenomenon, it also appears that those systems exhibit strong refractive index variations in the highly sheared band, which makes them observable in visible light as dark bands. The width of those dark bands is directly related to the width of the highly sheared band measured in the velocity profiles. At very high pressure drops, those dark bands start to fluctuate in space and time. We also study those fluctuations for both wormlike micellar systems.

[1] N.A. Spenley et al., Phys. Rev. Lett. 71, 939 (1993); [2] J. K.G. Dhont, Phys. Rev. E 60, 4534 (1999); [3] G. Degré et al., Appl. Phys. Lett. 89,024104 (2006).

Tuesday 10:45 Steinbeck CF25

Probing shear-banding transitions of entangled liquids using large amplitude oscillatory shearing (LAOS) deformation

Lin Zhou[1], Randy H. Ewoldt[2], L. Pamela Cook[1], and Gareth H. McKinley[2]

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Surfactant molecules (micelles) can self-assemble in solution into long flexible structures known as wormlike micelles. These structures entangle, forming a dense network and thus exhibit viscoelastic effects, similar to entangled polymer melts & solutions. However, in contrast to polymeric networks, wormlike micelles break and reform leading to a new relaxation mechanism. Steady shearing flows of these solutions exhibit spatial inhomogeneities in flow such as 'shear-bands' which have been well studied both experimentally and theoretically. Recent experimental studies with concentrated and highly-monodisperse polymer solutions have shown that, while not exhibiting breakage/reforming events, these systems can also develop similar banding inhomogeneities in steady and transient shearing deformations at sufficiently large applied strains. In the present work, we investigate numerically and analytically the dynamical response of two recently formulated constitutive models (denoted respectively VCM, PEC+M) under Large Amplitude Oscillatory Shear (LAOS) deformations. The VCM model is a two-species network mode which incorporates a discrete version of the micellar breakage and reforming dynamics originally proposed by Cates. The PEC+M model is a noninteracting two species limit of the VCM model that describes, at least qualitatively, non-affine tube deformation and chain disentanglement. The VCM model is formulated to capture the essential physics of wormlike micellar solutions, and the PEC+M limit captures the physics and flows of entangled solutions of monodisperse long chain polymers in an unentangled sea of short chains. In LAOS deformations both models predict that kinematic inhomogeneities develop across the gap for a wide range of strains and frequencies. Lissajous figures (of the oscillatory stress versus imposed strain or imposed shear rate) can be used to illustrate visually the complex dynamics of the entangled networks. Quantitative comparison of the model predictions with experimental measurements performed in oscillatory shear can be made using an elastic/viscous decomposition of the stress in conjunction with a Chebyshev polynomial expansion. The complex dynamics of shear-banding in this unsteady large amplitude deformation and the special limiting cases of linear viscoelasticity and steady inhomogeneous shear flow can be conveniently understood using a Pipkin diagram representation.

Tuesday 11:05 Steinbeck CF26

Taylor-like vortices in the shear-banding flow of giant micelles

Marc-Antoine Fardin[1], Sandra Lerouge[1], Médéric Argentina[2], Guillaume Grégoire[1], Jean-Paul Decruppe[3], and Olivier Cardoso[1]

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Many complex fluids often show original non linear responses when submitted to shearing forces. These non linear behaviors result from the coupling between the structure of the fluid and the flow and can sometimes lead to shear localization effects generally characterized by a splitting of the system into two macroscopic layers bearing different shear rates and stacked along the velocity gradient direction. This shear-banding transition has been observed in complex fluids of various microstructure such as, for instance, surfactant phases, soft glassy materials, granular materials or foams. In this work, we focus on the dynamics of the shear-banding flow of a semi-dilute wormlike micellar system made of cetyltrimethylammonium bromide with sodium nitrate in water. Using a Couette geometry, we showed recently that the interface between shear-bands becomes unstable and undulates with a wave vector along the vorticity axis. We also observed different patterns of spatio-temporal dynamics depending on the applied shear rate in the banding regime. Here we extend this study by following simultaneously the dynamics of the interface together with the dynamics of small reflecting tracers seeded in the sample. The organization of the tracers into stripes stacked along the vorticity direction strongly suggests that the flow is three-dimensional. Moreover, we show that the dynamics of the Taylor-like vortices is correlated with the one of the interface in the coexistence regime. These observations are combined with particle image velocimetry measurements which confirm the existence of recirculations in the sample. Finally, our results are discussed in the context of recent theoretical studies dealing with the stability of shear-banding flows.

Tuesday 11:25 Steinbeck CF27

Investigation of vorticity structuring in shear-banded flow of wormlike micelles using NMR velocimetry

Kirk W. Feindel and Paul T. Callaghan

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Shear-thinning wormlike micellar systems often exhibit a characteristic stress plateau above a critical applied shear rate, at which regions with widely differing local strain rates coexist under a common stress (i.e., shear banding)[1]. In addition, coupling between flow and microstructure of the system, manifest as intrinsic stress fluctuations, can cause spatio-temporal fluctuations of both the volume fractions and the shear rates of the bands.

A multitude of techniques have been applied to the study of shear banding; however, NMR techniques are particularly attractive for the study of shear banded flow as they are non-invasive and have the potential to spatially localize specific areas of interest in three dimensions. By combining conventional rheological methodology with magnetic resonance techniques (rheo-NMR), previously elusive information about the properties and behaviour of complex fluids can be garnered.

The majority of reports on shear banding have investigated the structure and behaviour of layer-normals in the flow-gradient direction. In some systems, however, flow induced heterogeneity has been reported in the vorticity direction[2]. For fluids in curved Couette flow, stacked Taylor velocity rolls can exist along the vorticity direction, the wavelength of which is loosely related to the width of the gap in the flow-gradient direction[3]. Recently, Fielding has suggested a novel mechanism for the formation of vorticity structuring in complex fluids in which undulations are introduced along the interface of the bands with wavevector in the vorticity direction [4].

We report experimental results from rheo-NMR investigations of vorticity structuring and fluctuations in shear-banded flow for a wormlike micellar solution. The system is 10% w/w cetylpyridinium chloride and sodium salicylate (molar ratio 2:1) in 0.5 M aqueous NaCl, which exhibits a flow curve with a wide stress plateau[5]. Rheo-NMR experiments were conducted using a 400 MHz vertical wide-bore superconducting magnet, Bruker Avance console, and a Bruker microimaging accessory. Steady shear deformation was performed using custom Couette cells with inner cylinder diameters of either 17 or 20 mm and gaps of 1 and 1.5 mm, respectively. We have employed a 2D slice selective RARE-based imaging sequence that is preceded by a PGSE encoding period to yield 2D velocity maps. Both time-averaged and real-time locally fluctuating velocity profiles are presented. Our results show the existence of a fluctuating vorticity structure which is coupled to applied strain rate.

[1] H. Rehage, H. Hoffmann. J. Phys. Chem., 1988, 92, 4712; [2] See for example, O. Diat, D. Roux, F. Nallet. J. Phys. II, 1993, 3, 1427; P. Fischer. Rheologica Acta, 2000, 39, 234; [3] P.G. Drazin, W.H. Reid. Hydrodynamic stability, Cambridge University Press, Cambridge, 2004; [4] S.M. Fielding. Phys. Rev. E. 2007, 76, 016311; [5] J.F. Berret, D. Roux, G. Porte. J. Phys. II, 1994, 4, 1261.

MF-3. Microfluidics: Surface Wettability

Organizers: Todd M. Squires and Annie Colin
Session Chairs: Patrick Tabeling and Annie Colin

Tuesday 9:45 Portola MF16

Probing nanoflows and nanoparticle interactions at less than 100 nm from solid surfaces

Cedric L. Bouzigues and Patrick Tabeling

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The observation of flows at a nanometric scale is crucial for understanding phenomena involving interactions between liquids and solid surfaces, such as slippage and electro-osmosis. Here we report a new method based on nanoparticle imaging by total internal reflection fluorescence, allowing the first observation of water flows between 20 and 300 nm from surfaces. We probed the energy landscape, leading to first local measurements of the Debye length and surface/nanoparticle interactions in a microfluidic channel. We determined velocity profiles in the same range of scales and provided an unambiguous determination (within 10 nm accuracy) of the slip length for different surfaces - wetting, non-wetting, hard, soft-. These results represent an improvement of one order of magnitude in terms of spatial resolution compared to existing velocity measurement techniques.

Tuesday 10:05 Portola MF17

Low-Reynolds-number hydrodynamics of “slip-stick” particles

James W. Swan[1] and Aditya S. Khair[2]

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The breakdown of the no-slip condition at fluid-solid interfaces generates a host of interesting fluid-dynamical phenomena. Here, we investigate a paradigmatic example of this by considering the hydrodynamic properties of a novel “slip-stick” spherical particle, whose surface is partitioned into “slip” and no-slip (or “stick”) regions. In the limit where the slip length is small compared to the particle size, we first compute the translational velocity of a particle due to the force density on its surface. Subsequently, we calculate the angular velocity and the response to an ambient straining field of a slip-stick particle. These three Faxen-type formulas are rich in detail about the dynamics of the particles: importantly, the translational velocity of a slip-stick sphere is coupled to all of the moments of the force density on its surface. Moreover, such a particle can migrate parallel to the velocity gradient in a shear flow. Perhaps most important is the coupling we predict between torque and translation (and force and rotation), which is uncharacteristic of spherical particles in unbounded Stokes flow and results directly from the broken symmetry of the slip-stick sphere. Lastly, we consider the rheology of a dilute suspension of slip-stick spheres and comment on possible microfluidic applications.

Tuesday 10:25 Portola MF18

Driven motion of non ideal fluids on substrates with spatially variable wettability

Bin Wu, Segun G. Ayodele, Fathollah Varnik, and Dierk Raabe
Max-Planck Institut fuer Eisenforschung, Duesseldorf D-40237, Germany

Guided motion of liquids is studied via lattice Boltzmann computer simulations. The focus of the work is on basic issues related to driving forces generated via a step-wise (abrupt) change in wetting properties of the substrate along a given spatial direction. We first give approximate analytic expressions for forces driving the liquid motion. These theoretical estimates show qualitatively different dependence of wetting gradient induced forces on contact angle and liquid volume in the case of an open substrate as opposed to a planar channel. These results are then examined via lattice Boltzmann computer simulations. Furthermore, we also investigate effects of a wetting gradient on internal droplet dynamics and the resulting dissipation losses.

Tuesday 10:45 Portola ⊛ MF19

Coating of model rheological fluids in microchannels

Michael W. Boehm and Kurt Koelling
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With the advent of lab-on-a-chip technologies, fundamentalists have strived to understand and quantify the dynamics within the myriad devices proposed and developed. Concepts such as fluid flow, mass transfer, molecule manipulation, and reaction kinetics must be understood in order to intelligently design and operate micro-devices. In addition to general engineering principles, intelligent design should also focus on material properties (e.g. density, viscosity, conductivity). One key property, viscosity, will play a large part of any micro-fluidic device, including biomedical devices, because the fluids used will, most likely, be non-Newtonian and therefore highly dependent upon the shear rate. Select model polymers can be used to investigate the dynamics within micro-devices, be it a biomedical or macromolecule separation device, or simply the processing of polymeric material.

Here, we present results for the processing of Newtonian and non-Newtonian polymeric fluids in micro-channels during multi-phase penetrating flow. The system investigated is a circular capillary 100 microns in diameter, which is pre-filled with a polymeric liquid. The polymeric liquid is either a standard photoresist, with a Newtonian viscosity, or the same photoresist with dispersed high molecular weight polystyrene, which exhibits viscoelastic behavior. A second, immiscible phase, silicone oil of low Newtonian viscosity is pumped into the system and subsequently cores the polymeric photoresist. The dynamics of bubble flow (e.g. bubble velocity and bubble shape) as well as the influence of rheology on coating will be investigated.

By studying these model systems, we will learn how complex fluids behave on progressively smaller size scales, and that will allow us to say something about complex biological systems, state-of-the-art micro-devices, and the processing of polymeric liquids on the micro-scale.

Tuesday 11:05 Portola ⊛ MF20

Spreading dynamics of non-Newtonian inkjet drop on solid surface

Yangsoo Son and Chongyoup Kim
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In this paper we experimentally investigated the spreading of inkjet droplets impinged on solid surfaces. The wettability of solid substrate was varied by adsorbing a self-assembled monolayer of octadecyltrichlorosilane followed by the exposure to UV-ozone plasma. To understand the effect of non-Newtonian characteristics of fluids on spreading, we chose several rheologically complex fluids in addition to two Newtonian fluids of ethylene glycol/water mixture and distilled water: aqueous solutions of xanthan gum, polyacrylamide and polyethylene oxide. The concentrations of xanthan gum and polymers were below C*. The result showed that the initial spreading characteristics were determined largely by the kinetic energy and the added polymers did not affect the spreading. However the oscillatory motion during the receding stage became weaker and more stable motions were observed when polymers were added. The suppression of the oscillatory motions was stronger in the stiff xanthan gum solution than in flexible polymer solutions. This implies that the extensional nature of the solutions strongly affect the spreading. However the equilibrium shape of drop was solely determined by the wettability of the solid substrate irrespective of the rheological properties of fluids such as viscosity, shear thinning and elasticity.

Tuesday 11:25 Portola ⊛ MF21

Anomalous reduction in pressure drops of the water flow through micro-orifices in high velocity ranges

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In recent years, much attention has been focused on the flow through micro-channels in experiments of chemical and biochemical processes. However, most of researches conducted so far have been limited in low velocity ranges, and experiments in high velocity ranges have been scarcely carried out. In the present study, pressure drops were measured for the water flow through micro-orifices in high velocity ranges: Orifice diameters ranged from 5 micron-meter to 1 mm, velocities were from 0.1 m/s to 200m/s, but Reynolds number was less than 1000 and then the flow was thought to be laminar. It was found that the measured pressure drops agreed with the conventional value for the orifices larger than 20 micron-meter , but they were reduced for the orifices smaller than 15 micron-meter. Especially the dimensionless pressure drops for 5 or 10 micron-meter orifices were two or three orders of magnitude smaller than those for the orifices larger than 20 micron-meter. This newly found huge reduction in pressure drop for micro-orifices was discussed for possible causes together with the result of similar reduction in jet thrusts for micro-orifices recently reported by the authors. Consequently, the most likely cause was the elastic property induced in an elongational flow in and about the orifice entrance.

EM-3. Amplitude Oscillation Shear Rheometry

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: Jason Stokes

Tuesday 9:45 De Anza I 💿 EM16

An ontology for large amplitude oscillatory shear flow

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The growing interest in nonlinear viscoelastic properties of biological and other soft materials drives the need for a consistent, quantitative, and low-dimensional framework to describe such behavior. A popular rheometric method for measuring nonlinear properties is large amplitude oscillatory shear (LAOS). However, a comprehensive framework does not currently exist to simultaneously identify elastic and viscous nonlinearities with LAOS, such as strain-stiffening/softening, and shear-thickening/thinning, which may occur both within a steady oscillation (intracycle nonlinearities) and between cycles (inter-cycle nonlinearities). For many systems we find the practice of reporting only "viscoelastic moduli" as calculated by commercial rheometers (typically the first-harmonic Fourier coefficients G1', G1") to be insufficient and/or misleading in describing the nonlinear phenomena. Many researchers also look beyond these first-harmonic coefficients and examine the higher harmonics of the material response. Although these higher-order Fourier coefficients capture the mathematical structure, they lack a clear physical interpretation. We introduce a framework for reporting and interpreting LAOS results which addresses both of these issues. First, the concern of arbitrarily defined viscoelastic moduli in the nonlinear regime is addressed. Our framework offers alternative techniques for estimating the first-order (linear) response to LAOS. These measures reduce to G', G" in the linear regime, but offer additional physical insight beyond G1', G1" for a nonlinear signal. Secondly, we offer a physical interpretation of higher-order Fourier coefficients. This portion of our analysis is founded on the geometrical interpretation of Cho et al. (2005) which decomposes a prototypical nonlinear stress response into elastic and viscous contributions using symmetry arguments. We introduce the use of Chebyshev polynomials to orthogonally decompose these stress components into nonlinear parameters that have a clear physical interpretation. We then relate these Chebyshev coefficients to the commonly reported Fourier coefficients. Furthermore, we address the inherent differences in LAOS tests performed under controlled-stress rather than controlled-strain. Although the theory of linear viscoelasticity does not distinguish between these testing methods, we show that nonlinear viscoelastic measures can be different for strain- and stress-controlled tests. The newly introduced viscoelastic parameters require slightly different definitions and interpretations with stress-controlled measurements. We apply this new framework to various systems in order to illustrate its efficacy. These new measures can be used to give a "rheological fingerprint" of an elasto-visco-plastic material, giving a comprehensive physical interpretation of both intracycle and inter-cycle nonlinearities when shown in the form of a Pipkin diagram formed from the two-dimensional parameter space of applied frequency and imposed strain-amplitude.

Tuesday 10:05 De Anza I 💿 EM17

Non-linear oscillation testing with a separate motor transducer rheometer

Aloyse J. Franck[1], Maik Nowak[2], and Ron F. Garritano[1]
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The benefit of the SMT rheometer design is the capability to measure the material's stress response unaffected by motor friction and inertia. SMT rheometers such as the ARES-G2 provide torque and displacement signals with minimum to no correction for instruments effects. The data acquisition of the rheometer used (ARES-G2) incorporates 5 fast channels for motor and transducer displacement, torque, normal force and an auxiliary signal with sample data at a rate of up to 8 kHz. Additional oversampling is used to reduce random noise of the raw signals to a minimum.

The non-linear material response in shear- and normal stress upon a sinusoidal strain input can be recorded and analyzed in two ways:

1) Fast sampling and saving of shear- and normal stress over time into a file for post processing: Discrete Fourier analysis of the measured stress or decomposition of the stress signal into an elastic and viscous component can be performed in a second step.

2) Direct correlation of the measured stress with the input strain to determine the magnitude and phase of the fundamental and harmonics up to the 9th order: This method can be conveniently integrated into standard test modes such as time, strain or frequency sweeps which provide the desired results (dynamic moduli G_n', G_n'' or magnitude ratio $I_n(\omega_n)/I_1(\omega)$) immediately.

The NIST standard PIB2491, a solution of 4wt% Xanthan gum and a commercial soft cosmetic cream have been subject of the non-linear oscillation measurements. Fourier coefficients of the stress signals are evaluated applying direct correlation or discrete Fourier transformation during post processing. The elastic and viscous non-linear contributions obtained from decomposition of the measured stress (K.S. Cho, K.H. Ahn) are fitted with Chebyshev polynomials (R. Ewoldt and G. McKinley). The relations between Fourier and Chebyshev coefficients are verified experimentally. The results obtained from the different test and evaluation methods are analyzed in terms of reproducibility and accuracy of the method, as well as practicality in a commercial rheometer.

Tuesday 10:25 De Anza I EM18

A study of polymer architecture with FT-rheology and large amplitude oscillatory shear (LAOS)

Henri G. Burhin[1], Christian Bailly[2], Roland Keunings[3], Nicolas Rossion[3], Adrien Leygue[3], and Henry Pawlowski[4]
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It is difficult to characterize Long Chain Branching (LCB) in polymers using only traditional rheological test methods. Many rheological measurements are affected by polymer characteristics other than LCB such as Molecular Weight Distribution (MWD). In this study, a new LAOS method is used to measure the presence and level of LCB, which is almost insensitive to MWD. A large amplitude sinusoidal strain on a sample generates a stress signal distortion that is sensitive to the presence and level of LCB and not to Average Molecular Weight (AMW) or MWD. The signal distortion is quantified using a Fourier transform. Since linear visco-elastic equations are not applicable to LAOS, the approach of Giacomin and Dealy is used. This considers the stress signal as a Fourier series. This series is used to calculate G'_n and G''_n. LCB was found to have a strong effect on G'_n and G''_n. Results show excellent sensitivity to LCB level. A graph of shear stress=f(shear rate) produces a Lissajou figure with secondary loops on linear polymers. Recent work at the Université Catholique de Louvain (UCL), Belgium has demonstrated the mathematical conditions for those secondary loops to appear. Important values for the presence of secondary loops are only the real components of the odd harmonics G'_1, G'_3 G'_5, etc. Secondary loops appear when the following condition is met: $-3=G'_1/G'_3=1$ A more sensitive alternate condition uses the ratio G'_1/G'_5 . The latter ratio remains constant for all linear polymers including polypropylene with modified MWD. Other linear polymers that produce secondary loops are polyisobutylene, polybutadiene and EPDM rubber. This work clearly establishes a mathematical relationship between Lissajou figure (shear stress=f(shear rate)) and Fourier spectrum, hence correlates with polymer architecture.

Tuesday 10:45 De Anza I EM19

Fourier transform rheology of metallocene LLDPE with controlled long chain branching

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In this paper, model metallocene linear low density polyethylene (m-LLDPE) resins were synthesized. The long chain branching (LCB) frequency and architecture were systematically varied by using different polymerization approaches. The set of well-controlled branched model polymers were used to establish clear relationships between polymer structure, processing and solid-state properties. These polymers were synthesized and fully characterized. The melt rheology part aimed at correlating the type and frequency of LCB in m-LLDPE to the shear and extensional properties of polymers. Classical dynamic and Fourier Transform rheology (FTR) measurements as well as extensional properties will be measured in ARES rheometer. FTR was used to characterize the LCB and correlate LCB to rheology in the linear and nonlinear viscoelastic range. Also, the influence of LCB on flow activation energy was assessed. The type and content of LCB was correlated to shear and extensional rheology of the model m-LLDPEs. The knowledge acquired from the different characterization techniques will be used to produce resins with enhanced processing properties and novel applications. Acknowledgement This project is supported by KFUPM under project # CHE/Metallocene/347.

Tuesday 11:05 De Anza I EM20

On the use of rheology for the investigation of the morphology of blends of natural rubber (NR) and polybutadiene (PB)

Julien Portal[1], Christian Carrot[1], Jean-Charles Majesté[1], Stéphane Cocard[2], Vincent Pélissier[2], Katia Baran[2], and Arnaud Lapra[2]
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The aim of this study is to describe how rheological techniques can be used to characterize the morphology of blends of two incompatible elastomers, natural rubber (NR) and polybutadiene (PB). Especially, dynamic mechanical spectroscopy in the melt and in the solid state are used to get information on the structure of unfilled and uncured blends. Melt blending was carried out in an internal mixer at 80°C. A complete composition range from 100% PB to 100% NR in steps of 10% (weight fraction) is studied. Rheological characterization in the melt was performed in oscillatory shear with a constant strain rheometer in the linear domain. At low frequencies and low volume fractions of the minor phase, the storage modulus shows an excess of elasticity that increases with the dispersed phase content. For a higher concentration of the minor phase, the excess of elasticity decreases in relation to the morphology. The rheological tests in the solid state were carried out in a controlled strain rheometer using rectangular torsion. The evolution of storage modulus of blends with the composition at the temperature of crystallization of polybutadiene is related to the morphology of this elastomer. The phenomenon of "fractionated crystallization" is evoked to explain the structure of polybutadiene in the NR/PB blends. The samples were also analyzed by TEM to confirm the morphology. Contrast between the phases is obtained using ultra cryo-microtomy carried out between the Tgs of the neat elastomers. Therefore, the elastomer with the higher modulus at the cutting temperature will be thinned by the cryo-ultramicrotomy. For that reason, it appears lighter in the micrograph and the contrast between phases is enhanced. The superposition of the three methods gives a nice picture of the morphology of unfilled and unvulcanized blends of natural rubber and polybutadiene on the entire composition range.

Tuesday 11:25 De Anza I EM21

Measurement of the rheological properties of magnetorheological fluids using a double concentric Halbach cylinder array

Vitor C. Barroso[1], Hanspeter Raich[2], Peter Blümler[3], and Manfred Wilhelm[1]
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A new experimental setup for measuring the rheological properties of magnetic fluids at variable magnetic fields is described. The proposed system consists of two concentric Halbach cylinders made from permanent NdFeB magnets. The permanent magnets are arranged in order to achieve a unidirectional homogeneous magnetic field inside each of the cylinders. The two cylinders can be rotated relatively to each other. Hence, the resulting field at the center is the vector sum of the two individual fields and varies sinusoidally with the displacement angle, covering a range of nearly zero to a total value of around B=0.6 Tesla, with a homogeneity around $\Delta B/B=0.3\%$. The proposed setup is mounted on a controlled-strain ARES rotational rheometer. This allows the measurement of the rheological properties of magnetorheological fluids for different applied magnetic fields, with enhanced magnetic field homogeneity. The measurement geometries consist of a bob-in-cup or vane-in-cup setup, and are made of a non-magnetic material (polyoxymethylene) in order not to disturb the magnetic field. Due to the particular Halbach arrangement, the magnetic stray field in the direction radial to the cylinders is greatly reduced. In the axial direction, the whole system is magnetically shielded with metal sheets in order to protect both the motor and the torque transducer of the ARES from any possible interference with the magnetic stray field. Experiments with magnetorheological fluids were performed both in steady and oscillatory shear regimes. The vane-in-cup geometry was found to be more adequate for the measurement under oscillatory shear regime. The deviation of the dynamic modulus from the linear regime was found to consistently shift to higher strains for increasing magnetic fields. A possible extension of the double concentric Halbach cylinder array for Rheo-NMR applications is also described.

SE-2. Foam Stability

Organizers: Denis Weaire and Lynn M. Walker
Session Chair: Denis Weaire

Tuesday 9:45 De Anza II SE10

Influence of interfacial and bulk rheology on stability of foam

Natalie Duerr-Auster, Tamara Eisele, Peter Fischer, and Erich J. Windhab
Institute of Food Science and Nutrition, ETH Zurich, Zurich, Switzerland

The properties of liquid foams are widely used in many applications including cosmetics, pharmaceutics and food. A key challenge for most applications is to carefully control foam stability to ensure a lifetime during which changes in foam structure are small. However, storage of liquid foams inevitably leads to microstructural development, which are mainly governed by coarsening, drainage and film rupture. Drainage and film rupture depend amongst other factors on the rheological properties of the continuous phase and of the surfactant-covered interface. In the present contribution, we report on the bulk and interfacial rheological properties of a model system and their influence on bubble coalescence. The model system consisted of air (dispersed phase) and an aqueous surfactant solution of a polyglycerol ester (PGE, continuous phase). Microstructural and rheological properties were probed using a combination of different bulk and interfacial techniques such as dynamic light scattering (DLS), confocal laser scanning microscopy (CLSM), oscillatory shear rheometry and Brewster angle microscopy (BAM). Coalescence stability of selected solutions was probed using a custom-built a coalescence cell. Using an excess amount of surfactant (than corresponding to full surface coverage), we show that the continuous phase of the model foam consists of an aqueous dispersion of multilamellar vesicles with a well-defined size distribution. At native pH, these vesicles have a net negative surface charge and show repulsive interactions. Altering the pH induces flocculation and weak gelation with a concentration dependent signal. Strain dependent dynamic experiments of the PGE-covered interface show that at equilibrium surface tension, the interface is characterised by a linear viscoelastic regime (LVE) at very small deformations. We performed frequency dependent dynamic experiments within this LVE region, which showed a transition from viscous to elastic behaviour within a narrow frequency range, characteristic of a transient interfacial gel. In contrast to oscillatory shear experiments, the dynamic dilatational behaviour is predominantly elastic throughout the investigated frequency spectrum, with E' an order of magnitude larger than E". Both dynamic moduli are frequency independent thus pointing towards a gel-like character of the interfacial film. Interfacial rheological properties were found to be pH independent. Coalescence experiments show that the gel-like character of both, the interface and the bulk face lead to increased bubble stability.

Tuesday 10:05 De Anza II SE11

Effects of film elasticity and surface forces on the stability of foams and lamellae films in the presence of non-ionic surfactants

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The stability of foams and froth plays an important role in flotation, in which bubbles laden with hydrophobic particles rise to the surface of a pulp, forming a three-phase froth, which is subsequently removed mechanically or by displacement. In flotation, small amounts of relatively weak non-ionic surfactants (frothers) are used to produce air bubbles and foams. In the present work, factors affecting the stability of the foams produced in the presence of common frothers, such as n-pentanol, n-octanol, methyl isobutyl carbinol (MIBC), and polypropylene glycol (PPG), have been studied. We used a model developed by Wang and Yoon (Colloids and Surfaces A: Physicochem. Eng. Aspects, 2006, 282-283, 84-91) to calculate the elasticities of the lamellae films. In addition, we used the thin film pressure balance (TFPB) technique of Scheludko-Exerowa type to measure film thicknesses and a microelectrophoresis technique to measure the zeta-potentials of air bubbles in aqueous solutions. The results were used to determine the contributions from the various surface forces to the disjoining pressures in the thin lamellae (foam) films formed between air bubbles, which are relevant forces governing the final drainage stage of foam films before reaching either equilibrium or rupture. The film elasticity and surface forces data were then compared with the foam stabilities measured in the present work in the presence of the various flotation frothers. It was found that foam stabilities are controlled both by film elasticity and by surface forces, the relative contributions of which change with frother type and concentration. In general, surface forces play a more important role at relatively low frother concentrations, while elasticity plays a more important role at higher concentrations. At the frother additions usually employed in the mining industry, MIBC stabilizes foams by increasing disjoining pressures, while PPG-400 stabilizes foams by increasing elasticities.

Tuesday 10:25 De Anza II SE12

Measurements of wall slip during rise of a physically blown foam

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Polymeric foam systems are widely used in industrial applications due to their low weight and abilities to thermally insulate and isolate vibration. However, processing of these foams is still not well understood at a fundamental level. The precursor foam of interest starts off as a liquid phase emulsion of blowing agent in a thermosetting polymer. As the material is heated either by an external oven or by the exothermic reaction from internal polymerization of the suspending fluid, the blowing agent boils to produce gas bubbles and a foamy material. A series of experiments have been performed to allow observation of the foaming process and the collection of temperature, rise rate, and microstructural data. Microfocus video is used in conjunction with particle image velocimetry (PIV) to elucidate the boundary condition at the wall. These data provide input to a continuum level finite element model of the blowing process. PIV is used to measure the slip velocity of foams with a volume fraction range of 0.50 to 0.71. These results are in agreement with theoretical predictions which suggest that at high volume fractions the bubbles would exhibit jamming behavior and slip at the wall. At these volume fractions, the slip velocity profile has a shear profile shape near the side walls and a plug flow shape at the center. The shape of the velocity profile is in agreement with previous experimental work investigating

different foam systems. As time increases, the available blowing agent decreases, the volume fraction increases, the viscosity increases, and the average slip velocity decreases, but the slip velocity profile maintains the plug-shear shape.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Tuesday 10:45 De Anza II SE13

Gas permeability of foam films stabilized with alpha olefin sulfonate (AOS) surfactants

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The interactions between foam films play an important role in interpreting the experimental data and developing general theories of foam rheology and motion. Foam films are suitable tools for studying the interactions between interfaces. The measurement of the gas permeability of the foam films gives valuable information about the stability and lifetime of the foams. Part of this information can be obtained from gas permeability experiments with foam or single foam films. Even more, as it was shown the interaction between the adsorbed monolayers forming the foam film changes the film structure and its gas permeability accordingly. Alpha Olefin Sulfonate (AOS) surfactants have shown outstanding detergency, lower adsorption onto porous media, high compatibility with hard water,good wetting and foaming properties. These make AOS an excellent candidate for foam applications in enhanced oil recovery. We measured the basic properties (thickness, contact angle, adsorption density) of foam films stabilized by an Alpha Olefin Sulfonate (AOS) surfactant. Furthermore, the gas permeability coefficient, k, of films was measured as a function of surfactant and salt concentration. It was observed that the thinner Newton Black Films (NBFs) are less permeable to gases than thicker Common Black Films (CBFs). This result was interpreted using adsorption densities calculated from measured surface tension data. It was concluded that the gas permeability of foam films is independent of the number of surfactant molecules adsorbed on the film surface. The interaction between foam films are most likely the reason for the unexpected permeability behavior of foam films stabilized with AOS.

Tuesday 11:05 De Anza II SE14

Injection of polyamide foam: Experiment and modeling

Sophie Redoutey and Jérôme Bikard
CEMEF UMR CNRS ENSMP 7635, Sophia Antipolis 06904, France

Polyamide cellular materials have interesting properties (acoustic and thermal isolation, shock absorber for crash application). The physical foaming (with supercritical fluids) is currently used to manufacture porous materials based on polyamide matrix. However, this kind of process leads to a very fast expansion. The objective of this study being to follow in-situ the PA foaming in order to enrich physical models [1,2], the chemical way has been preferred, using a PA6-based matrix. Foam structures have been realized using blowing agents, whose chemical decomposition is controlled by temperature. In such a process, because of the high fusion temperature and the low viscosity of polyamide, care must be taken to prevent the blow gas to escape out of the polymer liquid matrix. The quality of these structures (cellular size and homogeneity, mechanical properties) mainly depends on the conditions used for the process, in quasi-static conditions (expansion in a closed cavity) and dynamic conditions (reactive extrusion). The experimental observations are analyzed and a model developed by the authors [1,2] (describing the foaming of the polymer and taking into account chemical reactions) is used to predict the microcellular structure of the foam. The results are discussed.

[1] Bikard J., Bruchon J., Coupez T., Silva L. "Numerical simulation of 3D Polyurethane expansion during manufacturing process". Colloids and Surfaces A: Physicochem. Eng. Aspects 309 (2007) 49-63; [2] Bouayad R., Bikard J., Agassant, J.F. "Modelling and characterization of polyurethane foam expansion during moulding", Proceedings of the Polymer Processing Society 23rd annual Meeting, Salvador, Brazil.

Tuesday Afternoon – 5 August 2008

KL-5. Keynote Lecture 5

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Ralph H. Colby

Tuesday 1:15 De Anza I-II KL5

Independent control over the mechanical and electrical properties of solid polymer electrolytes for lithium batteries

Nitash P. Balsara[1], Ashutosh Panday[2], and Mohit Singh[2]

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The effect of structure on the mechanical and electrical properties of lamellar block copolymers doped with lithium salts is studied. Ion transport is restricted to one of the microphases while the other microphase is a hard insulator. We demonstrate that electrolytes with high conductivity and shear modulus are obtained by this approach. In solid electrolytes based on homopolymers, ion transport is coupled to segmental motion of the chain and this leads to an inverse correlation between ionic conductivity and shear modulus. The applicability of block copolymer electrolytes in solid-state lithium ion batteries will be discussed.

KL-6. Keynote Lecture 6

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Pier-Luca Maffettone

Tuesday 1:15 Steinbeck KL6

Modeling liquid crystal materials and processes in biological systems

Alejandro D. Rey

Chemical Engineering, McGill University, Montreal, Canada

Liquid crystal phases are found in DNA, proteins, lipids and polysaccharides. Frozen-in, chiral liquid crystal ordering also occurs in solid biocomposites such as insect cuticle, muscle, plant cell walls and collagen, where the helicoid structure is believed to arise by self-assembly processes. Spinning of silk fibers by spiders is another biological polymer process that relies on liquid crystal self-assembly. I will discuss the progress and challenges of modeling in three such applications: (1) Biological helicoids form by directed self-assembly. Theory and computer simulation of chiral phase ordering show that the directed self-assembly process reproduces the natural structures. The computational results shed light on the role of chiral ordering on the formation of helicoidal monodomains. (2) Spinning of spider silk involves a complex sequence of phase transitions that includes nematic phase ordering in the duct section of the spinning apparatus. Simulation of phase ordering under capillary confinement replicates the observed structures found in Nephila clavipes and other orb-weavers. The computational results shed light on the role of defect textures in the fiber spinning process. (3) Biological membranes are smectic liquid crystals that display flexoelectricity, or coupling between electric fields and curvature. Models based on smectic elasticity and polarization thermodynamics are used to derive the electroelastic shape equation, whose solution gives the membrane shape under external fields. The theoretical results shed light on the various ways electric fields affect membrane shape and functioning.

HS-4. Immiscible & Miscible Polymer Blends

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chairs: Arantxa Arbe and Nino Grizzuti

Tuesday 2:30 San Carlos IV 💿 HS22

Polypropylene-polyethylene melts: Phase structure determination by rheology

Cornelia Kock[1], Alois Schausberger[2], Nicolai Aust[3], Markus Gahleitner[4], Elisabeth Hebesberger[4], and Elisabeth Ingolic[5]

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The phase structure of polymer blends strongly influences the mechanical and optical properties as well as the performance of plastic materials. In principle three factors determine the phase structure: viscosity ratio λ between dispersed phase and matrix, surface tension α (phase compatibility), and deformation history.

In more complex PP-PE blends the surface tension is not a uniform parameter but depends on the molecular structure of PP and PE respectively. We study blends of 80 % base material (polypropylene-homopolymer or random-copolymer) and of 20 % modifier polymer (C2/C8-plastomer, linear low density polyethylene or high density polyethylene) in order to evaluate the different surface tensions and the influence of the viscosity ratio. For this purpose Palierne´s emulsion model[1] is used allowing the calculation of the dynamic moduli of a blend from the moduli of the components with given values of surface tension, particle size and volume fraction of the 2 phases.

In order to determine the surface tension the measured moduli of the blend are compared to the moduli calculated according to Palierne with given volume fraction and particle size. Both volume fraction and particle size are obtained from Transmission-Electron-Microscopy images. In blends with polypropylene-homopolymer as matrix the surface tension is stronger compared to blends with random-copolymer. The surface tension slightly decreases if the modifier is changed from the plastomer over the LLDPE to the HDPE. Furthermore the particle size increases with increasing surface tension and increasing viscosity ratio.

On all blends of this study the same mixing procedure is applied therefore the deformation history is not treated.

1. Palierne, J.F.; Linear rheology of viscoelastic emulsions with interfacial tension; Rheol Acta; 29; (1990); 204-214.

Tuesday 2:50 San Carlos IV HS23

Non linear viscoelastic behavior of polystyrene/polymethylmetacrylate blends

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In this work, the rheological behavior of polystyrene/polymethylmetacrylate (PS/PMMA) blends of several compositions, viscosity ratios and to which either random or block copolymer was added was studied. Small amplitude oscillatory shear tests, stress relaxation, single and double step shear rate tests were performed. The rheological results were explained in light of morphological observations. The relaxation spectra of the blends inferred from the small amplitude oscillatory shear tests presented either three (in the case of non compatibilized blends) or four relaxation times (in the case of compatibilized blends) depending on the blend concentration and concentration of compatibilizer added. The stress relaxation experiments revealed that all blends presented two relaxation steps: a first one which was similar to the one of the matrix and a second one which varied with blend composition, viscosity ratio and addition of compatibilizer. The results of single and double step shear rate tests were compared to Doi-Ohta Scaling laws.

Tuesday 3:10 San Carlos IV HS24

Morphology and rheology of cocontinuous blends

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Microstructure was related to viscoelastic properties of cocontinuous polymer blends during coarsening. Fluorescently labeled polystyrene (FLPS) and styrene-acrylonitrile copolymer (SAN) were imaged with laser scanning confocal microscopy (LSCM). Images were analyzed for time evolution of interfacial area, curvature and curvature distributions. Different regimes of coarsening were observed depending on the composition of the blend. For symmetrical blends a single regime was observed: self-similar growth. In the case of non-symmetrical blends the self-similar growth was followed by a slowing down of the coarsening and a subsequent transition to disperse morphologies (pinch-off) after sufficient annealing. These transitions were detected and quantified by measurements of the extra contribution to the elastic modulus due to the interface.

Tuesday 3:30 San Carlos IV HS25

The effect of 3rd component on the melt rheology of polymer blend system

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We investigated the effect of 3rd component on the melt rheology of polymer blend.Especially, we forcus on uniaxial elongational flow and meso-structure and report the melt rheology of ternary system.

Tuesday 3:50 San Carlos IV HS26

Microscopic observation of structural relaxations in systems with tunable confinement and dynamic asymmetry

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Self-assembly, confinement, nanophase separation and dynamic asymmetry (difference in timescales of motions in subsystems within the sample) are general concepts in multicomponent soft materials. However, these features are not exclusive for multicomponent systems but might also be present in some homopolymers, like the family of poly(n-alkyl methacrylates) (PnMAs)[1]. X-ray studies point to the aggregation of side groups of different monomers forming self-assembled alkyl nanodomains (called polyethylene (PE)-like), which size depends on the side-group length. The two glass-transitions detected by dynamic heat capacity presumably correspond to the freezing of motions within the alkyl nanodomain (PE-like, α_{PE}) and of the main-chain dynamics (α). It was suggested that the nanodomain structure imposes a self-confinement situation: the more mobile alkyl groups are confined by the slow main-chain segments.

Until now, PnMAs dynamics has been investigated by calorimetry, dielectric and mechanical spectroscopy, that are not selective for the processes at molecular level. In addition, x-rays cannot distinguish main-chain and side-group contributions. Neutron scattering combined with isotopic labeling allows isolately studying different components or molecular groups. Here, we have exploited these advantages to unveil the structure in PnMAs and selectively follow the collective dynamics of alkyl and main chain atoms.

Our structural study provides an unambiguous proof of the nanophase hypothesis and strongly supports the idea of self-confinement of alkyl nanodomains by the main chains. Peak I (at 0.2...0.8A^{-1}, side-chain length dependent) in the structure factor arises from correlations between the main chains (structural subunits conforming the confining matrix), while peak II (at about 1.4A^{-1}) reveals correlations between the side-chains within the confined system. The clear separation of these peaks in Q-space has facilitated the selective study by Neutron Spin Echo of the dynamics associated to each subsystem. At peak I, the dynamics always shows the features of a completely standard α-relaxation. This is also observed for the confined alkyl subsystem (peak II) in PEMA (2 carbons in the side group). However, the situation at peak II changes for higher order members (4 or more carbons in the side group): surprisingly, nearly perfectly logarithmic decays are found, strongly deviating from the typical expected stretched exponentials. This novel effect arises when the dynamic asymmetry in the system reaches about two orders of magnitude. The analogy with results reported for short-range attractive colloids[2] and model systems for polymer blends with high dynamic asymmetry[3] is discussed.

[1]M. Beiner and H. Huth, Nat. Mat. 2, 595(2003);[2]F. Sciortino et al., PRL 91, 268301(2003);[3]A.J. Moreno and J. Colmenero, J. Chem. Phys. 124, 184906 (2006).

Tuesday 4:10 San Carlos IV HS27

Submicronic gap of heterogeneous polymer between macroscopic particles: Viscoelastic analysis by a dynamic surface force apparatus

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Constant developments of surface force apparatus have permitted to transform them in nanorheometers and to investigate the dynamics of confined macromolecular systems at a molecular level.That is a situation which mimics dynamic interactions between particles at close contact.Surface treatments create strong attractive interactions between polymer chains and solid surfaces. They induce strong heterogeneity in the conformation and the dynamics of chains depending on whether they belong to adsorbed or grafted layers or to free polymer melt. We present the general formalism of a plane-sphere gap filled with an heterogeneous fluid whose properties vary with the distance to the surfaces. Then we apply it to the linear viscoelastic behavior of a polymeric system composed of two layers of tethered chains separated from free melt by two connecting zones or interfaces where free and trapped chains interfere. In particular we show that, even at large surface separations, we do not retrieve the bulk behavior of free chains.In some situations, the interfaces play the role of slipping planes. We illustrate our analysis with experimental data obtained with a nano-indentor used as a nano-rheometer, exploring the terminal and plateau relaxation modes by a frequency sweep. Samples are either drops of polybutadiene melt confined within the gap or end-grafted acrylate brushes with free acrylate melt.We also explore the situation of overlapping layers when the surface separation is lower than the thickness of both layers.We establish the expression of the global complex modulus of the gap which includes the elastic modulus of the compressed layers. We show how to connect it with the static force profile measured with a static force apparatus.

Tuesday 4:30 San Carlos IV HS28

Component dynamics in polyisoprene/poly(4-tert-butyl styrene) miscible blends

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Linear viscoelastic and dielectric measurements were conducted for blends of polyisoprene (PI; M = 20K) and poly(4-tert-butyl styrene) (PtBS; M = 16K) with various PI/PtBS compositions. In general, PI and PtBS exhibit the lower-critical-solution-temperature (LCST) type phase behavior. However, at temperatures examined, T = 125°C, our PI/PtBS blends were in a statically homogeneous state. The PI chain has the so-called type-A dipoles parallel along the backbone and its global motion activates prominent dielectric relaxation, while the PtBS chain has no type-A dipoles and its global motion is dielectrically inert. Thus, the blends exhibited the dielectric loss exclusively attributed to the PI chains therein. In the blends with high PtBS content, the dielectric loss obeyed the time-temperature superposition at high T but not at low T, despite the fact that the blend was statically homogeneous at all T. At low T, PtBS relaxed slower than PI (because Tg was higher for PtBS), as revealed from comparison of the viscoelastic and dielectric data of the blends. Thus, at low T, the large-scale motion of the PTBS chains would have been effectively quenched to give a heterogeneous frictional environment in the time scale of PI relaxation. The PI relaxation possibly detected changes of this heterogeneity with T thereby violating the time-temperature superposition. In contrast, at high T, the PtBS relaxation became equally fast compared to the PI relaxation. At such high T, the heterogeneity of the frictional environment was erased in the time scale of PI relaxation, thereby allowing PI chains to obey the superposition. The same situation was found for blends with low PtBS content (in which PtBS relaxed faster than PI at all T examined).

Tuesday 4:50 San Carlos IV 💿 HS29

Rheology/morphology relationship of immiscible EPDM/PP based thermoplastic elastomer blends

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Due to the existing lack of understanding in rheology/morphology relationship of immiscible polymer blends, more efforts are required to develop a quantitative outcome, facilitating the prediction of final properties of any polymeric blend. In this work, non-plasticized/plasticized EPDM/PP based thermoplastic elastomers (TPEs) were prepared using an internal mixer. Subsequently, single and multiple clockwise & anti-clockwise startup transient experiments have been performed to verify the effect of composition, plasticizer and shear rate in a homogeneous flow field. Due to the highly elastic nature of the elastomeric component, 0.1 s-1 and 10 min relaxation time were set for shear rate and the necessary relaxation time between each cycle, respectively. The complex morphological features (e.g., specific interfacial area and its orientation) and rheological responses of these blends are analyzed at the end of each transient experiment for modeling purposes. The morphologies observed in SEM micrographs are not remarkably different in plasticized and non-plasticized blends. However, despite various complications created with the addition of the plasticizer, the latter reduces the differences between rheological properties of both components and increases their deformability. To predict the rheology/morphology relationship, a phenomenological model based on Doi and Ohta [J. Chem. Phys. 95(2), 1242 (1991)] is used to couple the time evolution of the morphological features and the macroscopic overall stress response. Based on this approach, few model parameters are required to express the relative importance of different interfacial dynamics such as coalescence, shape relaxation and rupture of one phase in another. The modeling parameters are further employed to verify the applicability of the model in predicting the torque/morphology relationship for blends prepared in a conventional melt mixing equipment (e.g., internal mixer).

SG-4. Effect of Nanoconfinement on Dynamics

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Didier Long

Tuesday 2:30 San Carlos II SG22

Single sphere suspended in a liquid subjected to shear flows: Effects of confinement

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Motion of liquids in confined geometries is relevant in several microfluidic devices. A filler with dimensions comparable with that of the flow cell and suspended in a liquid matrix strongly affects the hydrodynamics. In this work we analyze the problem of the motion of a sphere suspended in a Newtonian or viscoelastic liquid subjected to shear flows in a confined geometry. The sphere is assumed to be inertialess and buoyancy is neglected. The steady state solution of the motion equations in 3D is obtained through a finite element code. The rigid-body motion of the sphere is imposed by means of constraints on the surface so the angular velocity is an additional unknown and is recovered by solving the system of equations. The effect of confinement is a slowing down of the rotation rate of the sphere with respect to the “unbounded” case. This slowing down is predicted for Newtonian as well as viscoelastic suspending matrix. Effects of confinement on local stresses and streamlines are also significant both for Newtonian and viscoelastic liquids.

Tuesday 2:50 San Carlos II SG23

Molecular dynamics of confined macromolecules: From the bulk down to polymeric sub-layers

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Confinement-effects on the molecular dynamics of thin polymer films are currently the object of an intensive scientific debate. The present paper contributes to this discussion and gives emphasis to the following topics:

(a) due to preparative factors, metastable states of the glassy dynamics may be induced in thin polymer films, which – similarly to confinement effects – exhibit shifts in the mean relaxation time of the dynamic glass transition. These shifts become weaker or even disappear after an extensive annealing.

(b) the mechanisms of the confinement effects can be revealed by analysing the changes in the distribution of the relaxation times in dependence on the film thickness. It will be shown, for instance, that an increase in the mean relaxation rate can originate from a suppression of the slower relaxation modes in confinement.

(c) different microscopic or macroscopic experimental methods do not necessarily deliver similar results when employed to investigate the molecular dynamics of confined polymers. For thin films of hyper-branched polymers it will shown that simultaneous dilatometric and dielectric measurements on the dynamic glass transition deliver diverging thickness dependencies.

(d) the interfacial dynamics of polymers in contact with solid substrates will be analysed in systematic dependence on the interfacial interactions. These investigations are enabled by a novel experimental approach which, using nano-structures as spacers, renders to Broadband Dielectric Spectroscopy the ability to measure molecular fluctuations in the immediate (nanometric) vicinity of solid substrates.

(e) measurements on the molecular dynamics in polymeric sub-layers exhibiting individually recognizable polymer chains will be presented and discussed.

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Tuesday 3:10 San Carlos II SG24

Segmental dynamics of nanostructured polymers

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A common feature of self-assembled nanostructured polymers consisting of two incompatible components is that the relaxation spectrum incorporates two dynamic glass transitions. The influence of domain size D on the segmental dynamics within the nanodomains is studied. Shear data and calorimetric results for nanophase-separated side chain polymers (0.5nm $< D <$ 2nm) and oriented microphase-separated block copolymers (10nm $< D <$ 30nm) will be presented. The results indicate a transition from cooperative segmental dynamics to more local motions in nanodomains smaller then two nanometers. This observation is discussed in the framework of concepts assuming that dynamic heterogeneities are an intrinsic feature of glass-forming liquids [1]. Similarities with the complex dynamics of native proteins and possible consequences for the efficient folding process of these biopolymers will be discussed [2]. Further parameters influencing the cooperative dynamics and equilibration phenomena in nanostructured polymers with components having significantly different glass temperatures T_g are investigated [3]. The influence of equilibration processes in the high T_g component on the segmental dynamics of the soft component is considered and the situation is compared with physical aging processes in glassy homopolymers.

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Tuesday 3:30 San Carlos II SG25

Effects of severe confinement on the structure and dynamics in polymer nanocomposites

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Mixing polymers with layered-silicates leads to the formation of organic/inorganic hybrids with enhanced properties and high technological potential. Three different types of structures can be identified in these systems depending on the organic - inorganic interactions: the phase separated microcomposites, where polymer and silicate are immiscible, the intercalated nanocomposites, where the polymer chains reside between the layers of the inorganic material forming 0.8-2.5 nm thin films, and the exfoliated ones, where the silicate layers are dispersed in the polymer matrix. The intercalated nanohybrids are especially interesting since they offer the opportunity to investigate the static and dynamic properties of macromolecules in nano-confinement utilizing, however, macroscopic samples and conventional analytical techniques. Hydrophilic polymers, like poly(ethylene oxide), PEO, can intercalate within hydrophilic silicates such as sodium montmorillonite, Na+MMT. In this work, we investigate the structure and dynamics of PEO/Na+MMT nanocomposites of various concentrations from pure polymer to pure clay by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC), Raman spectroscopy (RS), and Quasi-elastic Neutron Scattering (QENS). XRD measurements show that at concentrations up to 20 wt% PEO, the PEO chains within the galleries form either a single- or a double-layer structure of intercalated chains. Further increase of the PEO concentration reveals only double-layers of intercalated PEO chains confined within the 0.9nm gallery spacing. At these concentrations XRD and RS verify that the PEO chains within the galleries are disordered liquid-like despite the fact that the bulk PEO tends to crystallize easily. Moreover, for PEO content below 70 wt% no XRD peaks are observed that can be assigned to the crystalline structure of PEO, which, together with the absence of any DSC melting transition, reveal that the PEO chains remain amorphous. This is also verified by the observation of broad Raman lines by RS. It is only for PEO concentrations higher than 70 wt% that the diffraction peaks characteristic of bulk PEO are observed together with sharp Raman lines, which proves crystallization of only the excess polymer outside the completely full galleries. QENS was utilized to investigate the dynamics of the intercalated PEO chains. The data for the energy-resolved elastic intensity scattered from the samples (elastic scan) show right away the differences in the behavior of PEO in bulk and in confinement. The data for bulk PEO show the existence of dynamics between the glass transition, Tg, and the melting temperature, Tm, as well as an abrupt drop in the intensity at the bulk Tm, whereas the data for the 30% PEO are insensitive to the bulk Tm. A jump of the bulk PEO dynamics at Tm is also observed in the quasi-elastic measurements, whereas the dynamics of PEO in confinement shows only weak temperature dependence and goes smoothly through the bulk Tm, above which it is slower than that in the bulk.

Tuesday 3:50 San Carlos II SG26

Influence of confinement and substrate interaction on the crystallization kinetics of ultrathin films of poly(ethylene terephthalate)

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The structural dynamics of thin and ultrathin polymer films of poly(ethylene terephthalate) (PET) capped between aluminium electrodes was investigated by dielectric relaxation spectroscopy. The thickness of the films ranged between 0.25 mm and 10 nm. For films thinner than 35 nm a slowing down of the structural dynamics and a corresponding increase of the glass transition temperature Tg with respect to the bulk behaviour were observed [1]. This effect was interpreted in terms of a strong interaction between polymer and substrate, as verified by means of contact angle measurements, and the confined films was modelled as a multilayer structure, where the part closer to the substrate interface (reduced mobility layer) has a slower mobility than the bulk [1, 2, 3, 4].

In this communication we present further investigations carried out on films of PET, of the same thickness as above, deposited on different substrates (glass, aluminium, silicon, gold). In particular, we studied the cold crystallization kinetics by dielectric spectroscopy, X-ray diffraction and infrared spectroscopy (FTIR, ATR, RAIR). The crystallization kinetics shows a similar behavior as the relaxation dynamics and deviates from the bulk behavior below 100 nm. Moreover, a stronger slowing down of the kinetics was observed in films deposited on very interacting substrates, whereas negligible effects, or a speeding up, was found in the case of weakly interacting substrates.

The crystallization kinetics on the free surface of PET films was also studied by means of Atomic Force Microscopy (AFM). For thicker samples, the kinetics at the free surface is much faster than that of the bulk sample. For thinner samples, the crystallization kinetics slows down as the free surface becomes closer and closer to the reduced mobility layers up to prevent crystallization in very thin films (10 nm), deposited on strongly interacting substrates. Moreover, the morphology of crystallites agrees to that provided by recent molecular dynamics simulations [5].

[1] S. Napolitano, D. Prevosto, M. Lucchesi, P. Pingue, M. D'Acunto, and P.A. Rolla, Langmuir, 23, 2103 (2007); [2] D. S. Fryer et al, Macromolecules, 34, 5627 (2001); [3] J.L. Keddie, R A L Jones, R A Cory, Europhys. Lett. 27, 59 (1994); [4] C.J. Ellison and J.M. Torkelson, Nature Materials 2, 695 (2003); [5] Y. Ma, W. Hu e G. Reiter, Macromolecules, 39, 5159 (2006).

Tuesday 4:10 San Carlos II SG27

Aging phenomena in thin polymer films observed through volume and dielectric susceptibility

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Glassy dynamics was investigated for thin films of atactic polystyrene and poly(2-chlorostyrene) by complex electric capacitance measurements using dielectric relaxation spectroscopy. During the isothermal aging process the real part of the electric capacitance increased with aging time, whereas the imaginary part of the electric capacitance decreased with aging time. It follows that the aging time dependences of real and imaginary parts of the electric capacitance were primarily associated with change in volume (film thickness) and dielectric permittivity, respectively. Further, dielectric permittivity showed memory and rejuvenation effects in a similar manner to those observed for poly(methyl methacrylate) thin films. This means that the response to the external field can be rejuvenated by coolig to room temperature. On the other hand, volume did not show a strong rejuvenation effect, which is consistent with the fact that polymers usually show densification through the aging process below the glass transition temperature.

Tuesday 4:30 San Carlos II SG28

Aging in PMMA/toluene films

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If the glass transition and the physical properties of glassy polymers have been extensively studied using the temperature as a control parameter, few experimental studies have reported physical aging investigations in polymer solutions, using the activity as the control parameter. In that case the system is more complex that other glass forming materials since it involves two components. The understanding of the observed similarities and discrepancies is of great fundamental interest.

Gravimetric experiments in a well controlled environment have been performed to investigate aging for a glassy PMMA/Toluene film. The temperature is constant and the control parameter is the solvent vapor pressure above the film (i.e. the activity). Several experimental protocols have been used, starting from a high activity where the film is swollen and rubbery and then aging the film at different activities below the glass transition. Desorption and resorption curves have been compared for the different protocols, in particular in term of the softening time, i.e. the time needed by the sample to recover an equilibrium state at high activity. Several regimes have been obtained depending on the aging activity, showing a non monotonic dependence of the softening time with the aging activity and non trivial behaviors especially at small activities (deep quench).

We propose a simple model that accounts for the glassy dynamics of the solvent solubility. At high activity, thermodynamic equilibrium is reached and the Flory-Hugging model applies. Deep in the vitreous state, a pseudo-equilibrium state could be derived using the Leibler and Sekimoto model, which introduced an elastic term in the osmotic pressure. In order to account for both regimes, we extended the former model to viscoleastic materials. The evolution of the system structure during aging is taken into account using the Taman-Nayanawsami-Moynihan approach.

The model captures qualitatively most of the observed phenomena and underlines the crucial role of the non-exponentiality of the relaxation. However, some observations made using more complex aging histories at very small activities are not accounted by the model and ask for further theoretical and experimental investigations.

HP-7. Entangled Polymers I

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: David C. Venerus and Ole Hassager

Tuesday 2:30 San Carlos III HP43

Thermodynamically-guided nonequilibrium Monte Carlo method for generating realistic shear flows in polymeric materials

Chunggi Baig and Vlasis G. Mavrantzas
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We have developed an atomistic Monte Carlo (MC) methodology for simulating polymeric systems beyond equilibrium by expanding the statistical ensemble to include field variables that can drive the system to certain nonequilibrium states. In the new method, also termed GENERIC (General Equation for the Nonequilibrium Reversible-Irreversible Coupling) MC [1-3], the field variables are the thermodynamic conjugate variables (or Lagrange multipliers) to coarse-grained structural variables. The latter are selected, guided by principles of nonequilibrium thermodynamics, to be representative of the overall polymer conformation; for unentangled polymer melts, such a variable is the conformation tensor **c**. At present, for a given flow, the conjugate field variable corresponding to **c**, a tensor **a**, is determined iteratively so that the resulting system conformation is the same as that obtained through a direct application of the nonequilibrium molecular dynamics (NEMD) method [4]. We have demonstrated the applicability of the new method in simulations of three linear polyethylene melt systems, $C_{50}H_{102}$, $C_{78}H_{158}$, and $C_{128}H_{258}$ for the case of steady-state shear flow, for which the two methods (expanded or GENERIC MC and NEMD) provide identical results practically for any shear rate. At convergence, the non-zero components of the tensor **a** provide invaluable information for the true free energy function of the deformed systems relative to equilibrium as well as for the underlying friction matrix of the corresponding GENERIC equation; thus, they can be used as a guide for improving existing conformation tensor based viscoleastic models or developing new ones [5].

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Tuesday 2:50 San Carlos III HP44

Are entangled polymeric solutions different from melts?

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Recent experiments have shown that concentrated polymeric solutions and melts exhibit dissimilar rheological behavior under extensional flow, contradicting the theory of entangled poly- meric systems. In the present work, various entangled solutions of monodisperse Polystyrene and 1,4 Polyisoprene and room temperature melts of 1,4 Polyisoprene and Poly n-butyl acrylate have been analyzed under uniaxial extensional flow, using the Filament Stretching Rheometer. In exten- sional flow, no significant dfference in the rheological response of concentrated solutions and melts is observed. Collapse of elongational stress data is observed when plotted a Weissenberg number defined using Marrucci and Ianniruberto's [3] tube squeeze relaxation time, with the ratio of maximum segmental stretch ratio and the number of entanglements per chain as a parameter.

Tuesday 3:10 San Carlos III HP45

Nonlinear rheology of entangled polymer solutions in narrow gaps probed by confocal microscopy

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Unlike weakly and moderately entangled polymers (N/Ne = 11), the step-shear damping function, $h(\gamma) = G(t, \gamma) / G(t, \gamma_0)$, for polymers with high entanglement densities is more strain softening than the Doi-Edwards constitutive theory prediction, $h_{DE}(\gamma)$. Two likely causes of this behavior, termed Type C damping, are interfacial slip of the sheared polymer at a polymer/polymer or polymer-wall interface, and shear banding. In an effort to isolate and understand these mechanisms, we employ macroscopic rheometry as well as microscopic methods to directly visualize the flow. The latter is done in a planar Couette shear flow seeded with tracer particles. We discuss experiments performed with polybutadiene (M_w = 200K and M_w = 1.1M) solutions with varying polymer volume fraction, ϕ, i.e. different entanglement densities (28 = N/Ne = 71) in a narrow gap (~ 35 μm) planar Couette shear cell. We find that not only does the velocity at the boundaries not satisfy the no-slip condition, but that the velocity profiles corresponding to the fully developed flow regime are linear. This observation is inconsistent with a shear banding mechanism. It is nonetheless consistently observed for a range of applied shear rates. The local shear rates extracted from these profiles combined with the rheological shear stress data are used to investigate interfacial slip behavior in the polymer solutions and to characterize the critical conditions for slip onset.

Tuesday 3:30 San Carlos III HP46

Nonlinear behaviour of entangled polymers studied by local rheo-optics and velocimetry

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The transient and steady state behavior of highly entangled polymer solutions is studied using local rheo-optics and particle tracking velocimetry in Couette geometry. A previous study on entangled polybutadiene solutions shows no steady-state shear banding, even though the constructed flow curve has a nearly zero stress slope 1. Here we investigate the nonlinear behavior of more entangled solutions using spatially-resolved (local) rheo-optic techniques, in additional to local velocity measurements. Steady-state shear banding is observed in some highly entangled polymer solutions. With insights from the local chain structural information obtained from the rheo-optics, we critically examine the Tube model, and discuss whether our results can be interpreted within the Tube framework.

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Tuesday 3:50 San Carlos III HP47

Elastic yielding in entangled polymeric liquids: Exploring origin of flow inhomogeneity

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We will present an overview of the latest developments in the area of nonlinear flow behavior of entangled polymer solutions and melts, on both the experimental and theoretical fronts. From visualization-based experiments, we have derived a theoretical understanding of a host of striking flow phenomena ranging from elastic breakdown after a step strain, to emergence of shear inhomogeneity in startup and large amplitude oscillatory shear and universal scaling behavior associated with the yield point identified to be the force maximum during start flow. In our efforts, we address basic questions such as (a) where cohesion comes from in polymeric liquids, (b) how cohesive failure occurs during startup flow and after step flow respectively, (c) whether and how well entangled polymers as transient solids break up inhomogeneously first before forced to undergo flow deformation. Clearly, effects of chain entanglement are not only dynamical as recognized in the past but also mechanical, and we must be concerned about the cohesive strength of such "solids".

Tuesday 4:10 San Carlos III HP48

Scaling relations in large amplitude oscillatory shear (LAOS) of polymeric fluids

Kwang Soo Cho[1], Ki-won Song[2], Dong Jin Kim[1], and Gap-Shik Chang[2]
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Stress decomposition method provides decomposition of shear stress of LAOS into elastic and viscous parts, which allows us to apply well-defined analysis methods of linear viscoelasticity to LAOS. In this presentation, we investigate some scaling rules which deal with experimental variables such as frequency and strain amplitude as well as structure variables such as molecular weight, concentration, and so on. We define nonlinear functions for elastic and viscous stress which normalize the shapes of the stress components and investigate the relationship between the nonlinear functions and structure variables.

Tuesday 4:30 San Carlos III HP49

What is polymer systems' behavior in the vicinity of "spurt" regime?

Valery G. Kulichikhin
A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

In strong shear flow homogeneous and heterogeneous polymers suffer drastic changes consisting in texturing of individual melt or phase segregation of incompatible polymer blends and particulate composite precursors. The most evident indication on this kind of behavior is ring-like morphology formation in heterophase systems which is reached at definite combinations of shear rate and reached strain. We present examples of different stages of ring-like morphology evolution in transparent sphere-plate geometry and demonstrate this kind of behavior for varios nanocomposite and individual systems, such as for polyisobutylene (PIB) matrix filled with 7% of clay particles and for pure PIB melt.

In particular, the behavior of individual PIB melt in vicinity of "spurt" regime is accompanied by cohesion rupture of specimen. The general driving force of polymer systems' texturing can be attributed to the phase separation of pure polymer melt due to molecular weight polydispersity (or different direction of stretched macromolecules orientation in adjacent bands), as well as to the phase segregation of heterogeneous blends and composites. In the nanocomposite systems, texturing of polymer matrix due to phase separation results in ordered arrangement of solid particles. The same reason leads to the viscosity decrease with increasing content of nanoparticle precursors. This phenomena was observed in a variaty of nanocomposite systems. The rough estimation of the additive viscosity change in the case of phase separation indicates the essential viscosity drop.

V.Kulichikhin, A.Subbotin, L.Tsamalashvili, E.Plotnikova, Polymer Science, 2000, C., P.1392; V.Kulichikhin, A.Subbotin, E.Plotnikova, N.Plate, Rheol. Acta, 2001, V.40, P.49.

Acknowledgements RFBR for partial financial support (grants 04-03-32152 and 05-03-08028), NWO-RFBR project 047.017.033

Tuesday 4:50 San Carlos III HP50

Entangled polymer melts under simple shear: Interfacial and internal elastic breakdown

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Recent experimental findings based on particle tracking velocimetry (PTV) revealed that entangled systems such as polybutadiene [1], DNA [2] and wormlike micellar [3] solutions yield both during shear and after step strain. The observed shear inhomogeneity appears to result from elastic breakdown of the entanglement network [4]. Several key questions remained to be addressed: 1) Would well-entangled polymer melts show similar shear phenomenology as seen in solutions? 2) Is interfacial wall slip also related to the fact that entangled melts are incapable of flowing on short time scales? In the present work, we attempted to answer such questions by performing a series of interrupted startup shear experiments in conjunction with in situ PTV observations. At large amplitude of strains, the recoil-like macroscopic motions were observed at either interface or interior of sample during relaxation. In contrast with entangled solutions, chain disentanglement takes a finite time to nucleate and grow, leading to visible eventual structural breakdown of the entanglement network, which is phenomenologically similar to observations of the same melts under uniaxial extension [5].

[1] Tapadia and Wang, Phys. Rev. Lett. 96, 016001, Boukany and Wang, J. Rheol. 51, 217 (2007); Wang et al., Phys. Rev. Lett. 97, 187801 (2007); [2] Boukany, Hu and Wang, Macromolecules 2007, under review; [3] Boukany and Wang, Macromolecules 2007, under review; [4] Wang, Ravindranath, Wang and Boukany, J. Chem. Phys. 2007,127, 064903; [5] Wang et al., Phys. Rev. Lett., 2007, in press.

FR-1. Food Gels and Perception

Organizers: Erich J. Windhab and Jan Engmann
Session Chairs: Erich J. Windhab and Adam Burbidge

Tuesday 2:30 Bonsai I FR1

Towards a simple constitutive model for bread dough

Roger I. Tanner
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Wheat flour dough is an example of a soft solid material consisting of a gluten (rubbery) network with starch particles as filler. The volume fraction of the starch filler is high-typically 60%. A computer-friendly constitutive model has been lacking for this type of material and here we report on progress towards finding such a model. The model must describe the response to small strains, simple shearing starting from rest, simple elongation, biaxial straining, recoil and various other transient flows.

A viscoelastic Lodge-type model involving a damage function which depends on strain from an initial reference state fits the given data well, and it is also able to predict the thickness at exit from dough sheeting, which has been a long-standing unsolved puzzle. The model also shows an apparent rate-dependent yield stress, although no explicit yield stress is built into the model. This behaviour agrees with the early (1934) observations of Schofield and Scott Blair on dough recoil after unloading.

Tuesday 2:50 Bonsai I FR2

Rheology of model dough formulations

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Dough is a multicomponent complex fluid consisting of water swollen starch particles suspended in a hydrated elastic gluten matrix. Dough exhibits rheological features that are characteristic of soft materials. We examine the rheological properties of model dough compounds which consist of the individual components, i.e., aqueous starch dispersions and hydrated gluten, and their mixtures of different compositions. Rheological properties are probed using small amplitude oscillatory shear (SAOS), large amplitude oscillatory shear (LAOS), shear rate frequency sweep (SRFS), shear stress ramp and uniaxial extensional tests. Material functions obtained from the various rheological tests are related to dough composition, and this provides information about how starch interparticle interactions are modulated by gluten.

Tuesday 3:10 Bonsai I FR3

Significance of wheat flour dough rheology to gas cell structure development in bread and other baked products

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Wheat flour doughs are an extensively studied system in food rheology, with scientific work dating back to the 1930s and simple rheological measurements widely used in the bakery industry. The practical significance of these measurements is, however, mostly limited to empirical correlations between curve parameters derived from these measurements and product quality (e.g. loaf volume, fineness of bread crumb). A well-developed and robust quantitative theory linking rheological behaviour to structure development in dough during the proofing and baking stages is still not available, although some progress has been made in recent years (van Vliet et al., 1992; Dobraszczyk, 2004). Apart from the difficulty in achieving a precise and repeatable rheological characterisation for a material whose structure cannot be conserved over long periods of time, it is also difficult to simulate the thermal history experienced by dough during baking without encountering problems of drying, inhomogeneity and expansion. Finally, the complexity of describing the non-linear viscolelastic behaviour (Ng et al., 2006; Tanner, 2007) which is a rarely used concept in food research and in the case of dough combines with compressibility effects, has stifled progress. This paper will discuss which rheological material functions of wheat flour dough should be adequate to describe structure development in baked products under given processing conditions. It will primarily be concerned with bubble growth during dough proofing, driven by yeast, and during baking, where the bubble growth is driven by a combination of CO2 desorption, ethanol and water evaporation, and thermal expansion of the gas. Particular attention will be given to the time scales of these mechanisms in relation to the relaxation behaviour of dough and the consequences for the required rheological characterisation. Furthermore, conditions for coalescence between gas cells in dough will be discussed, in particular the applicability of a Considère criterion to predict the occurrence of coalescence between bubbles and its effect on loaf aeration.

Van Vliet, T., Janssen, A.M., Bloksma, A.H. and Walstra, P. (1992), Strain hardening of dough as a requirement for gas retention, J. Texture Stud. 23, 439-460; Dobraszczyk, B.J. (2004), The physics of baking: rheological and polymer molecular structure-function relationships in breadmaking, J. Non-Newt. Fluid Mech. 124, 61-69; Ng, T.S.K., McKinley, G.H. and Padmanabhan, M. (2006), Linear to non-linear rheology of wheat flour dough, Appl. Rheol. 16, 265-274; Tanner, R.I., Dai, S.C. and Qi, F. (2007), Bread dough rheology and recoil, J. Non-Newt. Fluid Mech. 143, 107-119.

Tuesday 3:30 Bonsai I FR4

Rheological changes in squid surimi made by two methods during frozen storage in the presence of different cryoprotectants

Laura Campo-Deaño and Clara A. Tovar
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Surimi is a concentrated of myofibrillar proteins obtained from mechanically deboned fish flesh, which is washed with cold water. It is served as a potential raw material for a variety of imitative seafood products. For processing surimi it is normally used proteins of fish muscle, however, the giant squid (Dosidicus gigas) muscle has the potential to be used for manufacture of surimi given that the muscle is white, has little flavour and virtually no fat and is in abundant supply throughout the world, especially on the Pacific coast of Mexico. Gel-forming ability and water holding capacity are important determinants of surimi quality, and they may be lost by the denaturation and aggregation of muscle proteins that occur during frozen storage. The addition of cryoprotectants is required in order to retain its functional properties. The objective of the present work was to investigate the ability of different kind of cryoprotectants to stabilize squid surimi as a function of elaboration method during six months of frozen storage. The first method is made by initial dispersion of muscle in a neutral salt solution and further isoelectric precipitation (Type A); the second one (traditional method) is made washing the minced muscle with a buffer citrate-phosphate at pH 5 (Type B). In both cases a decanter is used to collect the precipitate and then 8% of cryoprotectant and 0.25 of sodium Tripoliphosphate are incorporated. Samples (pH 7) were the following: A1 with 8% of starch, A2 (4% sorbitol + 4% sucrose), A3 (4% sorbitol + 4% trehalose) and A4 (8% of trehalose), whereas their method B counterparts were named B1, B2, B3 and B4. For the study a Bohlin CVO and RS600 Haake rheometers were used. In general, oscillatory dynamic tests (stress and frequency sweep) showed a decrease of the rigidity and firmness of the samples that could be provoked by proteolysis due to endogenous and microbial enzymes during frozen storage, in both kinds of surimi, A and B. Moreover, this rheological behaviour is more uniform throughout 24 weeks of storage in samples B, revealing a better interaction between cryoprotectants and actomyosin in surimi B, maybe due to the higher quantity of native protein for this kind of surimi. In addition, samples from traditional method showed a peculiar little protein aggregation after six months of storage, reflecting a new weak restructuring of the protein network, as shown by the significative increase of the coordination number from mechanical spectra.

Tuesday 3:50 Bonsai I FR5

Characterisation of fracture behaviour of starch gels using conventional fracture mechanics tests and wire cutting tests

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The fracture behaviour of two types of starch gels is investigated using conventional notched samples as well as wire cutting tests at various loading rates in order to determine the true fracture toughness of the materials and how it varies with starch type as well as with the starch/water weight ratio. In a parallel study on the same gels it was found that the behaviour at small strains was rate independent for both gels, whereas the stress and strain at failure increased considerably with strain rate. Therefore this comprehensive study on fracture will aim to explain this behaviour. The fracture toughness results from the notched samples will be used to verify the results obtained from the cutting tests which are performed with various wire diameters and cutting speeds. In agreement with the trend in the failure stress and strain rising with increasing strain rates, the cutting forces are also observed to increase with increasing cutting rate. The wire cutting test is simulated using Finite Element Analysis using two criteria for crack propagation: i) maximum strain criterion and ii) cohesive zone model. The unique set of parameters in the cohesive zone model as well as the coefficient of friction between the wire and the gels are determined by comparing the experimental data to the numerical predictions corresponding to all the wire diameters and cutting speeds. Lastly, a microstructural analysis of the gels is performed using light microscopy as well as cryo SEM in an effort to explain the important structure-property relationship.

Tuesday 4:10 Bonsai I FR6

First steps in understanding texture perception in the human mouth as an inverse bio-fluid mechanical problem

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We discuss approaching the question of sensory perception of in mouth texture, using the specific example of ‘grittiness’ from the perspective of an inverse problem in which the structural elements of a suspension interact indirectly with the sensory structures present in the human mouth. Firstly we verify the ‘resolution’ of these sensory structures by means of a simple experiment requiring subjects to distinguish between pairs of discs of different diameters or thickness. The results of this experiment prove to be surprisingly rich, and demonstrate that the brain uses a number of different data sources to make it's decision. Secondly, we hypothesise that 'grittiness' could at least in part be attributed to stress field perturbations due to the presence of finite sized particles in a non-simple flow field. Sample calculations are presented for squeezing flows between tongue and palate based on applications of Faxen's laws and singular solutions of the Stokes equation. Based on the physiological data available from the literature we can simulate the apparent stimulus applied to the various known bio-sensory structures present in the mouth (Merkel, Meissner and Ruffini cells) and compare our findings with previous physiological experiments.

Tuesday 4:30 Bonsai I FR7

Correlation of mouthfeel perceptions with bulk rheology and tribology (lubricity) in dairy emulsions

Stefan K. Baier[1], Brian D. Guthrie[1], Tim A. Lindgren[1], Steinbach J. Adam[1], Joost Vanhemelrijck[1], Stephane Debon[2], Joerg Laeuger[3], Patrick Heyer[3], and William R. Aimutis[1]
[1]Global Food Technology, Cargill, Inc., Wayzata, MN 55391, USA; [2]Global Food Technology, Cargill Europe BVBA, Vilvoorde, Belgium; [3]Anton Paar Germany GmbH, Ostfildern, Germany

Human perceptions of different mouthfeel attributes of a variety of liquid and solid foods were correlated with instrumental determinations of bulk rheology and tribology or lubricity. Traditional Quantitative Descriptive Analysis (QDA) was performed on dairy emulsions of varying fat contents. Mouthfeel descriptors were defined for each dairy emulsion. Lubricity, from Stribeck curves (friction coefficient as a function of sliding speed at a constant normal force) was determined using a newly developed tribology accessory. The mouthfeel attributes of each food were scored in triplicate. Flow curves (power law fit) were performed on the dairy samples. Correlation of the human and instrumental data was explored using PCA and PLS1 models. In general, neither rheology nor lubricity (tribology) alone correlated well with all of the mouthfeel attributes. Certain attributes, such as "thickness" correlated with the instrumental rheology measurements while attributes such as “slippery” and “creamy” were more correlated with lubricity. Total mouthfeel sensations seem to involve both the flow and lubricating properties of foods.

Tuesday 4:50 Bonsai I FR8

Viscosity and wine: A subtle and sublime connection

Ron C. Runnebaum[1], Robert L. Powell[2], Roger B. Boulton[3], and Hildegarde Heymann[1]
[1]Viticulture & Enology, UC Davis, Davis, CA 95616, USA; [2]Chemical Engineering, UC Davis, Davis, CA 95616, USA; [3]Viticulture & Enology; Chemical Engineering, UC Davis, Davis, CA 95616, USA

Previous work has not yet determined how individual constituents interact and combine to create the overall viscosity or body of a wine. This research used multivariate statistical modeling to identify significant correlations of several chemical and physical properties of wine with its perceived body. Seventeen white wines that span an anecdotal range of perceived viscous mouthfeel, including Chardonnay, Viognier, Pinot gris, Riesling, and Sauvignon blancs, were assessed using a descriptive analysis technique to determine quantitative ratings of viscous mouthfeel. These wines were also submitted to a wide range of chemical and physical property analyses, including capillary viscosity, density, ethanol by volume, total phenolics, organic acids (lactate, citrate, tartrate, malate, succinate), glycerol, sugars (fructose and glucose), total extract, and several inorganic cations/anions (K, Ca, Mg, Na, Cl). A multivariate statistical model has been developed that shows the viscous mouthfeel of these white wines is significantly correlated with physical properties, such as capillary viscosity and osmotic potential, and chemical properties, such as lactate, fructose, glucose, and total extract. This work also confirms previous results from other researchers indicating that ethanol and glycerol do not play an important role in viscous mouthfeel.

Tuesday 5:10 Bonsai I FR9

Rheological characterization of vegetal pear (*Sechium edule*)

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División de Estudios de Postgrado e Investigación, Instituto Tecnológico de Orizaba, Orizaba, Veracruz 94320, Mexico

The national production of Mexican vegetal pear (Sechium edule) is located at the present time in more than 130,000 ton / year. The vegetal pear that produced in the center zone of the state of Veracruz is known in international markets; however it is a product that practically has not been studied. This work identifies the rheological behavior of vegetal pear (Sechium edule). A rheometer MCR301 of Anton Paar was utilized for viscosity and shear stress measurements. The objective of this experimental was modeling the rheological behavior of vegetal pear suspensions at three concentrations (1, 2 and 3 % w/w), three particle size (1.00, 1.19 and 1.40 mm), at the same conditions of temperature (25, 40 and 70 ºC). The results showed that in all the suspensions there was a phenomenological behavior as a dilatant fluid ($n > 1$) the performance of flow was represented by the Herschel-Bulkley model, and present values of "yield stress" between 0.1 and 15 Pa for the different experiments. During evaluation of the activation energy of the suspensions of vegetal pear was found that decreases from 981.77 to 737.67 kJ/mol for a particle size of 1.00 mm to 1.40 mm, which implies that the effect of temperature is higher with smaller particles, in this case 1.00 mm. Furthermore, it assessed the effect of particle size performed by Péclet number, showing an increase of the viscosity when the Péclet number also increases.

BR-2. Rheology of Biomacromolecules

Organizers: James L. Harden and Christoph F. Schmidt
Session Chair: Maria Kilfoil

Tuesday 2:30 Redwood BR7

What do we learn rheologically from entangled DNA solutions?

Pouyan E. Boukany and Shi-Qing Wang
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Aqueous DNA solutions can be highly entangled at very low concentrations (~1 %) and are consequently an ideal model system to examine basic phenomenology concerning strong flows without complications such as edge fracture at the meniscus or Weissenberg rod-climbing. Indeed, several features showed up in our rheological and PTV measurements of entangled DNA solutions [1-3]. These solutions allow us to show that shear banding after startup shear would be permanent at a high enough level of entanglement and weakly entangled systems tend to undergo homogeneous shear. Many new exciting results will be presented and be published in the near future.

[1] Boukany, Hu and Wang, "Observations of shear banding in an entangled DNA solution", Macromolecules, submitted (2007); [2] Boukany and Wang, "Observations of shear banding in an entangled DNA solution: II. Effect of solvent", Soft Matt., to be submitted; [3] Boukany and Wang. "Observations of shear banding in an entangled DNA solution: III. Effect of chain entanglement density", J. Rheol., to be submitted.

Tuesday 2:50 Redwood BR8

Little shop of horrors: Rheology of the mucilage of *Drosera sp.*, a carnivorous plant

Philipp Erni[1], Matthieu Varagnat[2], and Gareth H. McKinley[1]

[1]Department of Mechanical Engineering, MIT, Cambridge, MA 02139, USA; [2]Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA

Drosera sp. (‘sundew’) are carnivorous plants; they capture insects using tiny drops of mucilage secreted by stalked glands on their leaf laminae. Prey gets trapped by the sticky viscoelastic liquid, initiating a metabolic cascade on the leaf that eventually results in the insect being digested by the plant. The mucilage droplets typically are in the size range of tens of micrometers; at these extremely small sample sizes, complex fluids are traditionally not amenable to traditional rheometry. In this contribution, we show how microrheometric techniques, in particular capillary breakup extensional rheometry (‘μ-caber’), can be used to test the nonlinear rheological properties of nanoliter volumes of such materials. We also discuss the applicability of complementary techniques for microrheometry, including particle-based methods and sliding plate microrheometry for measurements on plant mucilage and related small-volume biopolymer samples.

Tuesday 3:10 Redwood BR9

A viscoelastic deadly fluid in carnivorous pitcher plants

Laurence Gaume[1] and Yoel Forterre[2]

[1]University of Montpellier, AMAP UMR 5120, Montpellier, France; [2]University of Provence, IUSTI UMR 6595, Marseille, France

The Nepenthes pitcher plants, widely distributed in the Asian tropics, are among the most successful and diversified carnivorous plants. Since Darwin, their mechanism of insect-trapping has intrigued scientists but is still incompletely understood. The slippery inner surfaces of their pitchers have so far been considered to be the key trapping devices while the fluid contained in them has been assigned the sole function of digestion. Using a combination of insect bioassays, high-speed video and extensional rheometry measurements, we show that the digestive fluid of Nepenthes rafflesiana is a highly shear-thinning viscoelastic fluid and that this later property is crucial for the retention of insects in its traps. Trapping efficiency is shown to remain strong even when the fluid is highly diluted by water, as long as the elastic relaxation time of the fluid is higher than the typical time scale of insect movements (large Deborah numbers). This finding challenges the common classification of Nepenthes pitchers as simple passive traps and is of great adaptive significance for these tropical plants, which are often submitted to high rainfalls and variations in fluid concentration. Such large production of a highly viscoelastic biopolymer fluid in permanent pools is furthermore unique in the plant kingdom and suggests novel applications for pest control.

Tuesday 3:30 Redwood BR10

Non-linear viscoelastic models for random coil polysaccharide solution rheology over a broad range of concentrations

Wilco M.H. Verbeeten[1] and Gerrit W. Peters[2]

[1]Universidad Politécnica de Madrid, Madrid, Spain; [2]Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

The investigation deals with the modelling of the flow behaviour of aqueous random coil polysaccharide solutions using non-linear viscoelastic models. Up to date, most researchers and scientists use General Viscous Fluid models to describe the rheology of such biological macromolecular solutions, *e.g.* the Cross model. Although these types of models do an excellent job in modelling steady state simple shear viscosity, they are unable to describe the other three phenomena of viscoelasticity, *i.e.* time dependence, normal stresses in shear, and different behaviour in shear and elongation. Furthermore, these models are not able to describe satisfactorily the linear viscoelastic behaviour measured by dynamic oscillation experiments. Thus, when more complex flows have to be analyzed, *i.e.* flows where material elements experience various types of deformations in a transient sense rather than steady state, these General Viscous Fluid models do not suffice and more complex non-linear viscoelastic models are necessary.

A mastercurve can be constructed from experimental steady state shear data over a broad range of concentrations, from the dilute to the semi-dilute solution regime. Shift factors can be determined for the experimental data to transpose data and the linear relaxation spectrum to different concentrations, similar to the time-temperature-superposition.

The experimental linear viscoelastic and steady state shear data of various random coil polysaccharide solutions can be quantitatively predicted by the multimode Phan-Thien Tanner, Giesekus, and eXtended Pom-Pom non-linear viscoelastic models over a broad range of concentrations, from dilute to semi-dilute regimes, using a single set of parameters. Transient shear viscosity data is quantitatively and first normal stress coefficient is qualitatively predicted for a galactomannan guar solution.

Due to their proven performance in finite element simulations, these non-linear viscoelastic constitutive equations could help to improve predictive modelling of time-dependent complex flow problems for polysaccharide solutions. However, as a previous step, the performance of additional rheological experiments in simple flows, *i.e.* transient and steady-state extensional measurements, is recommended.

Tuesday 3:50 Redwood BR11

Viscoelastic properties of sodium hyaluronate solutions

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Sodium Hyaluronate (NaHA) is the sodium salt of hyaluronic acid which is a member of the glycosaminoglycans and is present in the human organism as part of the synovial fluid and the vitreous body. HA which is mainly commercialized as sodium or potassium salt is either extracted from cockscombs or nowadays more often produced by bacterial fermentation which guarantees a low protein content. Because of its natural origin and toxicological harmlessness, NaHA is used to a great extent for pharmaceutical and cosmetic products. In medical applications, NaHA is already being used as a component of flushing and stabilizing fluids in the treatment of eye cataract and as a surrogate for natural synovial fluid. Another growing domain in the commercial utilization of NaHA is the field of skin care products like dermal fillers or moisturizers. In this spectrum, NaHA is used in dilute over semi-dilute up to concentrated ($0 < c < 5$ wt %) and chemically crosslinked aqueous solutions. In order to optimize NaHA samples for their specific utilization and to find new applications, it is of great interest to understand its viscoelastic behavior. We therefore present in this contribution the results of a comprehensive investigation of the viscous and elastic material functions of different NaHA samples. This includes, besides shear flow and oscillatory experiments, the determination of the elongational flow behaviour, as well as the performance of rheo-optical measurements in order to determine the elastic component in the range of low shear rates and low concentrations. In addition, the data thus obtained from HA produced by bacterial fermentation or extracted from cockscomb will be compared with the viscoelastic material functions of normal and pathological synovial fluid of test persons with and without anthropathy.

Tuesday 4:10 Redwood 💿 BR12

Textural properties of agarose gels described by FT-rheology

Christopher O. Klein[1], Paul Venema[2], Leonard M. Sagis[2], and Erik van der Linden[2]

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Agarose is widely used in food systems as e.g. thickener, stabilizer. The use as a thickener has a desired influence on the rheology of food systems, like e.g. a change of the viscosity. Large Amplitude Oscillatory Shear was used to determine the non-linear rheological properties of such agarose gels. The focus of this analysis was on the mechanical behaviour in the non-linear regime, not including the fracture of the gels. The concentration was varied between 0.5% and 2.5% w/w. Special focus was laid on the texture of these gels. Texture and mouthfeel of food systems are of a special importance, because they strongly influence the perception of the food while eating. Both these processes can take place in the non-linear rheological regime. The group of Prof. Foegeding performed an analysis based on a second order polynomial to describe the rheological behaviour in the linear and non-linear regime of agarose gels. This analysis describes the stress as a function of the strain amplitude. In the linear term, the prefactor G describes the slope in the linear region of the stress-strain curve. The second order term contains a prefactor k that describes the change of slope of the stress-strain curve in the non-linear region. The non-linear rheological analysis performed in this work is based on the FT-rheology technique. In this method, the oscillatory stress-strain data is analysed by a Fourier transform. The non-linearity can then be described by the appearance of higher harmonics, in terms of their intensities and corresponding phases. Typically, the third harmonic is the strongest harmonic detected. As a simplification, the non-linearity can be described by the third harmonic alone. The adequacy of the third harmonic as a non-linear parameter for characterizing the rheological behaviour of agarose gels in the non-linear regime was tested, and the results are presented here. Keywords: FT-rheology, agarose, LAOS, non-linear regime, characteristic functions.

Tuesday 4:30 Redwood BR13

Strain-stiffening in networks formed by the self-assembly of biomolecules in organic solvents

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Strain-stiffening, i.e., an increase in material stiffness at large deformations, is a property of many self-assembled biopolymer networks. Currently, model systems for the study of this phenomenon are networks (gels) of semiflexible filamentous biopolymers such as actin, keratin, or fibrin. In this presentation, we will demonstrate that strain-stiffening is also a property of certain self-assembled networks formed in organic solvents. Specifically, we find strain-stiffening in mixtures of the biological surfactants, lecithin and bile salt, in a solvent such as cyclohexane. The self-assembled structures in these samples are reverse wormlike micelles, which are flexible cylindrical filaments. Moreover, the networks formed by these micelles are transient ones, and accordingly the samples behave as viscoelastic solutions, not as elastic gels. Thus, neither a permanent network nor a high filament rigidity are necessary requirements for strain-stiffening, in conflict with existing theories. It is also interesting and significant that a closely related class of reverse worms, formed by mixtures of lecithin and water in cyclohexane, does not show strain-stiffening. Taken together, the results imply that a different mechanism must exist for this unusual phenomenon, and we will discuss one such possible mechanism.

Tuesday 4:50 Redwood 💿 BR14

Vinculin contributes to cell invasion by regulating contractile activation

Claudia T. Mierke

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Vinculin is a component of the focal adhesion complex and is described as a mechano-coupling protein connecting the integrin receptor and the actin cytoskeleton. Vinculin knock-out cells (vin-/-) displayed increased migration on a 2-D collagen- or fibronectin-coated substrate compared to wildtype cells, but the role of vinculin in cell migration through a 3-D connective tissue is unknown. We determined the invasiveness of established tumor cell lines using a 3-D collagen invasion assay. Gene expression analysis of 4 invasive and 4 non-invasive tumor cell lines revealed that vinculin expression was significantly increased in invasive tumor cell lines. To analyze the mechanisms by which vinculin increased cell invasion in a 3-D gel, we studied mouse embryonic fibroblasts wildtype and vin-/- cells. Wildtype cells were 3-fold more invasive compared vin-/- cells. We hypothesized that the ability to generate sufficient traction forces is a prerequisite for tumor cell migration in a 3-D connective tissue matrix. Using traction microscopy, we found that wildtype exerted 3-fold higher tractions on fibronectin-coated polyacrylamide gels compared to vin-/- cells. These results show that vinculin controls two fundamental functions that lead to opposite effects on cell migration in a 2-D vs. a 3-D environment: On the one hand, vinculin stabilizes the focal adhesions (mechano-coupling function) and thereby reduces motility in 2-D. On the other hand, vinculin is also a potent activator of traction generation (mechano-regulating function) that is important for cell invasion in a 3-D environment.

MP-4. Extrusion

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: João M. Maia

Tuesday 2:30 Ferrante I-III 💿 MP22

On the study of the die swell of pure and filled linear polystyrene

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A rheo-optical study on both isothermal and non-isothermal die swell processes of pure and filled polystyrene (PS) melts is presented. The investigations, initially focussed on both nearly monodisperse ($M_W / M_N = 1.04$) and polydisperse ($M_W / M_N = 2.74$) linear polystyrenes, have been extended to filled systems comprising PS (matrix) and glass or highly cross-linked PS beads (fillers). Both the glass and PS beads had an average diameter of the order of 10 μm.

Die swelling experiments were carried out over a wide range of temperatures (~130-240°C) and shear rates (~0.1-200 s^{-1}), and the extrudate shapes were captured in real time using a video camera and a DVD recorder. Post processing of the video images was carried out using a specially written Labview code, enabling the various profiles to be determined with great accuracy.

The experimental results were compared with previously published theoretical models, which relate the die swell ratio ($\chi = d/D$, where d is the steady diameter of the extrudate and D is the tube diameter) to the first normal stress difference ($N1$). In order to obtain the time dependent compliance $J(t)$ (thus the linear viscoelastic properties) of the extruded polymer, in analogy to the stress creep recovery, a reinterpretation of the extrudate full profile measurements from the die exit is proposed.

In the case of filled systems, particular attention was paid to understanding the origins of the *cavitations*, which were observed to occur at a particular shear rate. Image analysis, performed on non-isothermal post-processed samples using both optical microscopy and scanning electron microscopy (SEM), suggests that the ratio $\omega_C / \dot{\gamma}_W$ (where ω_C is the low-frequency crossover between the elastic and viscous moduli, and $\dot{\gamma}_W$ is the wall shear rate) is the characteristic parameter determining the presence ($\omega_C / \dot{\gamma}_W < 1$) or the absence ($<\omega_C / \dot{\gamma}_W > 1$) of *cavitations*.

Tuesday 2:50 Ferrante I-III 💿 MP23

Correlations between high-density polyethylene viscoelasticity and annular extrudate swell

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Extrusion blow molding is an important polymer conversion process used to produce rigid packaging articles and other end user products. In 2008, approx. 21 billion lb high density polyethylene (HDPE) will be converted to finished products by the blow molding process. Control of the annular extrudate swell is an essential element of the blow molding process. Annular swell depends in a complex way on a combination of processing conditions (temperature, flow rate, die geometry) and polymer viscoelasticity. The effect of HDPE resin characteristics on extrudate swell is the subject of the work presented here. Extrudate swell of a large number of HDPE materials (in the order of 30), produced by gas phase and slurry processes was studied extensively on a newly developed lab-scale annular extrusion set-up. The goal of the study was to find universal relationships that express extrudate swell characteristics in terms of measured viscoelastic characteristics, independent of the synthesis process. For the rheological characterization of these resins, linear viscoelastic properties were determined via dynamic spectroscopy at various temperatures and creep and creep recovery, while non-linear viscoelastic properties were measured via uniaxial elongation tests. Advanced data analysis, supported by fundamental insights regarding the combined effect of viscosity and elasticity, was used to identify practical and relevant rheological parameters that relate to extrudate swell. It was found that diameter swell correlates well with recoverable compliance, whereas thickness swell correlates well with the ratio of storage to loss modulus (inverse tan delta). Compliance and tan delta are both measures for the elasticity of the material, but they have different weighting versus viscosity in the full viscoelastic parameter spectrum. The main effects of rheology on extrudate swell can be explained in terms of the variation in linear viscoelastic properties between the materials studied. The information derived from the non-linear data was found to be of secondary importance.

Tuesday 3:10 Ferrante I-III MP24

A new approach to non-Newtonian free-surface flows

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Two of the very few fluid flow situations in which the shear stress distribution is readily accessible are cylindrical pipe flow and planar or sheet flow, and many rheometric geometries have been developed from them. These two situations can be considered to form the extremes, with most real fluid flow applications lying somewhere between these two. Since intermediate flow situations have shear stress distributions which are not readily accessible, they are customarily simplified until either the pipe or sheet flow approach can be applied. Previous work on free surface flows has concentrated on the former – the so-called pipe flow paradigm. This approach was developed by assuming that the free surface flow is analogous with pipe flow, using the concept of an equivalent “diameter” derived from consideration of the cross-sectional flow area and the wetted perimeter. Whilst this approach has proved useful for Newtonian turbulent flows, it is less so for non-Newtonian laminar flows. Arguably, in these contexts, the pipe flow paradigm for free surface flow has been taken as far as it is useful. The objective of this paper is to develop the fundamentals of sheet flow into a form which can be translated into an appropriate laminar flow free surface flow model – the so-called sheet flow paradigm. This model has interesting industrial applications as diverse as mine tailings disposal and avalanche and debris flows. Previous work on the pipe flow paradigm is reviewed, and the limits of its usefulness are exposed. In particular, issues such as the inability to expose unexplained slope or hydraulic gradient effects are presented and discussed. A new approach to sheet flow is presented, and macro-flow parameters such as an expression for the bulk shear rate are developed from first principles, and related directly to the fluid rheology. This paradigm is then extended to a generalised laminar flow free surface flow model, incorporating the classical concept of the hydraulic radius. The usefulness of the new laminar sheet flow paradigm model is demonstrated using appropriate free surface experimental data, and is compared with pipe flow paradigm models.

Tuesday 3:30 Ferrante I-III MP25

On-line characterisation of small-scale polymer processing

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Extruders are a fundamental part of any extrusion and compounding line. Single-screw extruders are of general-purpose application, while intermeshing twin-screw machines have found special application niches, where their characteristics are used with greater advantage. Counter-rotating extruders are nowadays the standard choice for extruding PVC dry blends. The co-rotating solution is often used for compounding operations, mainly because of its good mixing capabilities, and the fact that characteristics like residence time or shear level can be controlled by exploring the geometrical flexibility of the equipment and the range of applicable processing conditions. These capabilities have led co-rotating extrusion to be the technique of choice in industrial applicability studies of novel systems, e.g., polymer/nanoclay and polymer/nanotube composites and reactive blends. However, due to either the small quantities of materials available or their high cost, it is often necessary! to have the capability to perform this work at small, laboratorial scales. The aim of this work is to meet the above goal with a novel small-scale modular single / twin-screw extrusion system, with well-controlled outputs in the range 100-500 g/h and the capability to perform material characterization on-line. This mini-extruder is equipped with ports that allow sample collection or non-intrusive analysis to be performed along its axis at desired locations. This system is coupled to a modular slit die that allows a wide range of rheometrical functions, e.g., shear viscosity and normal-stress differences, to be measured and rheo-optical experiments to be performed. Results are shown and the concept validated for a number of simple and complex systems, including different homopolymers and multi-phase systems (nanocomposites and reactive blends).

Tuesday 3:50 Ferrante I-III MP26

Using hollow microcapillaries to explore the extrusion rheology of polymer films

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It is possible to extrude a molten polymer film that contains a multitude of microcapillaries [1, 2]; this has been termed a microcapillary film or MCF. The presence of the microcapillaries can act as passive markers in the MCF [3] and be used to identify the nature of post extrusion processing deformation; for example from the form of the deformed capillary shape it is possible to identify regions of uniaxial or biaxial deformation. In this paper we report experimental results and some matching modeling to show how external deformation and rheology can influence the final hole size and shape of the capillary array within the MCF. This paper also explores ways in which voidage and hole size can be controlled by manipulation of both processing parameters and polymer rheology. Typical capillary diameters that can be achieved range from 800 µm – 5 µm with voidages ranging between 10 % and 70 %.

The melt rheology of the polymer was studied to provide rheological parameters that could be used both to gain an understanding of the character of the polymer and for modelling of the extrusion and drawing process. In particular, the temperature dependent nature of the rheology was investigated. Identifying the transition from viscous-dominated behaviour to elastic-dominated behaviour was important for the success of the hot drawing process by which capillary size reduction was achieved. X-ray diffraction (XRD) analysis of both drawn and undrawn low-voidage and high voidage MCFs was performed to get a qualitative measure of orientation in the final product.

Hallmark, B., M.R. Mackley, and F. Gadala-Maria, Hollow microcapillary arrays in thin plastic films. Advanced Engineering Materials, 2005. 7(6): p. 545-547; Hallmark, B., F. Gadala-Maria, and M.R. Mackley, The melt processing of polymer microcapillary film (MCF). Journal of Non-Newtonian Fluid Mechanics, 2005. 128(2-3): p. 83-98; Hallmark, B., Polym. Eng. Sci., In press, 2007.

Tuesday 4:10 Ferrante I-III MP27

Rheology at the interface and the role of the interphase in reactive functionalized multilayer polymers in coextrusion process

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Coextrusion technologies are commonly used to produce multilayered composite sheets or films with a large range of applications. The contrast of rheological properties between layers can lead to interfacial instabilities during flow. Few investigations in the literature have been dedicated to their physicochemical affinity at the interface. The present study deals with the influence of this affinity on interfacial instabilities for functionalized polymers. Multilayered structures, with varying viscosity and elasticity ratios, of polyamide (PA6) and either polyethylene functionalized (PE-GMA) or pure PE were studied. It was experimentally confirmed, in this case, that the interphase of non-zero thickness (corresponding to an interdiffusion/reaction zone) should be taking into account instead of a purely geometrical interface. As a first step, the rheological behavior of the multilayered cast films was investigated in order to probe (i) the competition between the interdiffusion/interfacial reaction and (ii) the influence of various parameters related with the process. The contribution interphase effect was also studied along with the increase in the number of layers. In order to quantify the contribution of the effect of the interphase triggered between the neighboring layers, an expression was developed to take it into account and to quantify its thickness. As a second step, an experimental strategy to optimize the process was formulated by listing the different parameters in control of the stability of the reactive multilayer flows. Coextrusion of bi-, tri- and fivelayered structures was carried out. The reaction rate /compatibilization plays a major role that must be taken into account. Furthermore, it is necessary to obtain links between the classic factors that are introduced in the evaluation of the theoretical stability charts and the obtained experimental ones. Hence, based on this analysis, guide-lines for stable coextrusion of reactive polymers were provided.

Tuesday 4:30 Ferrante I-III MP28

Effect of polymer processing aids (PPA) on the elimination of sharkskin defect in LLDPE extrusion: Influence of die surfacing

Claire Dubrocq-Baritaud[1], Nicolas Devaux[2], Evelyne Darque-Ceretti[1], and Bruno Vergnes[1]
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Surface defects (sharkskin) are the most limiting defects in linear polyolefin extrusion since they appear at low production rates. Since more than twenty years, polymer processing aids (PPA) have been commonly used to suppress sharkskin in extrusion. Fluoropolymer PPA act by covering the die walls, inducing wall slip, and simultaneously eliminating sharkskin defect and reducing die pressure. However, the mechanisms of coating and wall slip that control PPA performances are not still totally understood. The aim of this work is to study the influence of die surfacing on PPA efficiency and kinetics. For this purpose, we used a modular slit die that allows to measure die pressure and velocity profiles, and to characterize die coating. A linear low-density polyethylene (LLDPE) was selected for its wide range of shear rate with sharkskin. The tested fluoropolymer KynarFlex® (Arkema) is a thermoplastic copolymer of vinylidene fluoride and hexafluoropropylene. Extrusions of 250 ppm PPA were carried out on a laboratory extruder in line with a die with transparent side walls and removable steel inserts. Several die surfaces, prepared by resurfacing and/or diamond polishing, have been tested. LLDPE extrusions with PPA reveal that PPA efficiency strongly depends on die roughness and roughness topology. Sharkskin elimination and die pressure drop are quicker at increasing die roughness, but final pressure levels are similar when resurfacing is parallel to the flow direction. Deposits of fluoropolymer, observed by Scanning Electronic Microscopy (SEM) coupled with Elementary Dispersive X-ray analysis (EDX), also show similar morphology in equilibrium flow conditions reached with PPA: lines of 3-4 µm thick, parallel to the flow direction, recover the entire die surface. The observation of coating at different times reveals that the die surface is first covered by small elongated clusters of 300 to 800 µm long that grows up to 1 mm long. Then coating becomes continuous along the die with interconnected lines of fluoropolymer that induce wall slip and die pressure drop. Finally, in the new steady state, the density of coating appears stabilized with renewable deposits. When roughness due to die resurfacing is perpendicular to flow direction, it leads to a quicker sharkskin elimination and die pressure drop. Besides, die pressure at the new steady state is significantly lowered. In parallel, SEM observations show a very different PPA coating: it is composed by lines of fluoropolymer parallel and perpendicular to the flow direction, showing a denser and interconnected deposit. At the beginning of coating, elongated clusters are more numerous than in the previous case; they appear hanged at surface asperities. Then the interconnected square-shaped coating grows and leads to a sharp pressure drop. As a consequence, the comparison of the influence of different die surfaces on PPA action seems indicate that the fluoropolymer coating is mainly induced by mechanical links with die surface rather than chemical bonds.

Tuesday 4:50 Ferrante I-III MP29

Impact of elasticity on lubrication: Esters of PEG, silanol and their blends as polymer processing additives

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Polyolefins represent roughly 60 percent of all the thermoplastic polymers produced and sold in the world. The present revolution in polyolefins production is the development of metallocene catalysts. The polyolefins with narrow molecular weight distribution made by use of metallocene catalysts are tougher, stronger and cleaner than plastics made with conventional catalysts. Meanwhile they cannot be processed by extrusion without Polymer Processing Additives (PPAs). PPAs are lubricants to reduce extrusion pressure and eliminate extrusion defects, gel-streaking and pinstriping. Nature uses elastic gels as lubricants in joints of bones, and demonstrates excellent results in lowering of sliding friction. Human technologies differ very much from natural ones. Due to the historic development of technology, fluorinated polymers dominate the use of external lubricants and PPAs for polyolefins. The PPAs made from fluorinated polymers are inherently costly, but the main problem in the using fluorinated polymers is that they are not friendly to the environment. Taking from Nature the idea of elastic lubricants, we developed novel PPAs that do not contain fluorine. These lubricants are made from Polyethylene glycols (PEGs) and PEG-silanols blends cured by borates. The novel PPAs show better lubrication efficiency in comparison with conventional (fluorinated) PPAs and a very short conditioning time to suppress sharkskin flow instability. They are hydrophilic opposite to hydrophobic fluorinated PPAs. Other polyols, their derivatives and blends can be also used in the PPA composition. With the use of silanols cured by borates mechanical properties of the lubricant were changed by small variations of composition to investigate the impact of elasticity on lubrication and suppression of sharkskin. Both lubrication and efficiency to suppress sharkskin were considerably improved when more elastic lubricants were used while the chemical composition of the lubricants was nearly the same.

MP-5. Nanocomposites

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: Christopher Macosko

Tuesday 2:30 Colton I-III MP31

Simultaneous determination of electrical and rheological properties of polypropylene filled with carbon nanotubes

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Composites of isotactic polypropylene (iPP) and carbon nanotubes (CNT) of different concentrations were prepared via an in-situ polymerization using metallocene catalysts. Rheological properties and the electrical conductivity were measured simultaneously as a function of particle concentration and preparation conditions. The influence of various modifications of the CNT prior to the in-situ polymerization of the matrix of these quantities was studied.

A significant effect on the dynamic-mechanical behaviour was found even far below the concentration of the electrical percolation threshold. In addition, the influence of the CNT on the recoverable compliance was measured by creep recovery experi-ments. Particularly, for small shear stresses the increase of the recoverable compliance by the carbon nanotubes was very significant.

The calculation of retardation spectra revealed a shift of the retardation times to higher values and, furthermore, an increase of the retardation strength for long retardation times. This finding is explained by an interaction between filler and matrix, slowing down the mobility of those matrix molecules being in contact with the CNT, as a particle network can be neglected due to electrical measurements.

Tuesday 2:50 Colton I-III MP32

Rheological behavior of carbon nanofiber-reinforced polypropylene and polystyrene

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Carbon nanofibers (CNFs) represent a viable solution to the preparation of polymer nanocomposites with improved mechanical, thermal and electrical properties. The characteristic nanoscopic dimension together with a relatively low cost and the easy incorporation into polymers make CNFs an obvious candidate for the production of high performance light materials. The present study analyzes the rheological behavior developed by carbon nanofibers dispersed in two different polymer matrices. Polypropylene/CNF and polystyrene/CNF nanocomposites have been prepared by melt blending in a small scale internal mixer. Shear and elongational rheological behavior have been investigated in the linear and non linear regime. CNF composites based on both polymer matrices show the presence of a yield stress above a critical percolation threshold. Such a behavior, which is a signature of the formation of a network structure, is due to interconnections among nanofibers. The critical percolation threshold is extremely low, due to the high aspect ratio of the CNFs. The elongational viscosity of polystyrene/CNF nanocomposites has been found to be significantly affected by the amount of CNFs. More precisely, the dispersed phase decreases the strain hardening index of the polymer matrix.

Tuesday 3:10 Colton I-III MP33

Impact of rheology on meltblown polymer nanofibers

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Melt blowing, a commercialized polymer processing technique, is used to produce a majority of nonwoven fiber products. It utilizes a stream of hot air to attenuate an extruded polymer strand into a fiber that is typically larger than 1 υm in diameter. Recently, our group has demonstrated the capability of melt blowing various polymers into defect-free fibers with an average diameter of several hundred nanometers by using a lab-scale melt blowing device designed after a typical commercial instrument[1]. However, surface tension-driven instabilities are observed when the smallest fibers are generated, resulting in droplets dispersed in the fiber mat. It has been suggested[1,2] that altering rheological properties of the polymer can either delay or suppress these instabilities. A systematic study comprised of melt blowing bidisperse polymeric blends with different rheological properties, obtained by mixing a low and a high molecular weight polymer, will be highlighted to show the effect of rheology on average fiber diameter and its width of distribution.

[1] Ellison, C.J. et al. Polymer 2007, 48, 3306-3316; [2] Yu, J. H. et al. Polymer 2006, 47, 4789-97.

Tuesday 3:30 Colton I-III MP34

Effect of processing conditions on rheological and electrical properties of epoxy/MWCNT dispersions

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Ultra low electrical percolation in polymer/carbon nanotube dispersions can be achieved at particle loadings as low as 0.0025wt% by manipulating processing conditions such as shear, temperature and the state of aggregation of the carbon nanotubes. We report rheological, electrical properties and associated optical microstructure observations of multiwall carbon nanotubes (MWCNTs) suspended in an epoxy resin matrix using an optical shear cell. Above a critical concentration (Vc), network formation of aggregates of MWCNTs was observed. Above Vc, both electrical conductivity and viscosity increase rapidly. The rheological and electrical properties of epoxy/MWCNTs dispersions were governed by aggregation and de-aggregation of MWCNTs under shear. High shear results in de-aggregation of MWCNTs resulting in shear thinning and low electrical conductivity. Low shear results in shear induced aggregation of MWCNTs and high viscosity and high electrical conductivity. In the second part of this work we studied effect of concentration of MWCNTs on scaling of elastic shear modulus. The effect of different lengths of MWCNTs on the scaling behavior of the elastic shear modulus was also studied. The influence of individual MWCNT bending within an aggregate of MWCNTs on the elastic shear modulus will also be discussed. Finally, we carry out small angle neutron scattering (SANS) studies to better understand the aggregate structure of the MWCNTs and to establish a quantitative relationship between MWCNT microstructure and the corresponding rheological and electrical properties.

Tuesday 3:50 Colton I-III MP35

Processing of chlorosulfonic acid-SWNT solutions into neat SWNT fibers

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The remarkable intrinsic properties of single-walled nanotubes (SWNTs) make them an attractive macromolecular building block for a wide variety of applications. Their electrical and mechanical properties make them ideal for strong, ultra-light, multifunctional materials as well as high performance electromechanical actuators and sensors. A critical obstacle in the processing of SWNTs into macroscopic articles has been their poor dispersion in common solvents. It has been shown that super acids can disperse SWNTs by protonating SWNT side-walls and counteracting the strong attractive van der Waals interactions. In particular, chlorosulfonic acid has shown an extraordinary ability to disperse SWNTs and to form an aligned liquid-crystalline microstructure at high SWNT concentrations. This microstructure directly affects the alignment and properties of the macroscopic articles we can produce. Here we describe a process for coagulation spinning neat SWNT fibers from chlorosulfonic acid-SWNT dopes. We study the effects of SWNT concentration, coagulant, and process conditions on the morphology and properties of the final fibers.

Tuesday 4:10 Colton I-III MP36

New approach of ultrasonic blend process on PP/PC and its nanocomposites

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In previous research, it was possible to induce chain scission of the PP in a molten state by high intensity ultrasonic wave. Also, with the aid of a multifunctional agent (MFA) and ultrasound, a long-chain branched PP and its nanocomposites can be created without any decomposing agent. And recent paper is introduced a ultrasonic method by imposing ultrasound and MFA to modify linear PC into branched grade. From these results, It was expected that we may be able to provide a blend information associated with the development of ultrasonic process on structural modification. The MFA used in this study includes three arms and a double bond exists at the end of each arm. So, the three double bonds in chain ends of MFA were expected to act as sites for trapping macroradiclas of polymer during ultrasound-assisted blend process. When macroradicals of ultrasonic blend react with the end group of MFA, formation of branched structure can be prepared and enhanced chain combination of polymer blend during sonication. Another purpose of dosing high-intensity ultrasonic waves can be to enhance nano-scale dispersion during compounding of polymer and clay. The sonication during processing led to enhanced breakup of the clay agglomerates and reduction in size of the dispersed phase.

Tuesday 4:30 Colton I-III MP37

Epoxy/montmorillonite nanocomposite systems: Effect of the dispersion method and the clay modification on the rheological parameters of the curing process

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Nanocomposites based on polymers and inorganic layered clays have been the subject of increased interest in the scientific and industrial community because of their potential and promising properties. The dispersion of clay inside the epoxy matrix is very important to improve the impact resistance, thermal resistance and high deflection temperature of the matrix. The objective of this work is to present results regarding the effect of the clay dispersion procedure and also the curing agent influence on the rheological parameters of the curing process of the epoxy matrix. The epoxy-clay nanocomposites were prepared by the dispersion of organically modified layered clays in epoxy resin (diglycidyl ether of bisphenol A). The clays used in this work were Cloisite 20A and Cloisite 30B. Different methods of dispersion were employed, such as intensive mixing, sonication and mechanical mixing. In addition, two different curing systems, based on methyl tetrahydro acid anhydride and triethylene tetramine were employed. The first system was cured at high temperature (120°C) and the second system was cured at room temperature followed by a post-curing process at 120°C. The nanometer-scale dispersion of layered clay within the crosslinked epoxy resin matrix was confirmed by X-ray diffraction (WAXS) and small angle X-ray scattering (SAXS). The sonication procedure or intensive mixing was important in order to achieve an exfoliated clay inside the matrix. In addition, the curing with anhydride was more effective on the exfoliation process because it can promote an intergallery polymerization. On the other hand, the amine-based curing system, with a lower curing time, promoted an extragallery curing process. In both curing system, the presence of clay resulted in an acceleration of the curing process because of the presence of alkyl ammonium ions located in the galleries of the modified clays which participate in the curing reaction. Dynamic time sweep experiments were carried out with all the systems used herein and it could be observed that the clay amount and the clay dispersion method were very important to the cure and the rheological properties of the epoxy resin.

The authors would like to thank the financial support of the following Brazilian Agencies: CNPq, FINEP and FAPERJ.

SC-4. Jamming and Shear Thickening

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Matthias Fuchs and Jan Mewis

Tuesday 2:30 De Anza III SC22

The microstructure of shear thickening, near hard-sphere, colloidal suspensions

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Concentrated suspensions exhibit many complicated rheological behaviors, including shear thinning, shear thickening, thixotropy and yielding. These behaviors have their origin in shear-induced microstructural changes. Shear thickening is of interest in industry as it can pose a problem in coating processes and can even damage process flow equipment. More recently, shear thickening fluids have been used in composites with protective fabrics such as Kevlar® and Nylon to improve their response to ballistic and stab threats (Lee et al., J. Mat. Sci. 2003). Shear thickening in concentrated colloidal dispersions is known to result from the dominance of short-range lubrication hydrodynamics driving density fluctuations in the flowing suspension known as hydroclusters. The hydrodynamic forcing of these fluctuations has been validated by stress-jump and rheo-optical measurements, whereas rheo-optics and flow-SANS measurement have demonstrated the coexistence of such density fluctuations with rheological shear thickening. These lead to micromechanical theories that can predict the onset of shear thickening, however little is known about the structure of the shear thickening fluid. In this work we employ a new flow- Small Angle Neutron Scattering (SANS) instrument (Liberatore et al. PRE 2006) to directly measurement the flowing microstructure in the shear plane (1-2 plane) in the shear thinning and shear thickening regimes. Using model, near hard-spheres colloidal dispersions suitable for SANS probing, we employ this technique in addition to flow-SANS and flow-USANS to fully resolve the internal structure of flowing hydroclusters as well as their extent for direct comparison to simulation and theory. Using micromechanical theories (Maranzano and Wagner, JCP, 2003), the resultant stresses are calculated directly from these microstructural measurements and compared to rheological measurements. This provides direct evidence linking the shear-induced hydrocluster structure to the measured rheological properties. These microstructural measurements enable probing the entire stress tensor, including testing predictions for negative normal stress differences in the hydroclustered state. These measurements provide a complete elucidation of the microstructure of a flowing near- hard-sphere colloidal suspension through the shear thinning and shear thickening regimes and provide critical tests of micromechanical theories for dense suspension rheology.

Tuesday 2:50 De Anza III SC23

Connecting structure and rheology in sheared colloidal suspensions

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We investigate the shear properties of colloidal suspensions confined between parallel plates. When the distance between the plates is very small, i.e. approaching the size of the colloidal particles, a number of dramatic phase behaviors are observed, including buckling, shear banding, jamming, and crystallization. Since standard bulk rheometric techniques cannot detect these microstructural phenomena, little is known about their macroscopic consequences. Our experiment explores connections between microscopic structure and macroscopic flow by combining confocal microscopy and force measurement techniques in a custom-built shear cell. In this talk, we present results on shear-thickening phenomena observed in confined suspensions.

Tuesday 3:10 De Anza III SC24

Stress chains formation under shear of concentrated suspension

Didier Lootens[1], Nicos S. Martys[2], William George[2], Steve Satterfield[2], and Pascal Hébraud[3]
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Numerical simulation of highly concentrated suspension of spherical particles subject to a constant rate of strain is presented in this paper. Giant fluctuations of the shear stress and the first and second normal force difference is studied as a function of the shear rate. Simulations are compared with recent experiments made with a model system of mono-disperse silica-particles. The effect of the hydrodynamic lubrication forces between particles is studied with both simulation and experiments by modification of the particle surface roughness and manipulation of interparticle interactions. The shear rate dependence on flow anisotropy is studied. At low shear rates, the suspension exerts an attractive force between two opposite surfaces, whereas at higher shear rates it becomes dilatant. Finally, stress chain formation and evolution under shear are visualized in order to make the relation between the stress fluctuations and the suspension microstructure.

Tuesday 3:30 De Anza III SC25

Dynamics of transient vorticity-aligned structures and internal stresses in shear thickening colloidal gels

Chinedum O. Osuji[1] and David A. Weitz[2]
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Dilute dispersions of fractal colloidal particles in non-polar hydrocarbon solvents flocculate and form gels with typical scaling of elasticity with particle volume fraction. Surprisingly, these attractive systems display shear thickening in two distinct regimes. At low shear rates, shear thickening is concurrent with the formation of stable vorticity-aligned structures, a somewhat general phenomenon observed in other soft materials under flow, but not previously associated with shear thickening. At high Peclet numbers, shear thickening involves the breakdown of dense particle clusters into smaller aggregates. This is in contrast to hard-sphere systems where shear thickening is most often attributable to a pseudo-jamming transition that occurs with the growth of hydro-clusters under flow. Pre-shear within the high shear rate shear thickening regime leads to enhanced modulus gels where the storage modulus scales as a power law with the pre-shear stress. Shear-rate quenches from shear thickening flows into the quiescent state result in rapid gelation accompanied by slowly decaying internal stresses. Rate-controlled flow as well as strain controlled dynamic deformation of these shear-thickened, mechanically quenched gels is highlighted by the transient formation of highly anisotropic vorticity aligned structures and the relaxation of residual internal stresses. We report on the dynamics of the formation and eventual dissolution of these structures as a characteristic length scale and orientation rapidly emerge and then gradually recede with time and accumulated strain. We propose a mechanism to account for the observed behavior.

Tuesday 3:50 De Anza III SC26

Extreme velocity fluctuations: Transient jamming in concentrated suspension flow

Sandeep D. Kulkarni[1], Bloen Metzger[2], and Jeffrey F. Morris[1]
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A study is reported of the flow of a concentrated suspension of non-Brownian spherical particles driven by a steady imposed pressure drop through a channel constriction at low Reynolds number. The flow channel width in the constriction is 1/3 that of the original channel. The ratio of particle diameter to the constriction width, ε, is varied, with typical values of $\varepsilon = 0.05$. The suspension flows smoothly for $\phi < \phi_c$. For a narrow window around $\phi = \phi_c = 0.58$, the flow becomes intermittent, alternating between fast and slow motion with a typical ratio of average speeds 20 : 1. Surprisingly, this conversion from a liquid suspension into a thickened and `solid-like' system exhibits a well-defined periodicity. A systematic experimental study of the length and time scales relevant to characterize this `transient' jamming behavior and to determine the role of imposed driving pressure level and ε will be reported.

Tuesday 4:10 De Anza III SC27

Transient study on the shear thickening behaviour of surface modified fumed silica suspensions in polypropylene glycol

Francisco José Galindo-Rosales[1] and Francisco José Rubio-Hernández[2]
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The shear thickening behaviour of concentrated dispersions has been a major topic of interest for rheologists over the last two decades. Initially, the interest was derived mainly from its association with damage to processing equipment and dramatic changes in suspensions microstructure, e.g., particle aggregation, which is known to compromise a range of properties. Nevertheless, nowadays the highly nonlinear behaviour of shear thickening fluids (STFs) is being exploiting in the design of damping services, and more recently in the context of body armour, due to their ability of absorbing huge amounts of energy when impacted with high velocity projectiles. The term shear-thickening is typically used to refer to a non-Newtonian flow behaviour observed in which there is an increase in apparent viscosity when the applied shear rate is increased. Originally, shear thickening in colloidal suspensions was suggested to be a consequence of an order-to-disorder transition (ODT), but various subsequent studies have suggested an alternative explanation based on "hydrodynamic clustering". These clusters are composed of compact groups of particles formed as shear forces drive them to contact. A range of parameters control this behaviour, among the most important being particle size distribution, particle content, particle shape, particle-particle interactions, and the viscosity of the suspending phase. The accumulative effect of these factors determines the extent its characteristics. Although there is a substantial volume of literature in the field of STFs, most of works are related to understanding the phenomena and its dependence with those parameters previously mentioned. As it is a flow behaviour that appears as consequence of a self-organizing microstructure, it seems to be logical that it may exhibit time dependence under constant shear rate conditions. Characterizing properly this dependence with time may be very relevant, particularly in the context of applications as body armouring. In this work, we explore the time dependent behaviour of Aerosil®R816 suspensions in polypropylene glycol with different molecular weights. On that purpose, hysteresis loops and step-wise experiments are carried out inside the reversible shear thickening region. By means of the former, although the time dependence cannot be separated from shear rate, it can be observed rates of breakdown and rebuild of the "hydrodynamic clustering"; stepwise experiments let us analyse time response of these samples. It has been noticed that the lower the molecular weight of the polymer the quicker is the response of the sample, although it is weaker. The most relevant result is that these systems present the same "instantaneous" response when they are suddenly undergone to a certain value of shear rate, independently of the onset conditions. All rheological experiments have been carried out in a RheoStress 600 (Haake). The volume fraction and temperature have been kept unaltered, 5% v/v and 25.0±0.1ºC, respectively.

Tuesday 4:30 De Anza III SC28

Measurements of flow elasticity during shear thickening

Ryan J. Larsen[1], Jin-Woong Kim[2], Charles F. Zukoski[1], and David A. Weitz[3]
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One of the most striking of rheological phenomena is the ability of some liquid suspensions to become solid-like under stress. This property, known as discontinuous shear thickening or shear jamming is useful for various technologies including body armor, protective sports padding, and machinery damping. Effective engineering of shear-jammed materials requires methods for characterizing their solid-like mechanical properties. It is natural to characterize a solid-like material in terms of an elastic stiffness. We therefore propose a new technique for measuring the non-linear elastic stiffness of discontinuous shear thickening suspensions, while they are flowing. Our technique relies on observing the shear rate fluctuations that occur when these suspensions are sheared in a stress-controlled rheometer. During these fluctuations, energy is exchanged between the inertial energy of the rheometer bearing and the strain energy of the sample. We show that the resulting sample stress fluctuations possess a characteristic frequency. We propose that this characteristic frequency, together with the bearing inertia, can be used to estimate a typical flow stiffness of a shear-jammed suspension that is independent of the inertia of the bearing. The flow stiffness is an increasing function of the solids content of the shear-jamming suspension. This technique provides insights into the elastic mechanisms associated with shear thickening.

Tuesday 4:50 De Anza III SC29

Implementing the split-Hopkinson pressure bar technique for shear thickening fluid evaluation

Amanda S. Lim, Sergey L. Lopatnikov, and John W. Gillespie Jr.
Center for Composite Materials, University of Delaware, Newark, DE 19716, USA

The split-Hopkinson pressure bar experimental technique has been implemented to evaluate the high rate squeeze flow behavior of viscous fluids. In order to apply the classic Kolsky data reduction method, it is necessary to first ensure that the fluid specimen achieves equilibrium during loading. The timescales for the dynamic processes (formation of Poiseuille flow profile and pressure relaxation) are determined using a conservation law approach. Based on these findings, a criterion for specimen design has been developed and used to evaluate non-Newtonian materials. Recently, fabrics infused with discontinuous shear thickening fluids (STFs) have been recognized for their augmented protective capabilities over neat fabrics. STF-fabric composites have been shown to quantitatively outperform neat fabrics under spike, stab and low velocity projectile threats. This enhanced impact resistance is accredited to the addition of the STF, which thickens rapidly above a critical shear rate. The high rate mechanical response of this STF is the focus of this study. The SHPB experimental technique provides a means of evaluating the transient behavior of these materials. Through this research, it is possible to determine the time required for the fluid-solid transition to occur as well as the post-transition mechanical properties of these materials.

Tuesday 5:10 De Anza III SC30

Controlling suspension rheology with novel oligomeric dispersants

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Suspensions of strongly interacting or anisotropic particles can give challenging – and fascinating – rheology when formulated at high concentration. Rheological behaviour that is fun to measure in the lab may not be welcome in a manufacturing environment. The industrial scientist faces the challenge of keeping manufacturing engineers happy by designing formulations of concentrated suspensions that meet the requirements of the manufacturing processes (i.e. the challenge of acting as a rheological "killjoy"). However, the initial recipes arriving in the lab do exhibit fascinating rheological properties, such as jamming or shear thickening and there is satisfaction to be gained from keeping these phenomena away from the engineers. In our laboratory, we have characterized and then "tamed" the challenging behaviour exhibited by suspensions of cationic boehmite (Catapal 200) or anionic fumed silica in order to increase flowability (remove elasticity, reduce viscosity and eliminate dependence on storage and shear history) while increasing concentration. Addition of commercially available dispersants – small molecules and polymers – did not give sufficiently well behaved rheology. Our solution was to design and make oligomeric functional anchor buoy dispersants, and these did the trick. The dispersants are a combination of a simple, inexpensive oligomeric buoy that is soluble in the continuous liquid phase (typically 25-30 acrylamide units for water). The anchor group is specific to the surface of interest: acidic, basic or hydrophobic for cationic, anionic or hydrophobic surfaces, respectively. This presentation will describe some of the rheological challenges posed by the suspensions and the effects of the dispersants on rheology control. Further development of the dispersant chemistry to introduce environmentally specific rheological behaviour may also be described.

GR-4. General Rheology

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: A. Jeffrey Giacomin

Tuesday 2:30 Bonzai III GR22

Rheology of carbon fibre reinforced cement-based mortar

Phil F. Banfill, Gerry Starrs, and John McCarter
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Carbon fibre reinforced cement based materials (CFRM) are of interest because of their electrical conductivity which offers the possibility of fabricating "smart" conductive overlays, finishes or components. However, the ability to mould and form the material is vital and the rheology of the fresh mix is key to this. While some work has reported the effect of fibres on the workability of reinforced cement and concrete, using empirical or subjective assessment, no one has studied the rheology. This paper summarises recent results obtained with the Viskomat NT, a small and convenient mixer type apparatus. Calibration of the instrument with model liquids permits determination of the rheological parameters in fundamental units. The results show that CFRM conforms to the Bingham model with slight, but not significant, structural breakdown. Both yield stress and plastic viscosity increase with increasing fibre length and volume concentration. However, the percolation threshold for CFRM is about 0.5% volume concentration of fibres: only above this concentration is the electrical conductivity sufficiently reduced by the presence of the fibres to render the materials "smart". The instrument in its original form is unable to handle the stiff mixes at this concentration and the effect of a series of mechanical modifications is discussed. The results enable definition of the concentration dependence of CFRM rheology up to 1% fibre volume.

Tuesday 2:50 Bonzai III GR23

Transient droplet behavior and droplet breakup during bulk and confined shear flow in blends with one viscoelastic component: Experiments, modeling and simulations

Ruth Cardinaels[1], Kristof Verhulst[1], Yuriko Renardy[2], and Paula Moldenaers[1]
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In this work, we present the results of a microscopic study on transient droplet deformation and orientation after inception of shear, shape relaxation after cessation of shear and droplet breakup during shear, both under bulk and confined conditions. The studied blends contain one viscoelastic Boger fluid phase. A counter-rotating setup, based on a Paar Physica MCR300, is used for the droplet visualisation. For bulk shear flow, it is shown that the droplet deformation during startup of shear flow and the shape relaxation after cessation of shear flow are hardly influenced by droplet viscoelasticity, even at moderate to high capillary and Deborah numbers. Only close to the critical conditions, the effects of droplet viscoelasticity become visible and a novel break-up mechanism is observed. Matrix viscoelasticity has a more pronounced effect, causing overshoots in the deformation and significantly inhibiting relaxation. However, different applied capillary numbers prior to cessation of flow, with the Deborah number fixed, still result in a single master curve for the shape retraction, similar to fully Newtonian systems. The long tail in the droplet relaxation can be qualitatively described with a phenomenological model for droplet deformation, when using a 5-mode Giesekus model for the fluid rheology. Confining a droplet between two plates accelerates the droplet deformation kinetics, similar to fully Newtonian systems. However, the increased droplet deformation, due to wall effects, causes the steady state to be reached at a later instant in time. Droplet relaxation is less sensitive to confinement, leading to slower relaxation kinetics only for highly confined droplets. For the blend with a viscoelastic droplet, a non-monotonous trend is found for the critical Ca-number and the maximum stable deformation as a function of the confinement ratio. Finally, experimental data under bulk and confined conditions are compared with 3D simulations, performed with a volume-of-fluid algorithm.

Tuesday 3:10 Bonzai III GR24

Effects of particle hardness on shear thickening colloidal suspension rheology

Dennis P. Kalman, Brian A. Rosen, and Norman J. Wagner
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Concentrated suspensions undergo many types of complicated flow behavior, including shear thinning, shear thickening, and yielding. Shear thickening is of interest in industry as it can pose a problem in coating processes and can even damage process flow equipment. More recently, shear thickening fluids have been used in composites with protective fabrics such as Kevlar® and Nylon to improve their response to ballistic and stab threats. Our goal is to develop a predictive understanding of how varied particle properties effect the onset, severity, and ultimate limit of shear thickening, which should be controlled only by the hydrodynamics of the system according to the hydrocluster theory. Literature reports of a second shear thinning regime after shear thickening in dense colloidal dispersions are examined from the viewpoint of the material properties of the particle phase. We hypothesize that the particle modulus can limit the extent of shear thickening, and that the second shear thinning regime is a manifestation of particle softness. We test this theory against a number of particle systems in literature of varied particle hardness. In addition, model poly(methyl methacrylate) (PMMA) colloidal dispersions are synthesized and purified. Stable suspensions are shown to exhibit strong shear thinning and thickening, followed by a second shear thinning regime. Using roughened plates, we determine that the second shear thinning regime is not an artifact of slip, or adhesive failure with the rheometer tooling. A simple extension of elastohydrodynamic theory captures the essential behavior born by the experiments. To further demonstrate how particle properties limit the extent of shear thickening, "soft" and hard shear thickening fluids (STF) are fabricated into composites with ballistic materials. Testing of these composites in quasistatic puncture and ballistic testing indicates shows a correlation between the limiting suspension rheology and STF-composite performance. These results demonstrate the important role of particle hardness in dense colloidal suspension rheology and applications employing STFs. The effect of particle shape on dense suspension rheology and shear thickening is studied by measurements on model dispersions of at disc-like clay suspensions and cube-like zeolite suspensions. Particle shape is shown to affect shear thinning and shear thickening differently, such that dense suspension rheology can be controlled also via particle shape for specific applications.

Tuesday 3:30 Bonzai III GR25

Primary normal stress difference in concentrated, colloidal suspensions

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Shear thickening in concentrated suspensions is known to occur as a consequence of lubrication hydrodynamic forces driving the formation of density fluctuations in the flowing suspensions, denoted as "hydroclusters". Micromechanical theory, simulations, rheo-optical, flow-small angle neutron scattering (SANS) and rheological measurements have all demonstrated various aspects of these hydroclusters and their rheological consequences. One interesting prediction, that has only recently been explored experimentally, is that the primary normal stress difference in a concentrated suspension can become negative as a consequence of the hydrocluster formation. Concentrated suspensions are one of the few systems known to display a negative normal stress and are unique in that the source of this negative primary normal stress difference is hydrodynamic. We provide a systematic study of the primary normal stress difference in concentrated suspensions at various volume fractions, particle sizes, and particle shapes. Novel 1-2 plane flow-SANS experiments (Liberatore et al. PRE 2006) are performed on model suspensions to provide the internal structure of the hydroclusters, along with flow-USANS measurements of the extent of hydrocluster formation. These structural measurements coupled to micromechanical theories provide a micromechanical understanding of the source of these negative primary normal stress differences in shear thickening colloidal suspensions.

Tuesday 3:50 Bonzai III GR26

Shear and extensional rheometry of PDMS tamponade agents used in vitroretinal surgery

Michael Day[1], Rowan-Louise Blanchard[2], Robert J. English[2], Tom Dobbie[3], Rachel L. Williams[1], Michael Garvey[1], and David Wong[4]
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The emulsification of low molar mass silicone oil (PDMS)-based tamponade agents used in the treatment of complex retinal detachments is a significant clinical problem leading to the patient suffering impairment of vision whilst the tamponade is in place. This is particularly the case in temporal postoperative applications where the tamponade can remain in the ocular cavity for several months. The majority of clinicians prefer to use a PDMS fluid of kinematic viscosity 1000cS, which offers ease of manual injection. Work is progressing towards the development of tamponades with a reduced tendency to emulsify, through specific tailoring of rheology and interfacial properties. Greater knowledge of the mechanism of intraocular emulsification is being elucidated and has lead to the development of 'polymer modified' tamponades with enhanced performance. Such materials are formulated by the addition of a high molecular weight PDMS to the base PDMS oil. Measurement of the shear viscosity at moderate shear rates is useful in predicting performance during manual injection into the eye. However, the determination of the behaviour in both shear and extension at high strain rates is useful in predicting resistance to intraocular emulsification and in informing future modelling studies. Initial experiments focussed on rotational rheometry (shear) and capillary breakup rheometry (CaBER - extension). A range of polymer modified tamponades were characterised - based on PDMS base oils from 500-5000 cS and containing up to 30% by weight PDMS of molecular weight varying in the range 100000-800000 Da. Even though the volume occupancy of the polymeric additive ranged from dilute to significantly interpenetrated, a linear response was observed in each case. However, subsequent experiments using capillary rheometry lead to the observation of non-linear behaviour and significant differences between the formulations. In contrast to the base oils, the polymer modified formulations showed significant tension thinning. Systems with lower high strain rate tensile viscosities gave improved performance in invitro emulsification tests and are now the subject of clinical trials. The thermodynamic interaction between the polymeric additive and the PDMS oil 'solvent' was also considered. Interestingly, the PDMS base oils appeared to behave as relatively 'good' solvents, the chains of the polymeric additives being considerably expanded from their unperturbed dimensions.

Tuesday 4:10 Bonzai III GR27

Dynamics in confining nanoparticle dispersions

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The physical and chemical properties of nanoparticles are often very different from those of the bulk materials, displaying some unique properties that depend on their size, shape, surface functional groups, and so forth. Such nanoparticles are of great current interest; hence the interest also in their rheological and tribological properties. We have investigated rheological and tribological properties of nanospheres, nanorods and nanowires. We found that dynamics of nanoparticles is strongly dependent on the followings: (i) Nanoparticle geometry; (ii) Nanoparticle stiffness: surfactant-coated nanoparticles have a hard interior and a soft exterior, which provides them with a rigid shape but mobile, fluid-like surface; and (iii) Nanoparticle interactions: They have no or little adhesion to the surfaces or to each other. This provides them with good lubrication properties.

Tuesday 4:30 Bonzai III GR28

Flow instability of colloidal dispersions flowing through a very small orifice

Shinji Toga[1], Tomiichi Hasegawa[2], and Takatsune Narumi[2]
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Flow fluctuation through a very small orifice has been measured for dilute aqueous colloids including fine particles about 100nm in diameter. Their orifice flow is affected by the interparticle interaction, although they exhibit a Newtonian viscosity in shear flow. The flow character is divided into three classes depending on the feature of the interaction.

In the experiment, fine Polystyrene particles dispersed in water with 1% volume fraction are investigated utilized a orifice of 100 micrometer in diameter. A flow through holes such as orifice, nozzle and filter is composed of strong elongational property as well as shear property. Therefore, these flows are often used to estimate the extensional character of various fluids. Meanwhile, in dilute aqueous colloid, interaction forces among the dispersed particles are an electro-static repulsion and a van der Waals attraction. In order to clarify the influence of these forces on the flow, it is necessary to control these balance. In this experiment, the electrostatic repulsion was adjusted by the amount of the contaminant ions in the solvent. The decreasing of the contaminant ions enhances the electro-static repulsion and the addition of the ions inhibits it.

First, in the case of the colloidal particles having very strong electrostatic repulsion, the colloid applied pressures maintains the flow through the orifice for a few seconds or minutes but finally it stops the flow. Further we found the colloid having iridescence around the orifice. It is seems to the orifice flow generates colloid crystal and it stops up the orifice. Next, in case of adding ion in small amount, the colloid having relatively strong repulsive interaction continues flowing but it shows notable flow instability. On the contrary, the high ion concentrations inhibit the repulsion and enhance the attraction respectively. In this case, the flow instability shown in low ion concentrations disappear.

Border ion concentration whether the flow is stable or not is predicted by the comparison of the Second Minimum Location of the surface interaction potential between two particles and the mean surfaces distance of the particles.

CF-5. Shear Banding II

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Suzanne Fielding

Tuesday 2:30 Steinbeck 💿 CF28

Shear-banding: When can we ignore diffusion?

Helen J. Wilson
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It is well-known that the addition of a small amount of diffusion of some material property (stress, rate of strain, structure factor, etc.) can regularise a constitutive equation which permits shear-banding. Typically, in the absence of diffusion, these models are ill-posed and permit steady banded states of a sort not observed in experiment, with many sharp-edged, closely-spaced bands.

In Wilson & Fielding (JNNFM 138, 181-196, 2006) we looked at the two-dimensional linear stability properties of banded planar shear flow for two possible diffusive modifications to the Johnson-Segalman model. We were able to show that, for perturbations whose wavelength is not as short as the diffusion lengthscale, the diffusive stability calculation is a regular perturbation to the equivalent calculation for a non-diffusive fluid with a material interface between shear-bands.

In this paper we extend this result to more general models and geometries, essentially showing that, for the purposes of the linear stability properties, the effects of weak diffusion can be neglected and the stability or otherwise of the banding interface can be assessed using the simpler diffusionless model. The extensive literature on co-extrusion instabilities is therefore relevant to the mechanisms for breakdown and fluctuation of banded systems.

Tuesday 2:50 Steinbeck CF29

Banded and complex flow of model transient networks

Joris Sprakel, Evan Spruijt, Jasper van der Gucht, and Martien A. Cohen Stuart
Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen, The Netherlands

The non-linear rheology of transient networks formed by telechelic associative polymers has received much attention in literature over the past 15 years and it has been speculated that the corresponding flow curves show signatures of inhomogeneous flow. We will present the first direct experimental evidence of the shear banding transition in these networks of spherical micelles connected by polymer bridges. The banded flow starts with the formation of 2 bands of different shear rate. With increasing shear rate the fast band itself becomes unstable, and a 3-band structure develops. Chaotic transient stress responses and velocimetry experiments suggest that the banded structure is not stationary and shows large spatiotemporal fluctuations. At higher shear rates the flow becomes macroscopically unstable due to high normal stress differences, leading to a Weissenberg effect causing the liquid to escape from the Couette gap. We will qualitatively explain the occurrence of shear banding with a simple microscopic model for the constitutive equation specific for these systems, that will be complemented with Brownian Dynamics simulations to be carried out in the near future. Our results suggest that these systems are interesting alternatives from wormlike micelles for studying complex flow in complex fluids

Tuesday 3:10 Steinbeck 💿 CF30

Shear banding of repulsive particulate suspensions in rotating Couette flow

Kyung H. Ahn, Sunjin Song, and Seung J. Lee
School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea

Shear banding of repulsive particulate suspensions in rotating Couette flow has been studied by self-consistent particle simulation. The hydrodynamic interaction was considered in this algorithm by recursively solving the microscopic particle dynamics and macroscopic flow simulation. The flow field and the particle motion were coupled and solved self-consistently. The tangential velocity profiles were non-homogeneous and the shear banding was clearly observed. The band formation was affected by shear rate as well as volume fraction. An optimum shear rate region was found where the shear banding was most pronounced. The banding was found to evolve with stress growth, and the final form of shear banding was dependent upon the degree of stress relaxation. The mechanism of the band formation was explained in terms of the fundamental forces acting on the particle system. Contrary to previous understanding, the formation of shear banding was found to arise by hydrodynamic interaction rather than by particle configurational change or yielding. The occurrence of shear banding seems inevitable for dense suspensions in rotating Couette flow. Once it occurs, the shear band evolves with time.

Tuesday 3:30 Steinbeck CF31

Shear zones in the capillary flow of concentrated colloidal suspensions

Lucio Isa, Rut Besseling, and Wilson C. Poon
School of Physics, The University of Edinburgh, Edinburgh EH9 3JZ, UK

We image the flow of dense hard-sphere colloidal suspensions in a square capillary using fast confocal microscopy. For glassy samples (volume fraction > 0.58) the flow consists of a "plug" in the center while shear occurs localized adjacent to the channel walls, reminiscent of yield-stress fluid behavior. However, the observed scaling of the velocity profiles with the flow rate strongly contrasts yield-stress fluid predictions. Instead, the velocity profiles can be captured by a theory of stress fluctuations originally developed for chute flow of dry granular media. We verified this both for smooth and rough walls. Data for different channel sizes are also presented showing a linear scaling of the width of the shear zones with channel size at variance with what observed for dry grains.

Tuesday 3:50 Steinbeck CF32

Spatially-resolved microstructure in shear banding wormlike micellar solutions

Matthew E. Helgeson, Matthew Reichert, Norman J. Wagner, and Eric W. Kaler
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Recently proposed mechanisms of shear banding in worm-like micellar solutions (WLMs) involve coupling of shear-induced micellar alignment and banding to an underlying, equilibrium isotropic-nematic phase transition. Critical tests of such theories require *spatially-resolved* measurements of flow kinematics as well as the local mesoscale microstructure within the shear bands. We have recently developed such capabilities using a short gap Couette cell for flow-small angle neutron scattering (flow-SANS) measurements in the 1-2 plane of shear [Liberatore et al., Phys. Rev. E, 2006] with collaborators at the NIST Center for Neutron Research. This work combines such measurements with rheology, rheo-optics and velocimetry measurements to present the first complete spatially-resolved study of WLMs through the shear banding transition for a solution of cetyltrimethylammonium bromide (CTAB) close to the isotropic-nematic phase boundary. The shear rheology is well-modeled by the Giesekus constitutive equation, where the anisotropy parameter determined purely from the shear rheology can be used to predict the ability shear band. Incorporating stress diffusion into the model enables prediction of velocity profiles in the shear banded state in agreement with measured flow kinematics. The model is further tested by comparison to segmental alignment and orientation measured by flow-SANS in the 1-2 plane. In comparison across a number of systems, we observe a critical alignment for the onset of shear banding that is significantly lower than expected for an isotropic-nematic transition. Thus, the combination of flow velocimetry and 1-2 plane flow-SANS measurements of the fluid microstructure provide a critical test of mechanism-based theories for shear banding in such systems. Finally, methods for controlling and eliminating shear banding using these concepts by modification of the micellar network are demonstrated, including changes in composition as well as nanoparticle addition.

Tuesday 4:10 Steinbeck CF33

Flow analysis for wormlike micellar solutions in an axisymmetric capillary channel

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Flows of wormlike micellar solutions in an axisymmetric capillary channel were studied both numerically and experimentally. In the experiments, an aqueous solution of cetyltrimethylammonium bromide (CTAB) with sodium salicylate (NaSal) was used as a test fluid. The mol concentration of CTAB is 0.03 mol/l and that of NaSal is 0.06 mol/l. The velocity distribution was measured with a particle tracking velocimetry (PTV) and flow visualization experiments were performed. The velocity profile showed a plug-like shape and had inflection points where the velocity gradient rapidly changed. High shear rate regions near the channel walls spread with increasing the average velocity. Moreover, the flow turned to be unstable at high average velocities and when the flow was unstable, white turbidity was observed near the walls. Shear rates showing a white turbidity were included in the range of shear rate where a shear-rate-jump in a flow curve occurred. These results suggest that both the characteristic velocity profile and the emergence of white turbidity relate the shear-rate-jump property of wormlike micellar solution. In the numerical analysis, startup flows were considered. A modified Bautista-Manero (MBM) model was employed as a constitutive equation, and startup flows at a constant average velocity (U) or at a constant average pressure gradient (-Λ) were numerically simulated. The values of model parameter were decided considering both dynamic viscoelasticity and a flow curve measured with a cone-plate type rheometer. The velocity profile at steady state predicted by the numerical simulation adequately agreed with corresponding experimental data. In the constant-U case, the velocity profile changes from Newton-like to plug-like with time. The inflection points in velocity profile appeared and moved towards the center-side with time. Temporal changes in both velocity gradient and fluidity indicated that the behavior in velocity depended on the shear-rate-jump property of wormlike micellar solution. The velocity gradient rapidly changed around the point, and the range of velocity gradient corresponds to that where a white turbidity was observed in the experiments. In the constant-Λ case, the distribution of shear stress is unchanged with time, which is similar to a flow in a stress-controlled type rheometer. The flow rate temporally increased to reach a steady state value. The position of the inflection point slightly moved with time, while the change rate in velocity gradient increased remarkably. Contrary to the constant-U case, the region of high shear rate and fluidity did not spread with time and their profiles temporally changed within this region. The results in the present study showed the availability and effectivity of the application of this constitutive model to macroscopic analyses of complex flows of wormlike micellar solutions.

Tuesday 4:30 Steinbeck CF34

Ageing, yielding and shear banding in soft colloidal glasses

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Suspensions of multiarm star polymers are studied as models for soft colloidal interactions in colloidal glasses. Using an established pre-shearing protocol which ensures a reproducible initial state (the ``rejuvenation" of the system), we report here the stress evolution from startup for two different concentrations for a range of shear rates. We show the existence of critical shear rates which are functions of the concentration. When the suspensions are sheared at rates below the critical rates, the stress rises to a common value which is also a function of the concentra-

tion. The system thus evolves a yield stress. This behavior manifests itself as an evolution from a monotonic, slightly shear-thinning flow curve to a flow curve dominated by a stress plateau. We relate this bulk evolution to spatially and temporally resolved velocity profiles which clearly show an evolution to a strongly shear-banded state.

Tuesday 4:50 Steinbeck CF35

Spatial-temporal correlations at the onset of flow in concentrated suspensions

Nicos S. Martys[1], Didier Lootens[2], William George[3], Steve Satterfield[4], and Pascal Hébraud[5]
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The rheology of dense colloidal suspensions composed of attractive spherical particles under static and shear conditions is studied using numerical simulation. Under static conditions the evolution of particle organization with time is followed as equilibrium is approached. The time dependence of the radial distribution and organization of nearest neighbors is tracked as equilibrium is approached and then as a constant shear rate is applied. The dependence of nearest neighbor count and shear rate is shown. Also illustrated in the angular orientation of nearest neighbors. The dependence of rheological properties on equilibration times is described. The evolution of the complex modulus as a function of time is evaluated using the mean squared displacements.

Tuesday 5:10 Steinbeck CF36

Timescales and instabilities of shear thinning solutions of wormlike micelles

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Shear thinning solutions of surfactant wormlike micelles are multi-scale systems with complex rheology. Transient kinetics of semidilute solutions is studied using a simple rheo-optical device with cylindrical Couette geometry. During a start-up of flow experiment, we observe the nucleation of the induced structures followed by the organization of the flow into two bands. The building of this banding structure begins with the formation of a diffuse interface that rapidly migrates towards the inner wall and sharpens (typical time scale: 5s). When its profile is sharp, the interface continues to move slowly up to its stationary position in the gap (typical time scale: 20s). This process is followed by the growth of an interface instability with wave vector along the cylinder axis that saturates on time scale of the order of 40 – 50s. We reproduce this behaviour using a non-monotone constitutive model including diffusion terms to cope with the strong gradients in the region of the sharp interface. The second timescale, corresponding to the displacement of the sharp interface to its equilibrium position, is used to estimate the interface width and the stress diffusion coefficient. Finally, in order to identify the origin of the longest time scale we study the growth of the interface instability in the model.

MF-4. Microfluidics: Droplets

Organizers: Todd M. Squires and Annie Colin
Session Chairs: Shelley Anna and Paula Moldenaers

Tuesday 2:30 Portola MF22

Impact of viscosity ratio on the dynamics of droplet breakup in a microfluidic flow focusing device

Shelley L. Anna[1], Lynn M. Walker[2], and Wingki Lee[2]
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Microfluidic techniques have emerged as promising routes to fabrication of monodisperse emulsions, and the droplets formed in this way can be used as carriers and reactors for diverse applications ranging from nanoparticle synthesis to polymerase chain reaction. In some of these applications it is desired to use droplets that are in the nanometer size range, but most microfluidic techniques are limited to the production of droplets that are close to the size of the device itself. We have recently shown that a tipstreaming-like phenomenon occurs in microfluidic flow focusing experiments when dissolved surfactants are present in one of the liquid phases. In this mode of droplet breakup a strong elongational flow in the contraction region couples with strong surfactant concentration gradients along the interface, leading to the formation of submicron droplets that are orders of magnitude smaller than the flow focusing orifice. The process is observed to be periodic, in which streams of tiny droplets alternate with the formation of a large (50 micron diameter) droplet at a frequency on the order of hundreds of cycles per second. In this talk, we report our observations of the dynamics of this process, including measurements of the relevant timescales for the formation of a cone-like interface, the drawing and disintegration of a fine thread, and the period with which the process repeats. We relate these timescales to dimensionless flow parameters such as the capillary number and the flow rate ratio, as well as the characteristic timescales for transport of surfactants to and along the interface. In addition, we describe a simplified model for the process that we have developed based on an observed symmetric corner flow in the inner liquid during the formation of the thread. This model leads to predicted boundaries for when tipstreaming can occur, as well as scaling arguments for the ultimate droplet size. We compare the results from the simplified model with a large number of experiments varying the fluid properties, the surfactant properties, and the device geometry, and through these observations we suggest ways to extend the tipstreaming portion of the process to enhance the overall yield of submicron droplets.

Tuesday 2:50 Portola MF23

Double emulsions in a microfluidic system

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A double emulsion is a dispersion of two liquids in a third one. Medicine, printing, textile, food and cosmetic industries already use double emulsions which permit the control of the delivery of a substance. It has been pointed out [1] microfluidics is a very promising technology to produce controlled double emulsions. We are here interested in equilibrium and non-equilibrium morphologies of double emulsions in a microfluidic system.

The equilibrium sate corresponds to a minimum of the interfacial surface energy and three distinct equilibrium morphologies are possible according to the spreading coefficients : $S_i=g_{jk}-g_{ij}-g_{ik}$ where g_{ij} are the interfacial tensions between i and j fluids. With the convention $S_1<0$, the possible morphologies are complete engulfing ($S_2>0$, $S_3>0$), partial engulfing or "janus" ($S_2<0$, $S_3<0$), non-engulfing ($S_2>0$, $S_3<0$) [2].

Our experiments were realized in a device in PDMS using soft lithography technique. The channels have a cross section of about 100µmx100µm with a double flow focusing geometry : A/B emulsion is formed at a first junction and downstream a second junction gives rise to a A/B/C double emulsion. The liquids we used are alkanes, different oils and water with and without surfactants. Equilibrium morphology is observed in the reservoir without flow. Morphologies are deduced from interfacial measurements realized after the fluids have been in contact in order to reach equilibrium. Comparison between theory and experiment is done for more than thirty triplets of fluids. A good agreement is obtained, in particular when S_2 and S_3 spreading coefficients are important compared to the uncertainty. But we notice a deviation with the observation of some janus whereas encapsulations are expected with $0< S_3 <5$ mN/m. As a whole the equilibrium theory is then convenient to predict the morphologies of double droplets produced in a microsystem.

If we now focus on the morphologies in the channel, between the formation and the reservoir we observe non-equilibrium morphologies, where hydrodynamic shear forces are significant. Complete engulfing is observed even if the equilibrium state is partial engulfing or non-engulfing and we can measure the displacement of the internal droplet into the drop. We study the life time of the non-equilibrium morphologies considering effects of the velocity field into the drop on the transport of the internal droplet. These observations permit to consider production of new objects thanks to microfluidic technology.

[1] Nie et al., J Am Chem Soc, 127, 8058-8063 (2005); [2] Torza and Mason, J Colloid Interf Sci, 33(1), 67-83 (1970)

Tuesday 3:10 Portola MF24

Liquid crystal droplet production in a microfluidic device

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Liquid crystal drops dispersed in a continuous phase of silicone oil are generated with a narrow distribution in droplet size in microfluidic devices both above and below the nematic to isotropic transition temperature. Our experiments show that the surface properties of the channels can be critical for forming droplets. We observe different dynamics in liquid crystal droplet generation, coalescence, and distinct droplet morphology by altering the microchannel surface energy. This is explained by the thermodynamic description of the wetting dynamics of the system. The effect of the nematic-to-isotropic transition on the formation of liquid crystal droplets is also observed and related to the capillary number. We also investigate how the nematic droplet size varies with the flow rate ratio and compare this behavior with a Newtonian reference system. The effect of the defect structures of the nematic liquid crystal can lead to distinctly different scaling of droplet size in comparison to the Newtonian system. When the nematic liquid crystal phase is stretched into a thin filament before entering the orifice, different defect structures and number of defect lines can introduce scatter in the drop size. Capillary instabilities in thin nematic liquid crystal filament has additional contribution from anisotropic effects such as surface gradients of bending stress which can provide extra instability modes compared to that of isotropic fluids.

Tuesday 3:30 Portola MF25

Effects of surfactant and flow on drop dynamics

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Deformation and internal circulation of aqueous drops (with or without surfactant) in clear mineral oil are measured in pressure-driven two-phase microchannel flow, using particle tracers and drop shape analysis. Drop deformation dynamics, interfacial mobility and interfacial tension during Poiseuille flow and transient elongational flow are analyzed. Using a homologous series of surfactants, the effects of surfactant solubility and concentration are explored, as well as the effect of interface age. Flow kinematics are adjusted by microchannel geometry and relative drop size.

Tuesday 3:50 Portola MF26

Flow of oil-water emulsion through constricted capillary tubes

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The flow of oil-in-water emulsions through a constricted capillary tube was analyzed by experiments and theory. The experiments consisted of flow visualization and pressure drop measurements of the flow. Quartz capillary tubes with dimensions similar to a pore-throat in high permeability porous media were used to represent the pore neck-pore body geometry. The pressure drop between the inlet and outlet of the capillary was recorded as a function of time, for several values of the volumetric flow rate. A number of different emulsions, stabilized by a surfactant (Triton-100), were prepared using synthetic oils and deionized water. Two oils of different viscosity were use, while two distinct drop size distributions were obtained by varying the mixing procedure. The average oil drop size varied from smaller to larger than the neck radius. Emulsions exhibited shear-thinning behavior in the range of shear rates used in the experiments. The results show that at low capillary number, i.e. $Ca < 0.1$, the viscosity of the emulsion does not determine the pressure drop-flow rate relation when the mean drop size was larger than the constriction. Instead, we resorted to pore-blocking mechanisms to explain the observed pressure response. Fluid mobility, defined as flow rate over pressure drop, was used to quantify the magnitude of the pore-blocking caused by drops larger than the constriction radius. The effect of the interfacial tension and viscosity ratio between the two phases on the changes of the local mobility was determined by solving the flow of an infinite oil drop immersed in water flowing through a constricted capillary tube. The flow field and interface configuration were obtained solving the Navier-Stokes equation together with elliptic mesh generation, with appropriate boundary conditions, by the Galerkin / Finite Element Method. The resulting set of non-linear algebraic equations for the finite element basis functions' coefficients at each time step was solved by Newton's method.

Tuesday 4:10 Portola MF27

Coalescence of partially miscible polymer blends in a confined flow

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The influence of a confinement on the steady state morphology of two different emulsions was investigated. The blends are made of Polybutene (PB, Indopol H-25, BP Chemicals, UK; M_n=635) in polydimethylsiloxane (PDMS, UCT; M_n=62700), and Polybutadiene (PBD,Ricon 134, Sartomer; M_n=8000) in PDMS. The viscosity ratios (viscosity of drop over matrix) are 1.2 for the PBD/PDMS system, and 0.3 for the PB/PDMS system. The interfacial tension measurements at room temperature, at which the coalescence experiments are carried out, show that the PBD/PDMS system is slightly diffusive, while the PB/PDMS system is highly diffusive. However, given the long time of shearing needed to achieve a steady-state morphology in the final confined flow, we refer to the steady interfacial tension values, which are 4.2 mN/m and 2.2 mN/m, respectively. The samples were sheared between two parallel plates, mostly with a standard gap spacing of 40 μm, in the range of shear rates at which the transition from "bulk" behavior towards “confined” behavior was observed. For both cases, the influence of the concentration was systematically investigated, as well as the shear rate effects on the final steady state morphology. By decreasing the shear rate, for each blend, it was found that droplets arrange themselves into two layers. When the degree of confinement reached a critical value, a single layer of droplets was formed. The ratio between the drop diameters and the gap spacing at which this transition occurred was always lower than 0.5. While decreasing the shear rate, the degree of confinement increases due to drop coalescence. Droplets arranged themselves in superstructures like ordered pearl necklaces and, at even lower shear rates, strings. The aspect ratio and the width of the droplet obtained from optical micrographs acquired during shear, were compared to the prediction of the Maffettone-Minale model. It was found that the theory, derived for unconfined shear flow, is not able to fully predict the drop deformation in confined geometries. The partially mobile interface model succeeded to predict the average drop size except for the cases in which the diameter of the droplets was limited by the degree of confinement. Hence, the mean steady-state droplet radii are still governed by the relations that describe the structure development in non-confined situations.

Tuesday 4:30 Portola MF28

Pairing and collective dynamics of particles and deformable drops in parallel-wall channels

Pieter Janssen[1], Matthew D. Baron[2], Patrick D. Anderson[1], Jerzy Blawzdziewicz[2], Michael Loewenberg[3], and Eligiusz Wajnryb[4]
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Fluids used in microfluidic applications often consist of multiple phases, i.e. polymer blends, blood and biological mixtures. One application is the generation of a regular array by the use of T-junctions and flow-focusing devices. In this work, we focus on the pairing and collective dynamics of these trains, and in particular on the influence of the deformability of the dispersed phase, by comparing trains of solid particles and trains of drops. Numerical methods employed are boundary integrals for drops and Stokesian-dynamics techniques for solid particles. We show that isolated pairs of drops undergo pairing, while isolated pairs of rigid spheres do not cluster. By contrast, confined linear arrays of particles and drops always undergo pairing regardless of deformability. Depending on the deformability and the initial separation between the drops, the initial dynamics of the pairing behavior can be quite complex. At prolonged time scales, all drop pairs reach the same velocity, while particle pairs migrate at a different velocity due to different intra-particle distances. In addition, the response of linear arrays to particle displacements shows a qualitative dependence on deformability. For example, drops are self-centering between the bounding walls and therefore linear arrays of drops are more stable to displacements normal to the walls. Complex collective behavior is also observed for linear arrays with particle and drop displacements parallel to the walls.

Tuesday 4:50 Portola MF29

Steady state droplet deformation and orientation during bulk and confined shear flow in blends with one viscoelastic component: Experiments, modeling and simulations

Kristof Verhulst[1], Ruth Cardinaels[1], Yuriko Renardy[2], and Paula Moldenaers[1]
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Immiscible blends are encountered in a variety of applications, such as foods, paints, cosmetics and plastics. Up to moderate concentrations, the blend morphology typically consists of a droplet-matrix structure. While the behavior of simple Newtonian-Newtonian emulsions is rather well understood, for blends containing viscoelastic components a complete picture is still lacking. In addition, there is a trend towards miniaturization of industrial processes, leading to microfluidic setups in which the dimensions become comparable to the droplet size. In this work, we present a microscopic study of the steady deformation and orientation of droplets in shear flow, both under bulk and confined conditions. Blends with one viscoelastic phase, either a Boger fluid with a constant viscosity or a shear thinning viscoelastic fluid, are studied at a viscosity ratio of 1.5. The experiments are performed with a Linkam shearing cell and a counter-rotating setup, based on a Paar Physica MCR300. For bulk shear flow, it is shown that matrix viscoelasticity suppresses the droplet deformation and promotes its orientation towards the flow direction. Interestingly, these effects saturate at De-numbers above 2. For ellipsoidal droplets, viscoelasticity of the droplet fluid hardly affects the droplet deformation and orientation, even up to Deborah numbers as high as 16. Similar to fully Newtonian systems, confining a droplet between two plates increases the droplet deformation and its orientation towards the flow direction. The effect of component viscoelasticity under confined conditions remains qualitatively the same as under bulk conditions, up to the highest accessible confinement ratio 2R/H of 0.6. The experiments under bulk conditions are compared to the predictions of phenomenological models, such as the Maffettone-Minale model, for droplet deformation. The Shapira-Haber model, which analytically describes the effects of the walls on the droplet deformation for fully Newtonian systems, is used to describe the experimental results under confinement. Here, this model is combined with bulk phenomenological models that include component viscoelasticity. Under the present conditions, the adapted Shapira-Haber model describes the steady droplet deformation under confinement rather well. Finally, experimental data under bulk and confined conditions are compared with 3D simulations, performed with a volume-of-fluid algorithm.

Tuesday 5:10 Portola MF30

Hydrodynamic resistance of single confined drops in microchannels

Siva A. Vanapalli, Arun G. Banpurkar, Dirk van den Ende, Florent Malloggi, Michael H. Duits, and Frieder Mugele
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Transport of drops in fluidic networks underlies many lab-on-chip technologies involving biochemical analysis, protein crystallization, novel material synthesis and fluid logic devices. A crucial parameter influencing the transport behavior of drops is their hydrodynamic resistance. Here, we report a novel microfluidic comparator design that allows in situ, sensitive and dynamic measurement of hydrodynamic resistance of soft confined objects. We integrate this comparator into a microfluidic T-junction device and measure the hydrodynamic resistance of single non-interacting aqueous confined drops. Our experiments show that the resistance of bare drops decreases with increase in capillary number ($10^{-4} – 10^{-2}$). Moreover the resistance of these bare drops is found to be a weak function of the drop size (slug length). We will also discuss the role of channel geometry and surfactants on the hydrodynamic resistance of drops.

CF-6. Viscoelastic Turbulence

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Michael Graham

Tuesday 2:30 San Carlos I CF37

Near-transition dynamics of viscoelastic turbulence and drag reduction in plane Poiseuille flow

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Nonlinear traveling wave solutions have been found for the Navier-Stokes equations in all canonical parallel flow geometries. These solutions capture the main dynamical features of turbulent flows, especially for near-wall coherent flow structures. Our previous study of the effects of polymer additives on one class of these so-called exact coherent states (ECS) suggests that turbulent drag reduction can be better understood through these traveling waves. Many key aspects of experimental observations can be related with the existence and evolution of ECS solutions in viscoelastic flows. Guided by these results, we conduct direct numerical simulations (DNS) in a minimal flow unit that captures the smallest self-sustaining structure in turbulence. The simulations are performed in a parameter regime close to the laminar-turbulent transition, where our earlier results predict that the laminar-turbulent transition, the onset of drag reduction and the maximum drag reduction (MDR) regime are close to each other in Reynolds number. The connection between these DNS results and traveling waves will be described, and the dynamical structures outside of the existence boundary of ECS will also be investigated, the latter of which could be a good starting point of understanding the nature of MDR.

Tuesday 2:50 San Carlos I 💿 CF38

Inertio-elastic stability modifications with drag reducing polymeric solutions

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The cascade of transitions separating laminar and turbulent flow in the Taylor Couette geometry was examined with drag reducing polymer solutions in the regime where the magnitude of the elastic forces approaches that of the inertial forces, i.e. where the elasticity number (El) nears unity. The elasticity number, defined as the ratio of a polymeric time scale to the viscous time scale, greatly impacts the stability boundaries on isolated secondary flow features in both the co- and counter-rotating Taylor Couette flow regime. It was previously shown that for dilute poly(ethylene oxide) solutions with El << 1, that the elasticity effect was non-monotonic, mode-dependent, and more significant for higher order states. In this study, Re_{inner} vs Re_{outer} stability planes generated at El ~ 1 in concentric, independently rotating cylinders of radius ratio 0.912 and aspect ratio of 60.7 are compared to previous maps generated in the inertia-dominated regime (El ~ 0). As a result, the importance of elasticity with solutions of similar diluteness is illuminated for various flow transitions, including transitions to axisymmetric, wavy, spiraling and/or turbulent modes. Changes in stability during adiabatic increases of the inner cylinder Reynolds number were determined using flow visualization and spectral analysis. All flow states are characterized by symmetry/symmetry breaking features as well as azimuthal and axial wave numbers using a combination of flow visualization in 2D planes of radial, axial, projected azimuthal and time dimensions. Polymeric solution characterization includes dynamic, steady and extensional shears, light scattering, and sessile drop experiments, and addresses such issues as chain scission, aggregation, and temperature dependence.

Tuesday 3:10 San Carlos I 💿 CF39

Dynamic K-L analysis of the coherent structures in turbulent viscoelastic channel flows

Gaurab Samanta[1], Antony N. Beris[1], Robert A. Handler[2], and Kostas Housiadas[3]
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The turbulent dynamics corresponding to long-time Direct Numerical Simulation (DNS) data of viscoelastic turbulent channel flows is analyzed here through a projection of the velocity fields into a set of Karhunen-Loeve (K-L) modes, large enough to contain, on the average, more than 90% of the fluctuating turbulence energy. Previous(*) static K-L analyses have demonstrated a dramatic decrease in the K-L dimensionality (and, correspondingly, the number of modes carrying most of the turbulent energy) as viscoelasticity increases in turbulent channel flows; this is also consistent to the increasing importance of large coherent structures for viscoelastic turbulent flows, as was also revealed in previous flow visualizations of DNS data.

Here we use the K-L modes dynamically in viscoelastic turbulence to better understand the role of coherent structures and viscoelasticity. In particular, we calculate the viscoelastic conformation field developed in response to the velocity field reconstructed from selected KL representations and compare the results against the full DNS predictions. The significance of these results in building low dimensional models for viscoelastic turbulence is also going to be addressed.

*Handler RA, Housiadas KD, Beris AN, Karhunen-Loeve representations of turbulent channel flows using the method of snapshots, Int. J. Num. Meth. Fluids 52 (12): 1339-1360 (2006).

Tuesday 3:30 San Carlos I CF40

Hairpin vortex dynamics and polymer-induced turbulent drag reduction

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It has been known for over six decades that the dissolution of minute amounts of high molecular weight polymers in wall-bounded turbulent flows results in a dramatic reduction in turbulent skin friction by up to 70%. Further it has been established for a decade that first principles simulations of turbulent flow of model polymer solutions can predict the drag reduction (DR) phenomenon. However, the essential dynamical interactions between the coherent structures present in turbulent flows and polymer conformation field that lead to DR are not well-understood. We examine this connection via dynamical simulations that track the evolution of hairpin vortices, i.e., counter-rotating pairs of quasi-streamwise vortices whose nonlinear auto-generation and growth, decay and break up are centrally important to turbulence stress production. Specifically, in the dynamical simulations, an initial vortical structure, isolated from direct numerical simulations using a linear stochastic estimation technique [1], is evolved in the viscoelastic flow where the polymer stress is modeled by the FENE-P model. We find that the threshold of initial vortex strength for the auto-generation of new hairpins increases as the viscoelasticity increases, especially in the buffer layer. As found in the fully turbulent DR flows, the counter polymer torque reduces the vortex strength by opposing the vortical motions, which results in the suppression of the auto-generation of new vortices and vortex packet formation in DR flows. This leads to a decrease in the coherent as well as incoherent Reynolds stress and ultimately reduces the turbulent drag. The effect of polymer relaxation time and chain extensibility on hairpin dynamics will be discussed in detail.

1. K. Kim, C.F. Li, R. Sureshkumar, S. Balachandar and R. Adrian, Effects of polymer stresses on eddy structures in drag-reduced turbulent channel flow, J. Fluid Mech. 584, 281-299 (2007)

Tuesday 3:50 San Carlos I CF41

A priori DNS development of closure for the nonlinear term of the evolution equation of the conformation tensor for FENE-P fluids

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The DNS predictions of viscoelastic turbulent flows of fluids represented by the Finitely-Extensible-Nonlinear-Elastic constitutive equation with Peterlin's approximation (FENE-P) of Housiadas et al. (2005) and Li et al. (2006a, 2006b), amongst others, give insight on the physics of drag reduction by polymer additives and provide useful data for developing adequate turbulence models.

In the context of single point closures the Reynolds- average evolution equation for the conformation tensor (C_{ij}) contains a new nonlinear term that requires adequate closure to allow the calculation of the average polymer stress contribution to the turbulent momentum balance. This term, henceforth designated by NLT_{ij}, is the cross-correlation between the fluctuating conformation and velocity gradient tensors arising in the distortion term of Oldroyd's upper convective derivative. Additionally, using a priori analysis of DNS data, Pinho et al (2007) have shown that NLT_{ij} also appears in the closure for the viscoelastic stress work appearing in the transport equations of turbulent kinetic energy and of the Reynolds stresses. Hence, a crucial step in devising turbulence models for viscoelastic fluids described by the FENE-P rheological equation of state is the development of a closure for NLT_{ij}, which constitutes the aim of this work.

The exact equation for NLT_{ij} is derived first. Then, based on physical reasoning and DNS data for fully-developed channel flow of FENE-P fluids some of its terms are shown to be negligible while others are approximated using physically consistent arguments. The final result is an explicit expression for NLT_{ij}, which compares well with the DNS data without the need to bring new physical quantities, thus providing a closed expression together with the remaining equations of a single-point turbulence closure. The model is calibrated against two sets of DNS data pertaining to the low drag reduction regime. Both sets of data are for the same Reynolds number, $Re_{t0}= 395$, ratio of solvent to total zero-shear-rate viscosities of $ß= 0.9$ and maximum extension $L^2= 900$. One set of data has a drag reduction of 18% corresponding to a Weissenberg number, $We_{t0}= 25$, whereas the other has a drag reduction of 37% corresponding to $We_{t0}= 100$. In the near future, this closure needs to be extended to the high and maximum drag reduction regimes.

Housiadas KD, Beris AN & Handler RA. Phys. Fluids, 17 (2005) 35106; Li CF, Sureshkmar R & Khomami B. J. Non-Newt. Fluid Mech., 140 (2006a) 23-40; Li CF, Gupta VK, Sureshkmar R & Khomami B. J. Non-Newt. Fluid Mech., 139 (2006b) 177-189; Pinho FT, Li CF, Younis BA & Sureshkumar R. A low Reynolds number k- e turbulence model for FENE-P viscoelastic fluids. Submitted to J. Non-Newt. Fluid Mech (2007).

Tuesday 4:10 San Carlos I CF42

Numerical investigations of fully 3-D, time-dependent viscoelastic flows past bluff bodies at moderate to high Reynolds numbers

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With the goal of creating a robust numerical method for calculating fully three dimensional, time dependent, non-Newtonian flows, we have developed an unstructured, finite-volume code to compute a wide variety of viscoelastic flows over a large range of Reynolds (Re) and Weissenberg (Wi) numbers. Our method is based on a continuum implementation of the FENE-P constitutive model to describe the flow of dilute polymeric solutions, but the algorithm can be used for wide range of differential constitutive equations. An implicit time-stepping technique is utilized (in a manner that is consistent with our previous formulation in Dubief, et al. 2005) that properly maintains boundedness of the polymer stresses and conformation tensors even at high flow strengths. This formulation thus allows for the investigation of the flow of high molecular weight polymers (L up to 100 in the FENE-P model where L is the polymer length in number of Kuhn steps) as well as high polymer relaxation times (Wi on the order of 100). We will present the time-dependent, laminar viscoelastic flow past a circular cylinder at low to moderate Reynolds number ($10 < Re < 1000$). Within this range of Reynolds numbers, regular vortex shedding occurs, and the characteristic frequency of this shedding was found to decrease with increasing fluid elasticity. Furthermore, the coefficients of both friction drag and form drag are reduced with increasing Weissenberg number. Grid-converged calculations are compared to existing numerical results (Oliveira 2001). Additionally, new qualitative effects have been observed at large polymer lengths (L), where the recirculation region immediately behind the cylinder is nearly eliminated and the location of vortex development is shifted several cylinder diameters downstream. Physical mechanisms for this viscoelastic behavior will be proposed and discussed. Time permitting, additional topics will be discussed including the effect of polymer additives on flow drag in the transition to turbulent flow about the same cylinder. Existing experimental literature suggests decreases in drag reduction compared to Newtonian values at the same Reynolds numbers, however wake effects in these drag reductions will be discussed and analyzed.

Tuesday 4:30 San Carlos I 💿 CF43

Vortex shedding in confined swirling flows of polymer solutions with a partially rotating disc

Shinji Tamano, Motoyuki Itoh, Ayako Takagi, and Kazuhiko Yokota

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The study of confined swirling flows of viscoelastic fluids is attractive from a scientific point of view for constructing rheological models owing to the well-defined boundary condition, and its understanding is of great importance in many process engineering applications, fluid machinery such as viscous coupling and viscous heater that uses fluid friction, and rotary agitators of viscoelastic fluids. Therefore, many experimental studies have been conducted to examine the fundamental flow behavior in the confined swirling flow of a polymer solution which is a typical viscoelastic fluid (e.g., Hill 1972, Day et al. 1996, Escudier and Cullen 1996, Stokes and Boger 2000, Stokes et al. 2001, Moroi et al. 2001, Itoh et al. 2006). In our quite recent work [Tamano et al., Phys. Fluids, Vol.19, No.023103 (2007)], we investigated the unsteady confined swirling flow of polymer solutions with the shear-thinning property using the flow visualization technique and found an attractive phenomenon of vortex shedding. The ring vortex is formed near the center of the rotating disc and grows larger, and it is finally shed in the axial direction. This process is repeated periodically, and is totally different from the spiral instability (continuous vortex shedding) described in Day et al. (1996), Stokes and Boger (2000), and Stokes et al. (2001). In order to understand the mechanism of the vortex shedding enough, however, there has been lacking of experimental data on the effect of the size ratio of the rotating disc and the cylindrical casing on the vortex shedding. In this study, unsteady swirling flows of aqueous polymer solutions in a cylindrical casing with a partially rotating disc have been investigated. The ratio of disc radius Rd to container radius Rc, S=Rd/Rc, was 0.4, 0.6 and 1.0. As the aqueous polymer solution, 0.5, 0.8 and 1.0 wt% polyacrylamide (PAA) solutions were used. The behavior of flow has been investigated using sectional and three-dimensional flow visualizations, and the flow patterns were classified using the Reynolds number Re0 and the elastic number E0 which were based on the zero-shear viscosity. It was observed that at S=0.4 and 0.6, the ring vortex was formed near the partial rotating disc and it was shed periodically, as well as at S=1.0. We found that the relation between the lower-critical Reynolds number for the vortex shedding (Re0)c and the elastic number E0 was obeyed by the equation, (Re0)c = 10 E0^(-3/5), which was independent of the disc-to-cylinder ratio S. It was also found that the non-dimensional period of vortex shedding increased with the increase of Re0, which was independent of S. The diameter of the ring vortex B/(2Rc) increased with the increase of the Reynolds number Re0, in which the relation between B/(2Rc) and Re0 was dependent on the concentration of PAA solutions, not on S. Regardless of the solution concentration or S, in addition, the height of the vortex was about one-tenth the size of diameter of the rotating disc.

Tuesday 4:50 San Carlos I CF44

Non-linear stability analysis of viscoelastic fluid flows

Marc Habisreutinger, Nicolas Fietier, and Michel Deville

Mechanical Engineering, Ecole Polytechnique Federale Lausanne, Lausanne, Vaud CH-1015, Switzerland

The difficulty to compute numerically viscoelastic fluid flow problems is expressed in terms of the dimensionless Weissenberg number which is a measure of the elasticity of the fluid. For vanishing Weissenberg number, the purely viscous behavior is recovered while the elastic effects become more and more significant for increasing values.

The state-of-the-art numerical schemes fail to converge when dealing with highly elastic fluid flows. Instabilities in the numerical simulation of such flows are supposed to be either of numerical origin due to the lack of convergence of the discretization algorithms, or of a mathematical source induced by the constitutive laws based on continuous media models, or due to incorrect modeling of the fluid rheology.

Extensive analysis of the numerical simulations have been conducted for unsteady plane Couette and Poiseuille flows of viscoelastic fluids using the spectral element method. For both flows, depending on the value of the Weissenberg number, an instability of Hadamard type leads to the blow-up of the simulations.

Numerical results clearly show that this instability is induced by the accumulation of high frequency structures for all computed flow fields which reflects a transition from a laminar to a turbulent flow state, even for low Reynolds numbers and even though a steady laminar solution is expected. This phenomenon has also been observed experimentally by Groisman *et al.* [S. Grossmann. The onset of shear flow turbulence. *Rev. Modern. Phys.*, 72(2):603--618, 2000.].

In the case of plane flows such as those investigated, available linear stability analyses based on infinitesimal disturbances do not show any loss of stability, however it could happen that the flow be unstable to finite-amplitude disturbances due to non-linear effects. An investigation of the temporal behavior of such disturbances is proposed by solving the fully non-linear set of governing equations for the perturbation. Results obtained with this method allow to confirm and explain the aforementioned mechanism of transition to turbulence.

SE-3. Complex Flows in Surface Active Systems

Organizers: Denis Weaire and Lynn M. Walker
Session Chair: Phil Sullivan

Tuesday 2:30 De Anza II SE16

Effect of nanoparticle dispersion on rheological properties of flexible polyurethane foams

Mauro Zammarano[1], Sameer S. Rahatekar[1], Roland Kramer[2], Thomas J. Ohlemiller[1], John R. Shields[1], Richard Harris[1], and Jeff W. Gilman[1]
[1]NIST, Gaithersburg, MD 20899, USA; [2]Royal Institute of technology, Sweden, Stockholm, Sweden

Flexible polyurethane (PU) foams are widely used in mattress and furniture but they are highly flammable. Our work is focused on reducing the flammability of PU foams by addition of different types of nanoparticles in PU foams. We produced flexible PU foams nanocomposites with different types of nanoparticles nanoclays, nanofibers and carbon nanotubes. We discuss the effect of addition of nanoparticles on the rheological behavior of the Polyols (which are used as precursors for PU foams). The network formation of the nanoparticles in polyol significantly impacts the rheological properties and foaming ability. Depending on the aspect ratio and the compatibility of nanoparticles in polyols, each type of nanoparticles show different critical volume (Vc) to form a network in PU foam. The PU with nanoclay did not show significant improvement in flame resistance where as nanofibers were able to reduce the flammability PU foams significantly. The rheological characterization may be a useful tool to understand processability of nanoparticles/PU foams and may also be used to relate the rheological properties with improvement in flammability of nanoparticle/PU foams.

Tuesday 2:50 De Anza II SE17

Structure and rheology of particle-laden liquid foam

Reinhard Hohler[1], Sylvie Cohen-Addad[1], and Andrew Kraynik[2]
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Particle-laden liquid foams are concentrated dispersions of gas bubbles and solid particles in a surfactant solution. They are used in several large-scale industrial applications such as ore flotation and oil production. We present macroscopic rheological experiments and numerical simulations of the microstructure that show how and why the elasticity of foam is enhanced and jamming finally occurs as more and more particles are dispersed in a liquid foam (1). These results are discussed in the general context of jamming and rigidity percolation in soft solids containing rigid particles. We have studied aqueous foams containing particles of a variety of shapes and sizes by oscillatory shear experiments at low frequency. The linear shear modulus is found to scale with particle volume fraction as predicted by a rigidity percolation model. However, the shear modulus at a given particle volume fraction is found to increase strongly with the ratio of mean bubble size over mean particle size. This feature cannot be understood within the framework of continuum mechanics models and motivates our numerical simulations at the scale of the microstructure, aiming to provide further insight into the physical processes that determine macroscopic elasticity in these materials. Using the Surface Evolver software, we have studied the structure and quasistatic elasticity of model systems that consist of wet ordered 3D foams in which particles are periodically inserted. These simulations show that capillary interactions between neighboring particles can significantly enhance the elasticity of particle-laden foam. This is reminiscent of wet granular materials where percolating networks of liquid bridges between neighbouring grains are essential for cohesion. However, the pendular capillary bridges in wet granular materials contain a fixed amount of liquid. In contrast, in particle-laden foams, the bridges are characterized by a fixed liquid pressure since they are connected to the network of Plateau borders (2). This leads to qualitatively different interactions between neighbouring particles. In this context, we investigate the influence of particle size, particle wettability and liquid fraction. We also compare these findings to results obtained for dry disordered particle-laden foams where capillary bridges do not exist.

(1) S. Cohen-Addad, M. Krzan, R. Höhler, B. Herzhaft, Phys. Rev. Lett. 99, 168001 (2007); (2) Plateau borders are liquid channels at the junction of 3 neighbouring bubbles.

Tuesday 3:10 De Anza II SE18

Rayleigh instability in charged globules: Effect of electrolyte and interfacial rheology

Rochish M. Thaokar and Shivraj Deshmukh
Chemical Engineering, IIT Bombay, Mumbai, Maharashtra 400076, India

We study the Rayliegh instability of charged globules in the presence of an electrolyte, but absence of any external electric field. Conventionally, the instability is studied with perfect dielectrics or conductors, in which the electric field is solenoidal. We consider the biologically relevant case of these charged objects immersed in an electrolyte solution, where the electric field is described by the simplified Debye-Huckel theory. This would also occur commonly in liquid-liquid emulsions. The effect of interfacial properties on the instability is investigated to cover an entire range of physical situations encountered: from surfactant free drops (only surface tension) to vesicles (purely elastic). We use both linear (normal mode analysis) and non-linear theory (Boundary integral method) to construct stability diagrams. The study should be useful in understanding formation of micro-emulsions and several biological phenomenon like the instabilities in Golgi-apparatus in the context of Rayleigh instability

Tuesday 3:30 De Anza II SE19

Isotropic-nematic phase transition in a liquid-crystal droplet

Xuemei Chen, Ben Hamlington, and Amy Shen
Department of Mechanical, Aerospace & Structural Engineering, Washington University in St. Louis, St. Louis, MO 63130, USA

In this talk, we focus on the isotropic-to-nematic phase transition in a liquid-crystal droplet. We present the results of an experiment to measure the growth of the nematic phase within an isotropic phase liquid-crystal droplet. Experimentally, we observe two primary phase transition regimes. At short time scales, our experimental results R & t^{0.51} show good agreement with a Stefan-type model of the evolution of the nematic phase within the isotropic phase of a liquid crystal. As time progresses, the growth of the nematic phase is restricted by increased confinement of the droplet boundary. During this stage of growth, the nematic phase grows at a slower rate of R & t^{0.31}. The slower growth at later stages might be due to a variety of factors such as confinement-induced latent heat reduction; a change of type in the defect in the nematic phase during its evolution; or interactions between the defect and the interface between the liquid crystal and oil or between adjacent defects. The presence of two growth regimes is also consistent with the molecular simulations of Bradac et al., who identify an early stage domain regime and a late stage confinement regime. For the domain and confinement regimes, Bradac et al. obtain growth exponents of 0.49 ± 0.05 and 0.25 ± 0.05. These are remarkably close to the values 0.51 and 0.31 observed in our experiments.

Tuesday 3:50 De Anza II SE20

Morphology and rheology of polymer/liquid crystal blends

Wei Yu, Youjun Wu, and Chixing Zhou
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The morphology and rheology of immiscible polymer blends has been the subjects of many researches. It is well known that the properties of blends depend on the rheology of components fluids as well as the properties of interface. For blends composed of isotropic fluids, the capillary number, defined as the ratio between the shear stress and the interfacial stress, controls the behaviors of dispersed droplet under flow field. When one component becomes an anisotropic fluid, it is expected that the anisotropic interfacial properties would greatly affect the properties of the blends. The effect of anisotropic properties of interface between a polymer and a liquid crystal (LC) on the steady and transient behavior of morphological evolution and rheology properties is the main interest of the present work. The deformation and relaxation behavior of a LC droplet immersed in a polymer matrix is investigated and compared with the predictions of our recent model.

Tuesday 4:10 De Anza II SE21

Observation of shear flow for surfactant solutions with a rheometer of cone and plate type

Takashi Koshiba[1] and Takehiro Yamamoto[2]
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In the measurement of steady shear viscosity for concentrated surfactant solutions with a cone and plate device, shear viscosity behaves like polymer solutions and shows interesting rheological properties, shear thinning and shear thickening properties. These rheological properties were caused by a transition of micelle structure induced by shear flow. In this study, we measured the pressure variation at local positions on a plate to examine the details of the relation between a shear flow in a cone-plate and the shear induced structural transition for surfactant solution. Test fluids used were mixtures of CTAB and NaSal in distilled water. The pressure on the plate increased with increasing the shear rate and its profile was closely connected to results of the first normal stress difference for surfactant solutions measured by other way. Furthermore, we carried out the flow visualization in cone and plate under flow regime at a constant shear rate, and observed the liquid surface at the circumference of cone. It was confirmed that a fluctuation in free surface occurred at a critical shear rate which was higher than the value showing the shear thickening property in shear viscosity and led a flow pattern in a cone to the flow instability. These results suggest that the alignments of micelles to flow direction are fractured by a strong shear deformation, and are associated with the property of the second normal stress difference for surfactant solutions.

Tuesday 4:30 De Anza II SE22

Effect of surface treatments of rheometer fixture on nonlinear rheology measurements of thread-like micellar solutions

Tadashi Inoue
Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Effects of surface treatments of rheometer fixture on nonlinear rheology measurements or flow visualization of an aqueous solution of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) were examined. This type of surfactant solutions is known for marked strain hardening behavior for fast startup flows and the shear induced structures for strong steady flows. For flow visualizations or light scattering measurements under shear flows, glassy fixtures are often used to transmit the light. However, we found that the hardening was very weak when non-treated glassy cone-plate fixture was used because of slip of solution-glass interface. Chemical treatments of glassy fixture were found to be very effective to reduce the wall slip and the strongest shear hardening phenomena were observed when the surface of the glassy fixture was treated with trimethylchlorosilane. Contact angle measurements suggested that surfaces having the higher dispersion component of the surface energy was effective to reduce the slip at the fixture surface and leaded to nonslip flow patterns.

Tuesday 4:50 De Anza II SE23

Flow of viscoelastic wormlike micelle solutions through a periodic array of cylinders

Geoffrey R. Moss and Jonathan P. Rothstein
Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA, USA

Solutions of self-assembled wormlike micelles are used with ever increasing frequency in a multitude of consumer products ranging from cosmetic to industrial applications. Accordingly, a thorough understanding of their behavior in response to a variety of flow situations is required. Owing to the wide range of applications, flows of interest are often complex in nature; exhibiting both extensional and shear regions that can make modeling and prediction both challenging and valuable. Adding to the complexity, the micellar dynamics are continually changing, resulting in a number of interesting phenomena, such as shear banding and extensional flow instabilities. We present the results of our investigation into the flow fields generated by a controllable and idealized semi porous media: a periodic array of cylinders consisting of six equally spaced cylinders, arranged perpendicular to the flow at a single cylinder diameter-to-channel ratio. By systematically varying the Deborah number, the flow kinematics, stability and pressure drop were measured. For small cylinder separations, we present evidence of the onset of shear banding above a critical Deborah number as seen by a plateau in the pressure drop with increasing Deborah number. For larger cylinder separations where the flow is dominated by strong extensional flow in the wake of the cylinder the flow becomes unstable. A combination of particle image velocimetry (PIV) in conjunction with flush mount pressure transducers were used to fully characterize the flow, while flow induced birefringence measurements were used to determine the conditions necessary to induce elastic instabilities.

Tuesday 5:10 De Anza II SE24

Nanoparticle associated surfactant micellar fluids

Jason E. Maxey[1], James Crews[2], and Tianping Huang[2]
[1]Global R&D, Baker Hughes Drilling Fluids, Houston, TX 77073, USA; [2]Baker Oil Tools, Houston, TX 77073, USA

Surfactant micellar fluids, or viscoelastic surfactant fluids, have been used in the oil industry as completion and stimulation fluids. High fluid leakoff and low thermal stability at elevated temperatures have, however, limited their application for hydraulic fracturing and frac-packing applications. Improved thermal stability and rheological design of such viscoelastic surfactants is critical for non-formation damaging, high temperature well treatments. This paper will introduce the interaction of nanoparticles with micelles, which at low concentrations induce micelle-micelle associations and significantly improve the performance of viscoelastic surfactant fluids.

The unique association of viscoelastic surfactant micelles and nanoparticles has demonstrated improved viscosity, the formation of a "pseudo-filtercake", and enhanced thermal stability. Laboratory tests show the development of a pseudo-filtercake which significantly reduces the rate of fluid loss and demonstrates wall-building rather than viscosity dependant leak-off control. Rheological tests demonstrate long-term stability of viscoelastic behavior at 150°C for fluids with high surfactant concentrations. Temperature stability can be achieved up to 135°C using lower surfactant concentrations ($2\%_v$ - $4\%_v$) than conventionally known. In small amplitude oscillatory shear, a previously unobserved elastic behavior is noted at low frequencies, with the storage modulus constant and the viscous loss modulus approaching zero as angular frequency decreases.

An examination of the rheological and fluid loss behavior of these fluids will be presented.

Wednesday Morning – 6 August 2008

KL-7. Keynote Lecture 7

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Dimitris Vlassopoulos

Wednesday 8:30 Steinbeck KL7

Tailoring the rheology of soft particle dispersions

Michel Cloitre[1] and Roger T. Bonnecaze[2]
[1]ESPCI, Paris, France; [2]Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

Many complex fluids are dispersions of soft particles that share common features with polymers and colloids. Examples include polyelectrolyte micro-networks, multi-arm star polymers, colloidal particles covered with grafted or adsorbed polymer chains, block copolymer micelles... Such particles are inherently soft and deformable and at the same time they are impenetrable. One important consequence is that soft particles can be concentrated well above close-packing. Concentrated dispersions of soft particles display both solid-like and liquid-like properties with the solid-liquid transition taking a variety of forms. This property is central to the use of formulations containing soft particles in many technical applications. Yielding is also associated with many other fascinating properties such as shear thinning, aging and memory, wall slip or fracture. Understanding these peculiar rheological properties is an outstanding challenge for statistical and condensed-matter physics as well as for materials science and biology.

Recently it has been suggested that the close-packed, amorphous structure of colloidal dispersions lies at the heart of their behavior. At high volume fraction, the particles are jammed in cages and can flow past one another appreciably only if the applied stress is sufficiently large to distort and break the cages. This fruitful analogy with glasses and supercooled liquids capture several features of yielding and ageing in concentrated colloidal dispersions.

Another characteristic feature of soft particle dispersions in addition to disorder is the presence of specific interactions mediated by the solvent. For instance, we have shown that the slip behavior of microgel pastes and emulsions near surfaces results from elastohydrodynamic lubrication. Other generic properties also seem to be governed by these contact interactions between squeezed particles.

We shall show that the properties of soft particle dispersions originate from a subtle interplay between disorder and local interactions. Recent advances in this direction suggest novel strategies to design and synthesize complex dispersions with well-controlled properties.

KL-8. Keynote Lecture 8

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: David C. Venerus

Wednesday 8:30 Serra I *Bingham Lecture* KL8

Could we raise glasses?

Hans Christian Öttinger
Department of Materials, Polymer Physics, ETH Zurich, Zurich 8093, Switzerland

When investigating glasses, nonequilibrium phenomena are ubiquitous. Even if there was a glassy equilibrium state, the occurrence of enormously large relaxation times would force us to deal with the nonequilibrium approach to such an equilibrium state, or with nonequilibrium phenomena taking place during and on top of that approach. We hence apply a modern framework of nonequilibrium thermodynamics to find out whether we might be able to raise our level of understanding of glasses, both from the conceptual and from the practical points of view.

SG-5. Mechanics of Nanocomposites

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Leon E. Govaert

Wednesday 9:45 San Carlos II SG31

Soft glassy NIMS

Rajesh Ganapathy[1], Robert Rodriguez[2], Emmanuel P. Giannelis[2], Lynden A. Archer[3], and Itai Cohen[1]
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Nano-particle based ionic materials (NIMS) are hybrid structures that are comprised of a charged inorganic core surrounded by an ionically tethered oligomer canopy serving as the counter-ion. A novel feature that distinguishes these systems from conventional colloidal suspensions/colloid-polymer mixtures stems from the fact that the tethered oligomer serves as an effective solvent rendering the system with effectively zero vapor pressure. The wide tunability in the properties of the inorganic core combined with the solvent free characteristics of NIMS suggest potential applications as coolants, electrolytes for fuel cells, etc. and understanding their rheological behavior is vital to this.

In this talk, I will describe the rheological differences between NIMS and NIMS in a solvent of excess oligomer. To this end, we have carried out linear and nonlinear rheological measurements as a function of temperature and core weight fraction. The amount of excess oligomer decreases with increasing core weight fraction. We see a plethora of interesting rheological response characteristic of fluids, stiff gels and glasses. An anomalous behaviour displayed by the low core weight fraction samples is their increasingly glass like behaviour with temperature. We also see features characteristic of a re-entrant glass transition with increasing volume fraction. The "Soft Glassy Rheology" model captures the observed rheological signatures which include a peak in the G"(ω) in strain sweep measurements, power-law behaviour in the frequency response and aging in steady shear measurements.

Wednesday 10:05 San Carlos II SG32

Polymer dynamics in C60-polymer nanocomposites

Peter F. Green[1] and Jamie Kropka[2]

[1]Materials Science and Engineering, Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA; [2]Chemical Engineering, University of Texas at Austin, Austin, TX 78712, USA

A diverse range of complex dynamical processes occurs in polymer based nanocomposite systems. These include shifts in the glass transition temperatures, Tg, compared to the pure polymer, additional glass transition temperatures and changes in the mechanical properties (including the viscosity). We used dynamical mechanical analysis, rheology, differential scanning calorimetry and incoherent neutron scattering (INS) to examine three C60-polymer nanocomposite systems: C60-polystyrene, C60-poly(methyl methacrylate), C60-tetra methyl bisphenl-A polycarbonate. Rheological experiments show evidence of homogeneous, uniform, increases in the viscosity (including the longest relaxation time) and moduli; no evidence of heterogeneities in the dynamics was observed. A single, yet larger, Tg was observed in each of these systems. However, INS measurements of the temperature dependencies of atomic mean square displacements in the glassy state of these systems indicates that the atomic species in the nanocomposites are more strongly restricted than those in the pure polymer. In addition, the scattering spectrum in the melt suggests that the influence of C60 on polymer dynamics is limited to the vicinity of the particles at nanosecond time scales. A model is presented to reconcile the findings in these systems and our results are discussed in light of the observations in other systems.

Wednesday 10:25 San Carlos II SG33

Effect of silica nanoparticles on the local segmental dynamics in polyvinylacetate

R. B. Bogoslovov and C. M. Roland

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The effect of nanosized silica particles on the properties of polyvinylacetate (PVAc) was investigated for a range of silica concentrations encompassing the filler network percolation threshold. The quantity of polymer adsorbed to the particles (“bound rubber”) increased systematically with silica content and was roughly equal to the quantity shielded from shear stresses (“occluded rubber”). A variety of experimental techniques was employed including pressure-volume-temperature measurements, broadband dielectric spectroscopy, thermal analysis (modulated DSC), dynamic-mechanical spectroscopy, viscometry. The glass transition properties of PVAc, i.e. the glass transition temperature and the changes in the thermal expansion coefficient and heat capacity at Tg, as well as the isothermal compressibility and the volume sensitivity of the local segmental dynamics of the polymer chains in the presence of the polymer-filler interface are discussed. The implication of this result and possible directions for new research are considered.

Wednesday 10:45 San Carlos II SG34

Reinforced elastomers: New insights on local stress heterogeneity and on long time relaxation phenomena; experiments and modelling

P Sotta[1], S Dupres[2], S Merabia[3], P A. Albouy[2], and Didier R. Long[1]

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Reinforced elastomers are disordered nanocomposites materials made of an elastomer matrix filled with nanometric solid particles or aggregates. They exhibit remarkable properties which are still far to be completely understood: a large, temperature dependent increase of the elastic modulus, large non linear effects at medium/high strain amplitudes, large energy dissipation and irreversibility. Important progress has been achieved recently in the understanding of these properties [1]. A model based on the presence of glassy layers related to the shift of Tg in the elastomer matrix has been proposed [2]. In model reinforced systems, it was shown that this model explains quantitatively reinforcement curves as a function of temperature and filler volume fraction [1]. Here, we shall present an ensemble of experimental results which give some new insight on the microscopic mechanisms of reinforcement, by combining various techniques. The results have been obtained in elastomers filled with carbon blacks of various morphologies. These systems are close to those used in tyre applications. The talk may be focussed on two particular aspects. First, we have investigated the differences in local strain amplification measured by different techniques (namely: mechanical measurements, deuterium NMR in stretched samples, onset of strain induced crystallization measured by Xray diffraction); these differences give indication on local stress heterogeneity, which depends on the morphology of the fillers. On the other hand, we have investigated slow relaxation phenomena: stress relaxation, memory effects and irreversibility effects [2], such as plasticity, long time evolution of SAXS pattern. These long time phenomena emphasize the importance of glassy regions within the elastomer matrix. Related to these and other experimental results, we have developed a new mesoscale modelling of reinforced elastomers which takes into account the slow (glassy) dynamics in the elastomer matrix. The model gives a unified picture of an ensemble of complex phenomena in both the linear and nonlinear regimes of reinforced elastomers: reinforcement over a large temperature range, Payne and Mullins effects, plasticity [3].

[1] Gradient of glass transition temperature in filled elastomers, J Berriot, H. Montès, F. Lequeux, D. Long, P. Sotta, L. Monnerie, Europhys. Lett. 2003, 64, 50-56; [2] Heterogeneous nature of the dynamics and glass transition in thin polymer films, S. Merabia, P. Sotta, D. Long, EPJ E 2004, 15, 189-210; [3] Non linear and Plastic Behaviour of Soft Thermoplastic and Filled Elastomers Studied by Dissipative Particle Dynamics, D. Long, P. Sotta, Macromolecules 2006, 39, 6282-6297.

Wednesday 11:05 San Carlos II SG35

The rheology and solid-state properties of polypropylene-silica nanocomposites prepared via in-situ synthesis

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It is well established that, above a certain threshold value for the molar mass M_c, the terminal viscosity of polymer melts scales with molar mass to the power 3.4. The strong increase of the viscosity with increasing molar mass is related to the presence of physical entanglements. The viscosity/molar mass rule implies that polymers of low molar masses are preferred for processing; however, high molar masses are required for materials' properties rendering the production of polymer products an area of unfortunate compromises.

One way to improve the properties of polymeric materials other than increasing its molar mass is to use additives such as nanofillers. This nanocomposite approach has advantages over traditional composites, especially when the length scale of the morphology and the fundamental length scale of the physics of a given property coincide [1]. Well-known examples are (exfoliated) clays and carbon nanotubes (CNT). However, no significant improvements in properties have been observed yet [2], though it may be too early to discard the theoretical potential of nanofillers, as many hurdles are still to overcome, especially regarding the dispersion and the processing of these materials. Mackay et al. [3] reported recently on a drop in the viscosity of nanoparticle-filled polymer melts produced by blending organic nanoparticles, synthesized by intramolecular crosslinking of single polystyrene chains, with linear polystyrene. This observation is in contradiction with the expression derived by Einstein describing the increase of the viscosity as a function of the volume fraction of fillers and the matrix viscosity, suggesting that this expression does not appear to hold in the case of nanoparticles. The decrease in the viscosity was attributed to excluded free volume induced around the nanoparticles. This is, however, accompanied with a significant decrease in the glass transition temperature, which is detrimental for the final properties.

We found a significant improvement of both processing and performance for a silica nanoparticles-filled polypropylene (PP). To facilitate dispersion of the nanoparticles, we developed a novel approach by using solid-state modification of porous, semi-crystalline PP powder with the in-situ preparation of silica nanoparticles by sol-gel chemistry [4]. In this presentation, we will show how shear-induced crystallization studies using small-angle X-ray scattering (SAXS) to probe the structure development were very useful to elucidate the mechanism for the improvement in processing and performance.

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HP-8. Polymer Solutions

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Claude Cohen and Patrick S. Doyle

Wednesday 9:45 San Carlos III HP52

Rheology of dendrimers in solution via Brownian dynamics simulations

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Dendrimers represent a special class of hyperbranched polymers. Their unique topology results in their unusual transport properties. The solubility, viscosity, and diffusivity of dendrimers differ significantly from the properties of molecules with more traditional architectures. This leads to many possible applications of dendrimers as additives, viscosity modifiers, or building blocks in nanostructures. Full control during the synthesis of dendrimers allows the design of molecules with mechanical or chemical properties in a wide range. The architecture and mechanical properties also affect the rheology and flow-induced deformation of molecules. For example, the varied length and flexibility of branches of a dendrimer results in a transition from the behaviour typical for colloids to polymer-like properties.

In this contribution we build a generic coarse-grained freely-jointed bead-spring chain model of a dendrimer with long flexible branches. Excluded volume interactions capture the quality of the solvent. With the aid of Brownian dynamics simulations, we investigate the effect of the molecular topology on the structural and dynamic properties of the polymers. Dendrimers with varied generation numbers and molecular weights are studied along with linear chain polymers with comparable molecular weights. Simulations are performed at equilibrium as well as away from it.

The effect of the topology, fluctuating hydrodynamic interactions, and solvent quality on the viscosity and transport properties of molecules are investigated. For molecules of the same molecular weight, with increasing degree of branching, a decrease in the intrinsic viscosity and an increase in the translational diffusivity are observed. In the free-draining case at the Θ state, the structural and dynamic properties are found in very good agreement with the predictions of the Rouse model. Incorporation of hydrodynamic interactions enables and is sufficient to reproduce the maximum in the intrinsic viscosity of dendrimers observed experimentally. Hydrodynamic interactions also, through a reduction in drag, lead to an increase in the translational diffusivity. This effect is stronger in dendrimers than in linear chain systems.

The rheology of dendrimers in solution subjected to planar shear and elongational flows is also studied. Results of the non-equilibrium Brownian dynamics simulations of dendrimers and linear chain polymers subjected to flow in a wide range of strain rates are reported. The flow-induced molecular deformation of molecules is found to decrease hydrodynamic interactions and lead to the appearance of shear thickening. Branching in dendrimers reduces the extent of shear-thickening. To investigate the effect of concentration on the rheology of dendrimer solutions, multiparticle systems have been also studied and preliminary results will be presented.

Wednesday 10:05 San Carlos III HP53

Shear thickening of an amphiphilic polymer solution as studied by large amplitude oscillatory shear flow

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Associating polymers based on a weakly charged hydrophilic backbone bearing grafted hydrophobic moieties show a pronounced shear thickening (rheo-gelation) above a critical shear rate which depends primarily on concentration for a given chemical structure . It scales as a power law (exponent -4) with concentration.

The shear induced gelation is a brutal phenomenon which is difficult to study since the gels show a pronounced Weissenberg effect and wall slip. In order to obtain a deeper insight, the polymer solutions have been submitted to large amplitude oscillations. In this way, frequency as well as strain or shear stress can be varied. Shear thickening is observed under large amplitude oscillatory shear, since after a linear regime, dynamic moduli increase significantly above a critical stress, whatever the frequency (regime I). This phenomenon is eventually preceded by a slight decrease of the moduli at low concentrations and/or low frequencies (regime II). It is shown that this phenomenon appears, for a given concentration, at a critical stress which increases when frequency decreases. It can therefore occur even at frequencies much lower than the critical shear rate observed under shear flow. The behaviour at a given concentration (regime I or regime II) depends on the relative frequency ω/ω_c where ω_c is associated to the crossing of the dynamic moduli in the linear regime. It is thus related to the dynamics of the system.

The data in shear flow or in large amplitude dynamic measurements coincide when the viscosity and the complex viscosity are plotted versus stress. Dynamic measurements allow us to study intermediate states whereas continuous flow leads essentially to the gelled state. Thus, the shear stress appears to be the parameter controlling shear thickening.

Wednesday 10:25 San Carlos III HP54

Competitive hydrogen-bonding in polymer solutions with mixed solvents

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Polymer coil size is investigated in a mixture of solvent molecules capable of cooperatively hydrogen-bonding with each other, as well as with polymer chains. A minimum in zero shear rate viscosity of poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) in water/methanol occurs at a molar ratio of ca. 2:1 water:methanol. This viscosity coincides with a minimum in PEO gyration radius and occurs near the solvent conditions where water/methanol mixtures deviate most markedly from ideal solution behavior. This behavior is investigated as a function of molecular weight and polymer concentration. A minimum in polymer radius of gyration is predicted for ternary polymer solutions composed of two hydrogen-bonding solvents.

Wednesday 10:45 San Carlos III HP55

Shear and temperature induced conformational changes in entangled xanthan solutions

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High molecular weight (~2x10^6) xanthan gum is a biopolymer commonly used as a drag reducer, viscosity enhancer in food applications, and as a drilling fluid in enhanced oil recovery. Polymer concentrations ranging from dilute to concentrated in water and electrolyte solutions are studied using rheology and rheo-optics over a range of temperatures. Xanthan solutions exhibit a Newtonian plateau at low shear rates followed by a region of shear thinning simply described by a Cross model. The overlap and entanglement concentrations in water are determined to be 140 and 1235 parts per million by weight. A crossover in the dynamic moduli (G',G") is observed for concentrations above the entanglement concentration while below the overlap concentration no crossover is observed. Furthermore, xanthan undergoes a temperature-induced conformational change between the native helical structure and a solution of random coils. The transition occurs in the range of 40 °C to 60 °C as evidenced by a sharp reduction (~50%) in the solution viscosity over a period of 12 to 18 hours. The conformational change is time dependent and partially reversible. The incomplete reversibility suggests imperfections in the structure when the random coils reorganize into helices. An increase in both the overlap and entanglement concentrations is observed at 60 °C following the conformational change. The imperfections in the reorganized structures are also responsible for the increase in both the overlap and entanglement concentrations in the renatured state at 25 °C. Increasing the solution ionic strength following the conformational change increases the viscosity of the solution upon cooling to room temperature. In addition, dynamic light scattering (DLS) and rheo-SALS quantify the change in the polymer's structure and conformation at temperatures both above and below the critical transition temperature. Polymer alignment in both the coil and helical conformations are quantified using birefringence studies. Birefringence measurements will also identify shear-induced conformational changes as a function of shear rate and temperature. The effect of solvent ionic strength on rheology is also investigated. Polymer solutions with 0.1M NaCl stabilize the native xanthan configuration, delaying the temperature-induced conformational change to much higher temperatures (~80 °C). Solutions of xanthan to which NaCl is added following the conformational change are stabilized and recover more of the original solution viscosity than those with no salt added. In total, a more complete understanding of the entangled polymer structure of xanthan gum under various solvent, temperature, and flow conditions will be elucidated.

Wednesday 11:05 San Carlos III HP56

Probe dynamics in semidilute polymer solutions and gels

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We investigate the dynamics of tracers in semidilute polymer matrixes while the matrix is being crosslinked. Tracers considered are fluorescently labeled linear macromolecules as well as labeled spherical particles, whose diffusion coefficient is readily determined via fluorescence recovery after photobleaching. We make use of a highly selective photoaddition reaction to achieve progressive crosslinking of the suitably functionalized matrix polymer. That way we can start from a semidilute solution which contains the tracer molecules or tracer particles. After measuring the diffusion coefficient of the tracers in solution, the system is irradiated to attain a certain conversion of the crosslinking reaction. The conversion is then determined by UV spectroscopy, and subsequently another measurement of the diffusion coefficient is performed. This sequence of irradiation, characterization, and measurement steps is repeated until complete conversion of the photoreaction is achieved. By separate dynamic mechanical measurements, the sol-gel transition is indicated and the rising crosslink density of the matrix is quantified. Parameters varied beyond the gradual increase of the degree of crosslinking are the concentration of matrix polymer and the molecular weights or hydrodynamic radii, respectively, of the linear or spherical tracers.

The polymers used are slightly modified poly(acrylamides) prepared by radical copolymerization. The matrix polymer is a PAAm copolymer containing about 1.5 mol-% repeat units carrying dimethylmaleimide (DMMI) groups. In the presence of a thioxanthone sensitizer in aqueous solution, irradiation with light of wavelength 382 nm induces dimerization of the DMMI moieties and thus leads to crosslinking of the correspondingly functionalized PAAm chains in a highly efficient and well controlled manner.

The tracers employed were linear polyacrylamides with different molar masses labeled by rhodamine B. By using labeled PAAm tracers in a PAAm matrix, the difference in chemical structure could be minimized in order to exclude perturbations due to possible thermodynamic incompatibility. Commercially available polystyrene microspheres having particle radii similar to the dilute-state hydrodynamic radii of the linear tracers were used for comparison.

The major observations are summarized as follows:

- In semidilute polymer solutions, the mobility of hard spheres is markedly smaller than that of flexible linear macromolecules having a similar coil size in terms of radius of gyration.
- Also, the concentration dependence of the diffusion coefficient in solution is much stronger for spheres than for flexible linear chains.
- Crosslinking of the semidilute matrix has only a minor influence on the mobility of linear tracers or no effect at all, while the spherical tracers get completely immobilized when the degree of crosslinking exceeds a certain threshold, provided that the sphere size is perceptibly larger than the mesh size of the network.

Wednesday 11:25 San Carlos III HP57

Linear to non-linear rheological behavior of water-soluble polymers with different structures for EOR

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Water-soluble polymers are broadly used in the field of enhanced oil recovery. Rheological properties are one of the primary considerations in selecting a fluid for use in petroleum recovery operations. This paper presents the rheological behavior of three commercially available polymers with different structures (Sample1, partially hydrolyzed polyacrylamide, Sample2, modified partially hydrolyzed polyacrylamide, Sample3, hydrophobically associating polymer) in solution. Steady shear experimental results obtained by using ARES show that the rheological curves are of pseudplastic pattern for all polymers, and Carreau model can fit the experimental data well. However, there is a significant difference in the shape of shear rate versus first normal stress difference for sample 3 compared with the others. To character the linear viscoelastic behavior of the polymer solutions, oscillatory shear experiments were also carried out, and which can be described by the General Maxwell Model. The behavior of polymer solutions in elongational flows was determined using a Capillary Break-up Extensional Rheometer (CaBER). An Elastic (Exponential) model can be used to fit the experimental data. The first normal stress difference as well as the relaxation time of the sample 1 is greater than that of the others, but both of its loss modulus and the viscosity at higher shear rate are lower. In contrast to sample1, the sample 3 gets the highest viscosity, but the lowest first normal stress difference. The experiment results indicate that the microstructure mechanism is responsible for the rheological behavior, which was explained and discussed in terms of molecular structure and solution properties. The results should be beneficial to synthesizing new polymers and designing new EOR projects to further increase the recovery of oil fields.

FR-2. Food Dispersions

Organizers: Erich J. Windhab and Jan Engmann
Session Chairs: Jan Engmann and Erich J. Windhab

Wednesday 9:45 Bonsai I FR10

Effects of sugar content and temperature on rheology and microrheology of Israeli honey

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The rheological properties of selected Israeli honeys were evaluated using both rheology and microrheology. Most honeys are Newtonian; their viscosity ranges over 3-4 orders of magnitude and the water content is typically between 17-23%. The viscosity of honey is determined by the temperature, the relative amount of water/sugar, and the molecular chain length of sugars present in the honey, which is correlated to the origin of the honey. Effects of temperature and origin of the honey were determined with rheology and compared to microrheology to distinguish any local heterogeneity. Rheological measurements were correlated with the moisture content, as determined by refractometry. After the base-line behavior had been established, sugars were added to floral-origin standard and reduced-calorie honeys, to determine the effect of supplementary sugar on the rheology. This approach may be used to determine whether sugar content of a honey, or similar materials, has been altered; this could be especially valuable for non-homogeneous materials, such as jams with solid particles.

Wednesday 10:05 Bonsai I FR11

Rheology of coating materials and their coating characteristics

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A huge variety of particles used in the food industry are coated with a protective layer to avoid reactions between particles in a mixture and to act as a spacer between particles to avoid agglomeration and compaction. Besides a temperature controlled release of particles can be realised when the temperature exceeds the melting point of the coating material.

The rheology is an important parameter to characterise coating materials and their behaviour during the coating process. The elastic and viscous behaviour of coating materials gives information about the hardness and brittleness of the coating film. Rheological measurements as standard quality control for coating materials can avoid considerable production problems. Production errors while the coating process induces most times a completely failed charge. Also the product development for new coating substances using rheological measurements is cheaper and simpler than using coating experiments in pilot plants.

Investigations performed with different coating fats have shown that it is not sufficient to measure the composition, the melting point and the viscosity of the coating material to predict the porosity, the film thickness and the abrasion resistance of coatings. For example two different fats with similar melting points indicated completely different coating results. One product had an extreme porous film and the other product was coated with an absolute non permeable fat layer. One reason for this phenomenon that is investigated can be the gradient of the storage modulus G´ and loss modulus G´´ at the solidification point. The gradient shows how fast the solidification is downed.

To declare the abrasion of different fats the storage modulus G´ and the loss modulus G´´ are also suitable parameters. The magnitude of the loss modulus G´´ and the storage modulus G´ gives evidence about the hardness and thus about the abrasion stability of a substance. Also the maximal deformation of the linear viscoelastic range gives information about the brittleness of the coating material.

The porosity, the film thickness and the abrasion are important parameters to protect coated products adequate. Rheological measurements are a method to predict the quality of the coating film with relatively simple procedures. The magnitude of the storage modulus G´ and the loss modulus G´´, their gradient and their ratio are adequate parameters to predict the porosity, the film thickness and the abrasion of new coating materials for the pharmaceutical and food industry. With rheological measurements new coating materials can be investigated without coating experiments that takes a long time and costs plenty of money.

Wednesday 10:25 Bonsai I ⊛ FR12

Ultrasound based in-line rheometry of complex fluids

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The trend within fluid industry is towards continuous production, leading to an increasing demand for new and improved methods that allow real-time monitoring of quality parameters and fast process control. The consistency and viscosity can be described by fluid rheology and are frequently used as quality control parameters. Rheological properties can be correlated with product microstructure, they govern the performance of unit operations and detailed knowledge is fundamental for the design of new process equipment and for predicting e.g. heat transfer. The determination of rheological properties in-line, in real time, thus has a great economical impact and is important from a quality perspective for the development of innovative and competitive products and a prerequisite for efficient process control.

A method for in-line rheometry combining the Doppler-based Ultrasound Velocity Profiling (UVP) technique with Pressure Difference (PD) measurements, commonly known as UVP-PD, has recently been developed. The UVP-PD method developed at SIK allows measurements not possible with common rheometers such as radial velocity profiles and yield stress directly in-line. Furthermore, it has advantages over commercially available process rheometers and off-line instruments in being non-invasive, applicable to opaque and concentrated suspensions, having small sensors dimensions and relatively low cost.

The UVP-PD methodology and system developed at SIK has been successfully applied to a range of model and industrial fluids and suspensions, including fluids containing large particles and fibers. Changes in rheology can be monitored in real-time directly in the process line, with respect to changes in profile shape and in rheological parameters. UVP-PD can be used to monitor changes in rheology in industrial unit operations such as rapid start-up or shutdown of the process, liquid displacements during rinsing or product change and in-line mixing. In addition, Simulatneous measurements of the attenuation of transmitted ultrasound and changes in sound velocity provide an interesting option for determining particle concentration (e.g. solid fat content SFC) in-line.

Wednesday 10:45 Bonsai I ⊛ FR13

Deformation and break-up of suspension droplets sheared in an immiscible fluid

Melinda Desse[1], Sandra E. Hill[2], John R. Mitchell[2], Bettina Wolf[2], and Tatiana Budtova[1]

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The deformation and break-up behaviour of suspension droplets immersed in an immiscible fluid has not been widely studied albeit such systems are frequently encountered in every day multiphase products such as foods and cosmetics. Starch is a common thickener used in the food industry. Starch suspensions have shown to offer better flavour perception than polymer thickened solutions; a better understanding of their behaviour under flow would be beneficial in terms of advancement on product formulation. Deformation and break-up of a droplet of swollen-in-water starch granules placed in high viscosity silicon oil was visualised using a counter-rotating parallel-plate shear cell. The silicon oil had a high viscosity to induce shear stresses high enough to deform the droplet (only a limited range of shear rates can be applied in the cell used); it is also transparent and inert towards the studied system. The starch suspension was prepared to have a volume fraction of 100% swollen granules, i.e. that all water was bound within the swollen starch granules. However, the latter were deformable enough to form a spherical droplet in the silicon oil. The shear flow behaviour of this starch suspension is characterised by an apparent yield stress, shear-thinning and first normal stress differences. The rheo-optical experiments were conducted as start-up flow experiments applying shear stresses above the apparent yield stress. A constant shear stress throughout the experiment allows a constant viscosity of the droplet and therefore rules out the shear thinning aspect. Analysis showed droplet break-up at critical Capillary numbers close to those reported for Newtonian fluids whereas it has been shown that viscoelastic polymer solutions break up at higher critical Capillary numbers. The results demonstrate that the droplet break-up behaviour in a complex emulsion system submitted to shear flow may not be fully described by the rheology of the individual phases alone but may require a microstructure component.

Key words: Starch, suspension rheology, viscoelastic, counter-rotating rheo-optical cell, single droplet break-up, critical Capillary number.

Wednesday 11:05 Bonsai I FR14

Rheological measurements of an emulsion with matrix viscoelasticity and droplet morphology compared with model predictions

Andre Braun, Marco Dressler, and Erich J. Windhab

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Emulsions are an important form of foods and widespread in food industry. To produce tailored food emulsions, it is important to understand the development of the macroscopic and microscopic properties during the process flow. Simulations and model predictions are an inexpensive and timesaving way to get an insight into production processes. Therefore, a rheological model describing emulsions with droplet morphology was recently derived within the framework of non-equilibrium Thermodynamics by Dressler and Edwards [1]. The model allows to investigate the difficult interplay between fluid dynamics, droplet microstructure, and the non-linear viscoelastic properties of the emulsion. The complex set of nonlinear and coupled differential equations were solved numerically for various isothermal flows, i.e. for homogeneous as well as for complex process flows. Within this presentation, we will discuss uniaxial shear flow in order to compare model predictions with experimental data. Rheological measurements were performed to obtain the viscosity and normal stress difference functions of the emulsion. These transient and steady state shear tests were carried out using a strain controlled rheometer with cone-plate geometry at room temperature. The model emulsion with matrix-phase viscoelasticity was composed of a guar gum solution as continuous phase and silicon oil as disperse phase. The zero shear viscosity of the Biopolymer guar is strongly concentration dependent. A high concentration was chosen to increase viscoelastic effects. A surfactant was added to stabilize the two immiscible fluids. The model parameters (i.e. the power law index, elastic modulus, and relaxation time of the matrix phase as well as the relaxation time of the droplet deformation, interfacial tension, and viscosity ratio of the two phases) were experimentally determined instead of fitted to avoid obtaining any illegitimate parameters during the fitting process. The model predictions are in good agreement with the experimental data.

[1] M. Dressler, B. Edwards. Rheology of polymer blends with matrix-phase viscoelasticity and narrow droplet size distribution, J. Non-Newtonian Fluid Mech., 120 (2004) 189-205.

Wednesday 11:25 Bonsai I FR15

Novel rheology in a structured food product - Marmite^{TM}

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Marmite^{TM} is a popular yeast extract spread in the UK. Fundamental understanding of its rheological behaviour is required by its manufacturer, Unilever UK, to underpin process improvements and design decisions relating to storage and flow of the product and its intermediates. The objective of this research is to characterise the basic rheology of this semi-solid material. Steady-state data were obtained from temperature-controlled stress and rate sweeps over two decades of shear stress or shear rate using Bohlin controlled-stress and ARES controlled-strain rheometers. Cone-and-plate and Searle systems were employed in the Bohlin while a parallel-plate system was used in the ARES. The Bohlin device was also operated in controlled-rate mode. Data from all systems, modes of operation and rheometers exhibited good consistency and negligible slip. The results indicated a structured, thixotropic material with a viscosity in the order of 100 Pa s at ambient temperature and 1 s^{-1} shear rate. On being sheared from rest the material exhibited shear-thinning characterised by a power law index of ~ 0.7; once broken down, the material was almost Newtonian. At higher temperatures the viscosity and extent of thixotropy decreased and overall behaviour approached Newtonian. The extent of breakdown on restructuring exhibited a dependence on both stress and strain. Non-steady-state data acquired by shearing the material from rest indicated a period of shear-thickening creep at shear rates around 0.01 s^{-1} and below, i.e. below the regime at which shear-thinning occurs. An apparent yield stress could not be detected, but creep tests indicated a noticeable transition between solid and liquid regimes at a critical stress that is a strong function of the solids content of the sample. However, this was not the same stress at which the material changed from being shear-thickening to shear-thinning. The data presented in this work indicate that the product exhibits novel rheology, with the presence of both shear-thickening and shear-thinning regions within a thixotropic material that, once broken, rebuilds its structure over a timescale of hours. This poses challenges for certain aspects of plant operation and the behaviour may apply to other structured foodstuffs.

BR-3. Physiological Fluids I

Organizers: James L. Harden and Christoph F. Schmidt
Session Chair: Wendy Krause

Wednesday 9:45 Redwood BR16

Analysis of shear-dependent erythrocyte aggregation characteristics in a microfluidic rheometry

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The aggregation characteristics of red blood cells (RBCs) play an important role in the microvascular flow system and increased RBC aggregation has been observed in various pathological diseases, such as thrombosis and myocardial infarction. The present study investigated shear-dependent aggregation characteristics of RBCs in a microfluidic rheometry. Using a shear-decreasing mechanism, red blood cells passing through microchannel, which are exposed to a wide range of shear stresses, tend to disaggregate and re-aggregate depending on the applied shear stress on RBC aggregates. Backscattered light intensity and shear stress were measured in a microchannel with respect to time. The time recording of the backscattered light intensity (syllectogram) yielded an upward convex curve with a peak point, which reflects the transition from disaggregation- to aggregation processes in the RBC-plasma suspensions. The critical time and critical shear stress corresponding to the peak point, as newly-proposed indexes of aggregation in the present study, were in good agreement with conventional aggregation indices. We found that the new indices could quantitatively represent the aggregation characteristics of RBC-plasma suspensions with variations of fibrinogen concentrations. The present microfluidic application of RBC aggregation offers a quick and easy method in the study of blood rheology and has great potential for point-of-care use.

Wednesday 10:05 Redwood BR17

Modeling the vortical structures in hemodynamics of small vessels and capillaries

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The paper is concerned with the experimental and numerical investigations of biofluids dynamics in micro-branches configurations. The aim of the study is to examine the hemodynamics in vessels of health and mal tissues, in relation to the specific morphological changes in capillaries architecture due to the presence of gastric tumors. Based on the confocal endomicroscopy protocol (the original pictures of vascular tissues are obtained using the in vivo imagines obtained with Confocal Laser Endomicroscope from Pentax at the Fundeni Clinic Institute from Bucharest) the flow geometries are digitally reconstructed and generic capillary branches are obtained for normal and tumoral tissues. From the geometrical point of view the main remarkable difference is the 3D development of branches from the premalign micro-vascularization lesions, in comparison to the almost planar bifurcation of micro-vessels in normal tissues. Experimentally, the flows in two corresponding branches were investigated using a classical microscopic device equipped with a controlled flow rate set-up. The tested geometries are basically planar and curved bifurcations with nominal dimensions in the range of 0.1 mm to 0.5 mm. The investigations are limited to the Reynolds number 1 and the tested samples are weakly elastic polymer solutions. Numerical solutions are obtained for the Newtonian liquid, the shear thinning fluid (Carreau model) and the viscoelastic Giesekus model. The focus of investigation is to model the vortex configuration in a close branches of the analyzed micro-bifurcations, in particular to observe the influences of fluid elasticity and branches curvature on the vortical structure. The study emphasis the differences in local hemodynamics due to capillaries architecture, a geometrical parameter which is straight connected to the evolution of gastric tumors. The results of the present work are used in supporting two hypothesis: (i) the presence of vortical structures in branched capillaries changes qualitatively the mass transfer between the red blood cells and the tissue, (ii) the twisted and curved capillaries are dominant in premalign and malign tissues, this type of local architecture being responsible with the generation of vortical structures at small Reynolds numbers

Wednesday 10:25 Redwood BR18

Flow through evolving porus media, specifically aneurysm, using entropic Lattice Boltzmann method

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Modeling and simulation of blood flow has become an important tool to analyze various biomedical application. In case of “Aneurysm”, a bulge is formed at weaker part of the vein. Blood clotting in the bulge is essential in order to prevent its further growth and thereby avoid lethal consequences. When blood clot is formed it acts as porous media, with blood flowing through it. To understand the phenomena as well as to decide upon appropriate remedy, understanding of blood flow through such an evolving porous medium becomes important. This paper particularly attempts to model the blood flow through the porous media using Entropic Lattice Boltzmann method (ELBM). Lattice Boltzmann has emerged as one of the most powerful tools to simulate complex flows through complex geometries. ELBM has now been suggested to rectify most ills in LBM regarding instability of the method at high Reynolds numbers. We employ an ELBM code and validate against experimental as well as simulation data for “Backward Facing Step” flow. Blood flow thorugh complex evolving porus media is then addressed in the ELBM framework and found to be computationally competitive and superior to existing techniques of simulation for flow through evolving porus media.

Wednesday 10:45 Redwood 💿 BR19

Rheometrical studies of blood clot formation by oscillatory shear, thromboelastography, Sonoclot analysis and free oscillation rheometry

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We report studies of the coagulation of samples of whole human blood by oscillatory shear techniques, including Fourier Transform Mechanical Spectroscopy (FTMS). These techniques are used herein to identify the Gel Point of coagulating blood in terms of the Chambon-Winter Gel Point criterion which provides a rheometrical basis for detecting the establishment of an incipient clot. A comparison of the results of FTMS with those obtained from measurements involving a Thromboelastograph (TEG) and a Free Oscillation Rheometer (FOR) indicate that the latter techniques are not capable of detecting the incipient clot, whose establishment occurs several minutes prior to TEG or FOR-based assessments of clot formation time. The results of the present study suggest that FTMS is a useful tool in blood clotting research, being capable of providing a global coagulation profile in addition to detecting the instant of incipient clot formation.

Wednesday 11:05 Redwood BR20

Rheo-SANS probe of the structure and mechanical properties of fibrin clots

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Small angle neutron scattering (SANS) and ultra small angle neutron scattering (USANS) experiments are used to probe the structure of fibrin networks (clots) over broad length scales (1-20,000 nm). SANS probes the rich internal structure of the fibers (protein arrangement, fiber porosity) while USANS provides valuable information on the structure of the bifurcating fibrin network (correlation length and fiber flexibility). Furthermore, the high penetration capacity of neutrons allows probing of the mechanical properties (rheology) of the clots while simultaneously obtaining structural information from SANS. This powerful feature allows us to correlate directly the structure of these important materials to their unique mechanical properties (elasticity and strain hardening). We will also discuss the changes in the structure and rheology of fibrin networks that are formed in a shearing environment.

Wednesday 11:25 Redwood BR21

Structure and dynamics of the red blood cell cytoskeletal membrane

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This talk will describe recent experimental work using optical tweezers and video tracking, to measure the mechanical viscoelastic properties of biological structures. Results will be reported on the dynamical mechanical properties of human red blood cells, which are one of the simplest types of cells. The quasi-static mechanical modulus of red blood cells has been known for the past 10 years from micropipette experiments, but new experiments with the optical trap allow the dependence of the cell stiffness on the dynamics of deformation to be probed.

Colloidal beads are attached to opposite ends of a blood cell, they are manipulated through the trap to stretch the cell. Both the stress relaxation following a fast deformation, and the effect of varying the strain rate have been experimentally investigated. A power law decay of the stress as a function of time, down to a plateau stress, has been found, and also a power law increase of the cell's elasticity as a function of the strain rate. Interestingly, the exponents of these quantities violate the linear superposition principle, indicating a nonlinear response.

We propose that this is due to breaking of a fraction of the crosslinks during the deformation process. The Soft Glassy Rheology Model accounts for the relation between the exponents we observe experimentally, indicating a similarity between the response of the red blood cell and the nonlinear dynamics in other soft matter systems. This picture is consistent with recent models of bond remodeling in the red blood cell's molecular structure. We have performed experiments over a variety of physiological conditions (age of cell, presence of varying amounts of glucose, availability of additional ATP, and shape of cell), to elucidate the importance of these parameters on the remodelling of the cytoskeleton. The main effect we have seen is the dependence on the age of the cell after it is drawn, with older cells becoming significantly softer.

Aside from the details of the nonlinear deformation model just described, our results show very clearly that the blood cell's mechanical behavior depends strongly on the deformation process, a simple fact that seems to have been overlooked until now.

MP-6. Other Processes

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: Dennis Siginer

Wednesday 9:45 Ferrante I-III MP40

Interplay of inertia and elasticity, enhanced heat transfer and change of type of vorticity in tube flow of nonlinear viscoelastic fluids

Dennis A. Siginer
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The fully developed thermal field in constant pressure gradient driven laminar flow of a class of nonlinear viscoelastic fluids with instantaneous elasticity in straight pipes of arbitrary contour with constant wall flux is investigated. The nonlinear fluids considered are constitutively represented by a class of single mode, non-affine constitutive equations. The driving forces can be large. Asymptotic series in terms of the Weissenberg number Wi are employed to expand the field variables. A continuous one-to-one mapping is used to obtain arbitrary tube contours from a base tube contour. The analytical method presented is capable of predicting the velocity and temperature fields in tubes with arbitrary cross-section. Heat transfer enhancement due to shear-thinning is identified together with the enhancement due to the inherent elasticity of the fluid. The latter is to a very large extent the result of secondary flows in the cross-section but there is a component due to first normal stress differences as well. Increasingly large enhancements are computed with increasing elasticity of the fluid as compared to its Newtonian counterpart. Order of magnitude larger enhancements are possible even with slightly viscoelastic fluids. The coupling between inertial and viscoelastic nonlinearities are crucial to enhancement. The asymptotic independence of Nu = f(Pe,Wi) from elasticity Nu= f(Pe)with increasing Wi is shown analytically for the first time. Isotherms for the temperature field are discussed for non-circular contours such as the ellipse and the equilateral triangle together with the behavior of the average Nusselt number Nu, a function of the Reynolds Re, the Prandtl Pr and the Weissenberg Wi numbers. The physics of the trends of the behavior of Nu with increasing Wi and Pe is governed by the change of type of the vorticity equation. The implications on the heat transfer enhancement of the change of type of the vorticity equation is discussed in particular for slight deviations from Newtonian behavior where a rapid rise in enhancement seems to occur as opposed to the behavior for larger values of the Weissenberg number where the rate of increase is much slower. The asymptotic independence of Nu from elasticity with increasing Wi is related to the thickness of the supercritical region around the tube axis controlled by the interaction of the viscoelastic Mach number M and the Elasticity number E. The physics of the interaction of the effects of the Elasticity E, Viscoelastic Mach M, Reynolds Re and Weissenberg Wi numbers on generating the heat transfer enhancement is discussed.

Wednesday 10:05 Ferrante I-III MP41

Three dimensional flow effects in contraction flows of branched and linear polymer melts

Harley Klein[1], Rosen Tenchev[2], Tim D. Gough[3], Oliver G. Harlen[4], Peter K. Jimack[2], Mark A. Walkley[2], and Tom C. McLeish[1]
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Contraction flows of polymeric fluids have been extensively studied as prototypes for the complex flow fields containing both shear and extension that are encountered during melt processing. The velocity and stress fields in these flows depend critically on the branching topology of the polymers with large upstream vortices observed for polymers with long chain branching. Even greater constrast between materials are seen in the flow induced birefringence, which provides a direct measure of the stress anisotropy. However, unlike fluid velocities that can be measured along the centre-plane, birefringence is determined from an integral across the depth of the channel and so is more susceptible to wall effects. The different molecular physics between branched and linear polymers are captured in recent tube based constitutive models for entangled polymers. The Pompom model accounts for the restriction on reptation due to branching in long chain branched polymers, while the Roliepoly incorporates both reptation and chain stretching in linear polymers. Multimode versions of these models can give good simultaneous fits to both shear and extensional rheology. In this paper we compare flow birefringence and fully 3-d velocity measurements on a branched LDPE and linear polystyrene melts with two and three dimensional calculations of the fluid velocity and birefringence using the Pompom and Roliepoly constitutive models respectively that are fitted to the shear and extensional rheology of the polymer melts. As well as assessing how well these models are able to predict both the velocity and birefringence patterns quantitatively, we also compare two and three dimensional simulations to determine the significance of wall effects. With the three dimensional code we are also able to compare calculated velocities with measurements away from the centre-plane and to calculate the birefringence pattern seen along a plane perpendicular to that of the flow symmetry.

Wednesday 10:25 Ferrante I-III 💿 MP42

Planar extensional viscosity of polystyrene and polystyrene/CO_2 solution

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The planar extensional viscosity of a foaming-grade polystyrene, with and without blowing agent, was determined using a rectangular die consisting of a hyperbolic inlet followed by a high-aspect-ratio rectangular channel. With the hyperbolic geometry, the fluid along the inlet centreline was subjected to a constant rate of extension. The die is 30 mm wide throughout. In the converging section, the cross dimension decreases from 10 mm to 0.8 mm. The 0.8 mm thickness continues in the downstream channel, yielding an aspect ratio of 37 for the rectangular cross-section and generating close to two-dimensional flow in the channel. Three pressure transducers were flush mounted along the die, one immediately before the converging section, one immediately afterward, and one at the downstream end of the channel. The first and second transducers were used to determine the extensional viscosity, and the second and third the shear viscosity. Measurements were made for a range of flow rates. The planar extensional viscosity was found from the difference between the total entrance pressure drop (the pressure difference between the first and second transducers) and the calculated pressure drop due to shearing. The extensional viscosity was calculated as a function of the extensional rate, assuming that this property depends on the extensional rate only. As for the shear viscosity, values of this property determined from flows in the channel compare well with values from commercial rheometers. Values of the planar Trouton ratio were found.

A solution of 5% supercritical carbon dioxide ($scCO_2$) in the polystyrene was prepared using a tandem extrusion system and a high-resolution gas pump. Similar pressure measurements were made for flows of this material in the die. The shear viscosity was found to be lower than that of the polystyrene. From values at different temperatures, a master plot of solution shear viscosity was developed using time-temperature superposition, and this plot was used to subtract shear flow effects in the entrance flow. The planar extensional viscosity was calculated as before, yielding values of the planar Trouton ratio of the foamed plastic melt.

Wednesday 10:45 Ferrante I-III MP43

Simulations of the industrial casting processes of cementitious materials

Nicolas Roussel

LCPC, Paris, France

This paper provides a general overview of the present status regarding computational modeling of the casting of fresh cementitious materials. These materials are thixotropic yield stress fluids, which contains coarse particles, the characteristic size of which is not far from the size of the element to be cast. The computational modeling techniques that can be found in the literature may be divided into three main families: single fluid simulations, discrete particle methods and numerical techniques allowing the modeling of particles suspended in a fluid. The general concept behind each family of techniques is described and examples and references to applications to fresh cementitious materials are given. These methods can be considered as practical tools allowing for the prediction of the industrial casting process. Moreover, they contribute to bringing rheology from research and development into the field of practical civil engineering applications.

Wednesday 11:05 Ferrante I-III 💿 MP44

Numerical simulation and application research on the effect of temperature for deep-drawing process for TC1 Ti alloy sheet

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Press-working of sheet metal is an important part of press-working technology, the process, which is leaded by dies under pressure, is a quite complex physical process. Because of the influence of die's geometry, forming temperature, forming rate, entering angle and pressure-pad-force, wrinkling and splitting usually appears during the processes. In this paper, the numerical simulation of deep-drawing thermo-rheological forming of TC1 titanium alloy was done by using software STAMPACK based on actual production. The influences of forming rate and temperature, to the rectification hood's forming quality are discussed. Two kinds of main invalidation, including wrinkling and splitting are analyzed, so that, it is not difficult to see that both of the forming rate and temperature are important factors for deep-drawing thermo-rheological forming. At the same time, the effective method for heightening flowability of the material is obtained. By analyzing the results of FEM numerical simulation of the thermo-rheological forming process, changing the forming temperature and forming rate of TC1 Ti alloy rectification hood, wrinkling and splitting phenomena are controlled effectively during forming process, and it provides important parameters for its' production. Numerical simulation researching results provided some important variables for module's designing, improved the performance of parts and the qualified ratio of products.

Wednesday 11:25 Ferrante I-III MP45

Thermoforming troughs: Verifying analytical solutions

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Analytical solutions for thermoforming troughs from uniformly thin, highly viscous Newtonian polymer sheets are presented including both free and constrained forming, and these are compared to finite element simulations employing Polyflow(tm). Free forming means before the melt touches the prismatic mold, and constrained forming, afterward. Our study focuses on how quickly forming progresses under a given gas pressure, the driving force for thermoforming. Translating cylindrical coordinates are used to find the developing thickness profile, stress, manufacturing time and the trough's edge sharpness. We employ a dimensionless approach resulting in universal results. Worked examples demonstrate how practitioners can use these results.

CG-1. Slow Dynamics, Aging and Transitions

Organizers: Dimitris Vlassopoulos and Wilson C. Poon
Session Chairs: Peter Schurtenberger and George Petekidis

Wednesday 9:45 San Carlos I CG1

Viscoelasticity, gelation and vitrification of suspensions of nonspherical colloids

Kenneth S. Schweizer[1], Galina Yatsenko[1], and Mukta Tripathy[2]
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The quiescent and mechanically driven slow center-of-mass translational dynamics of glassy isotropic fluids composed of rigid nonspherical objects is studied based on a nonlinear stochastic Langevin equation of motion that includes activated barrier hopping [1]. Suspensions of hard core diatomic, triatomic and spherocylinder shaped colloids of variable aspect ratios are predicted to exhibit ideal kinetic glass transition (simplified mode coupling) boundaries which are distinct nonmonotonic functions of shape anisotropy [2]. Rather remarkably, the ideal nonergodicity boundaries closely resemble the maximum packing fraction jamming behavior of isotropic granular ellipsoids and spherocylinders. A strict nonergodicity transition is avoided by noise-induced activated barrier hopping, and hence the emergence of an ideal glass state signals a dynamical crossover. The consequences of particle shape anisotropy on the entropic barrier height, alpha relaxation time, transient localization length, elastic shear modulus, and yield strain and stress have been determined as a function volume fraction. The magnitude and volume fraction dependences of many properties for different aspect ratio systems collapse reasonably well onto master curves based on a reduced volume fraction variable that quantifies the distance from the ideal glass transition. The theory has also been generalized to systematically investigate the structure, diffusion, relaxation, vitrification and gelation of suspensions composed of objects of one (rods, rings), two (planar disks) and three (e.g. cubes, octadechedron, tetrahedron) dimensional character [3]. For purely excluded volume interactions, the effective object dimensionality is the primary variable controlling the ideal glass volume fraction and entropic barrier height. Subtle effects occur within a fixed dimensionality class (e.g., triangles versus hexagons) which are strongest for the compact 3-dimensional shapes. In the presence of short range inter-site attractions, vitrification competes with gelation, and a re-entrant glass-fluid-gel behavior is predicted at high volume fractions the quantitative aspects of which depend on colloidal shape. Correlations of the slow dynamics with the number of sticky contacts between the nonspherical objects have also been investigated. A new unified understanding of how barriers and relaxation times in colloidal gels depend on local structure, attraction strength and volume fraction has been achieved based on a collisional perspective which suggests analogies with repulsion-dominated glasses.

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Wednesday 10:05 San Carlos I 💿 CG2

Age-dependent relaxation times of soft colloidal suspensions with tunable glassines

Dirk van den Ende[1], Eko Purnomo[1], Siva A. Vanapalli[2], and Frieder Mugele[2]
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We studied both the macro- and micro- rheology of soft thermosensitive microgel suspensions that can be tuned continuously and reversibly between the glassy state at low and the liquid state at high temperature. In the glassy state, the rheological properties (G' , G'' , and J) of the suspensions depend strongly on their age [1,2]. They can be described quantitatively by the soft glassy rheology (SGR) model [3]. The underlying mechanism for the aging is the increase of the structural relaxation time τ as the system ages. However, τ is experimentally inaccessible by small amplitude frequency sweep experiments. Therefore we tested the recently introduced strain rate frequency superposition (SRFS) technique [4] which is based on the idea that relaxation process can be accelerated by applying a larger strain rate amplitude. The evolution of τ as determined with SRFS is remarkably consistent with the predictions of the SGR model based on the linear measurements [5]. This implies that no macroscopic inhomogeneities occur in the sample. To test for microscopic inhomogeneity, the relaxation time τ is also determined from the mean square displacement (MSD) of probe particles, embedded in the system. The MSD values were obtained from particle tracking using a Confocal Scanning Laser Microscope. This technique provides not only the MSD values but also the displacement distributions, which are indicative for heterogeneity of the suspension.

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Wednesday 10:25 San Carlos I CG3

Slow dynamics and ageing in soft colloidal dispersions

Jyoti Seth[1], Roger T. Bonnecaze[1], and Michel Cloitre[2]
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Disordered solid-like materials are ubiquitous in colloidal science. These materials, which have countless applications, include foams, soft particle dispersions like concentrated emulsions and micellar solutions, and colloidal glasses. They share in common a very peculiar dynamics that seems to vary in time and to depend strongly on preparation and measurement history. In fact these time-dependent phenomena exhibit all the main features of ageing in glassy systems. The properties depend essentially on the time elapsed after flow cessation, the so-called "age" of the system and follow universal scaling laws. Although a lot of effort has been spent to characterize the phenomenology of ageing little is known about the physical mechanisms at the origin of ageing.

We shall focus on concentrated dispersions of polyelectrolyte microgels that form soft glasses at high volume fraction. Combining several experimental tools that probe simultaneously the structure and the local dynamics at a local scale (Diffusive Wave Spectroscopy, microrheology and confocal microscopy) with particle dynamic simulations of interacting soft dispersions, we show how the relaxation of trapped internal stresses

following the cessation of flow inside the materials causes ageing. Scaling laws of the ageing and microscopic models of their origins are presented and supported by experimental and computational simulations.

Wednesday 10:45 San Carlos I CG4

Ageing under shear: Effect of stress and temperature field

Asheesh Shukla and Yogesh M. Joshi

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Utter Pradesh 208016, India

In this work we study ageing behavior of soft glasses of aqueous suspension of laponite under oscillatory shear stress of varying magnitude at different temperatures. In order to erase ageing and deformation history of the samples that render them a uniform initial state, a well defined shear melting protocol was employed on the three week old samples. Subsequent stress controlled oscillatory shear experiments show dominating G" at small age, demonstrating the sample to be in the liquid state. As system ages, G' increases with age and eventually crosses G". Increase in the magnitude of shear stress prolongs increase in G' such that the crossover modulus (G' = G") increases exponentially with stress. Interestingly, increase in temperature has an opposite effect to that of shear stress, which tends to accelerate the ageing process. It is generally accepted that in soft glassy (non-ergodic) materials, process of ageing occurs via activated dynamics of constituent elements so as to lower their potential energy with age. At any instance there exists a distribution of potential energy that particles possess, which is also know as energy landscape. Application of deformation field pulls the particle up the potential well and eventually overcomes the same by causing a local yielding event. As applied stress increases, more and more particles undergo local yielding events continuously thereby retarding the ageing process. Increase in temperature decreases relative depths of energy landscape uniformly; however, it accelerates the activated dynamics thereby accelerating the overall ageing process. We propose a simple scaling model based on these ideas to understand the observed behavior. We analyze these results from a perspective of ageing dynamics of soft glassy materials.

Wednesday 11:05 San Carlos I CG5

Rheology of frustrated self-assembly of nano-clay/end-functionalized polybutadiene oligomer gels

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We studied the rheology of gelation, reverse gelation, structural recovery, and ageing of an exfoliated nano-clay/end-functionalized polybutadiene oligomer suspension using time-resolved mechanical spectroscopy, birefringence, and static light scattering. The organo-clay/polymer composite forms a gel upon exfoliation of the clay sheets followed by aggregation. The gelation time was found to significantly decrease with temperature, possibly due to a lowering of energy barriers that would suppress exfoliation. A higher clay concentration also led to faster gelation due to shorter diffusion distances. The self-assembling process is disrupted by the liquid to solid transition so that no long range order can develop. We assumed a gelation process that combines two mechanisms: one is the interaction between the end-functionalized polymer with organo-clay, which is temperature sensitive and a relative fast process. The other is the diffusion of the layered clays, which is concentration sensitive and a relatively slow process. The synergy of the two connectivity mechanisms results in a three-dimensional network structure. The fragile gel structure "melted" upon strong shearing and gradually resumed connectivity upon stopping the shear. The "shear melted" gel could rejuvenate upon moderate shearing at certain temperatures when the interaction between the end-functionalized polymer and the organo-clay surface is strong enough.

Wednesday 11:25 San Carlos I CG6

Soft glassy rheological behavior of smectic liquid crystals in silica gels

Ranjini Bandyopadhyay[1], Dennis Liang[2], Ralph H. Colby[3], James L. Harden[4], and Robert L. Leheny[2]

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Many complex fluid mixtures form soft glassy phases. These phases are distinguished by their novel rheological properties, which include an apparent finite yield stress, thixotropic response to induced flow, and anomalous frequency dependence of viscoelastic moduli. Recent work has suggested that such mechanical properties are associated with metastable, heterogeneous structure in these systems that slowly evolve with time. This talk will present experimental studies of the rheological behavior of the liquid crystal octylcyanobiphenyl (8CB) entrained in colloidal dispersions of aerosil (AS). Aerosil consists of nanoscale silica particles with surface siloxane groups and forms soft hydrogen-bonded thixotropic gels when mixed with 8CB. These AS/8CB gels are rheologically simple in the isotropic and nematic phases of 8CB and dominated by the elastic behavior of the AS network. However, with the onset of smectic order, the magnitude of the linear storage modulus $G'(\omega)$ grows approximately linearly with decreasing temperature, reaching values that exceed by more than 3 orders of magnitude the values for pure 8CB. Associated with this transition is the suppression of collective dynamics of the 8CB, as measured by dynamic light scattering. The storage modulus at low temperatures also possesses a power-law component, $G'(\omega) \sim \omega^{\alpha}$, with an exponent α that approaches zero with increasing gel density, a hallmark of soft glassy rheological behavior. The amplitude of G' and its variation with temperature and gel density suggest that this low temperature response is dominated by a dense population of screw dislocations in the smectic A phase arising from quenched disorder imposed by the presence of the AS dispersion.

SC-5. Yielding and Thixotropy II

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chair: Saad Khan

Wednesday 9:45 De Anza III SC31

A pairwise theory for the rheological properties of soft particle pastes

Roger T. Bonnecaze[1], Jyoti Seth[1], and Michel Cloitre[2]
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Soft particle pastes (SPPs) are composed of deformable particles randomly packed into a dense suspension. Examples soft particles include polymer coated colloids (R~20 microns), polyelectrolyte microgels (R~200 nm) and star polymers (R~10 nm). In spite of the differences in the particle sizes and source of elasticity, all of these materials show similar rheological characteristics and aging behavior. That is, their microstructure and rheological properties change slowly with time without apparent end.

A pairwise interaction theory is developed to predict the elastic moduli, shear stress and normal stress differences of soft-particle pastes. The theory is based on the equilibrium radial distribution function and its perturbation due to flow, which is convoluted with the appropriate elastic and hydrodynamic pairwise interaction to compute the properties of interest. As part of this theory, a methodology is presented to compute a priori the radial distribution function for the quiescent or glassy SPPs based on free volume considerations and energetic constraints. The theory is compared to experimental observations and computational simulations of the viscoelastic properties of the paste, including the effective viscosity, yield stress and normal stress differences. Ageing of the paste is discussed in terms of the evolution of the pairwise distribution function following cessation of flow.

Wednesday 10:05 De Anza III SC32

Exploring origins of yield behavior in nanosuspensions

Xin Li[1], Pouyan E. Boukany[1], Xiaorong Wang[2], and Shi-Qing Wang[1]
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Yield-stress materials are everywhere. Many filled systems including carbon black filled rubbers in tires are structured materials that exhibit jamming characteristics and thus are unable to flow unless sufficient stress is applied to cause yield. The present study applies an effective particle-tracking velocimetric (PTV) method, along with in situ conventional rheometric measurements, to visualize origins of yield behavior in nanosuspensions [Yu and Wang, J. Rheol., 47, 483 (2003)] made of nanoclay particles exfoliated in aqueous media at different loading levels undergoing different types of shear deformation: creep, startup shear, large amplitude oscillatory shear and step strain. Cohesive breakdown is observed to result in the fluidity and nonlinear responses according to our PTV observations. In contrast, a second nano-granular material made of nano-sized polymer spheres show nonlinear behavior without displaying any discontinuous structural response. In other words, our PTV observations of polymer gels made of nanospheres reveal no shear inhomogeneity although the sample responds nonlinearly to external deformations of various types. Thus, these two model systems illustrate the two extremes where PTV observations play an important role in revealing to actual responses of these highly elastic structured fluids.

Wednesday 10:25 De Anza III SC33

Microstructures and mechanical properties of dense particle gels: Microstructural characterization

Iwan Schenker[1], Frank T. Filser[1], Tomaso Aste[2], and Ludwig J. Gauckler[1]
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The use of an internal gelation method (DCC = Direct Coagulation Casting [1]) permits to control the microstructure of densely packed gels with solids contents up to 60 vol%. It allows for an in situ and thereby undisturbed development of gel microstructures by either shifting the pH of the solution to the isoelectric point or by increasing the ionic strength. The first method results in homogenous, the second one in heterogeneous microstructures [2,3]. Heterogeneous microstructures express up to ten times higher elastic properties than their homogeneous counterparts [4,5].

Our goal is to correlate the microstructural differences to the different macroscopic mechanical properties. For this we've developed a new way to characterize the microstructures. The "straight path" method characterizes quasi-linear arrangement of contacting particles. We've applied this method to homogeneous and heterogeneous microstructures generated by Brownian dynamics simulations [6]. The straight path statistic presents important differences between homogeneous and heterogeneous microstructures: heterogeneous colloidal microstructures have a significantly higher straight paths density and exhibit longer straight paths than their homogeneous counterparts.

These differences in straight path number and length are suitable to differentiate between these structures possessing highly different mechanical properties. The number of straight paths follows an exponential distribution similar to the distribution of the force chain lengths in mechanically loaded granular material. The quasi-linear structures of the straight paths correspond to the geometrical shape of force chains that are well known to determine the load bearing capacity of granular matter. We conclude that the straight paths may capture best the characteristic microstructural features which are relevant for the mechanical properties of destabilized colloidal suspensions.

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Wednesday 10:45 De Anza III SC34

Very concentrated plate-like kaolin suspensions under large amplitude oscillatory shear: A microstructural approach

Frederic Bossard[1], Michel Moan[2], and Thierry Aubry[2]

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Very concentrated kaolinite suspensions (f > 0,4) undergoing large amplitude oscillatory shear (LAOS) are known to exhibit a peculiar nonlinear viscoelastic behavior, characterized by a hump in G" modulus, whose microscopic origin is still a matter of debate.[1-3] In this work, a microstructural interpretation of this nonlinear behavior is proposed.[4] For this purpose, the viscoelastic behavior of suspensions has been investigated as a function of volume fraction, ionic strength and in the presence of polymer at various concentrations, in order to monitor the influence of both the nature and the intensity of interparticle interactions. The cohesive energy density Ec and the intensity of the strain hardening in G" are greatly enhanced by increasing volume fraction and decreasing ionic strength. From a microstructural point of view, the strengthening of cohesion has been attributed to the combined increase of excluded volume and repulsive electrostatic interactions between neighboring particles. The increase of the strain hardening in G" modulus may originate from an increase of both electro-viscous dissipation, through the deformation of the diffuse charge clouds surrounding particles, and excluded volume interactions, induced by the significant fluctuation of the inter-particle distance in the nonlinear regime. In the presence of polymer, additional interactions of bridging, steric and lubrication type, appear. Adsorption measurements have been performed to estimate the saturation concentration, corresponding to the total coverage of kaolinite particles by polymer chains. The increase of Ec and of the strain hardening in G" is favored by bridging and steric interactions of confined polymer chains, while the presence of non-adsorbed chains induces lubrication effects that weaken the intensity of the hump in G".

[1] Jogun, S. M et al, J. Rheol. 40, (1996); [2] Jogun, S. M. et al, J. Rheol. 43, (1999); [3] Yziquel, et al, J. Non-Newtonian Fluid Mech. 86, (1999); [4] Bossard et al., J. Rheol. 51, (2007).

Wednesday 11:05 De Anza III SC35

Transition pathways between solid and liquid states of dense suspensions in transient and oscillatory shear flows

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Suspensions containing rigid monodisperse spherical particles in a Newtonian carrier liquid are investigated experimentally, providing evidence for solid and liquid states in transient controlled shear rate (TCSR) experiments from rest [1] and in CSR oscillatory shear flows. In TCSR experiments it has been found that between solid and liquid states a transition takes place; the transition pathways from solid to liquid and from liquid to solid being different. The dynamics of the transition are shown, with the material in this regime reacting as a highly nonlinear system. A key feature of the transition regime is an intrinsic material instability with a negative slope of the flow and deformation curves in a certain range of shear rates and shear strains, respectively. The instability is caused by a collapse of the particle network structure due to shear.

CSR oscillatory shear experiments for suspensions with various solid volume concentrations have been carried out with varying shear strain amplitudes and angular frequencies. The raw input strain and stress response signals were analyzed by the method of Fourier transform rheology. At low amplitudes only the fundamental frequency component is relevant. At higher shear strain amplitudes the intensity of the higher harmonic overtones increases and reaches a maximum at a given shear strain amplitude. In this case, the whole frequency spectrum must be taken into account to calculate the complex modulus. Comparison of this result with that of the TCSR experiments shows that the amplitude range of maximum non-linearity corresponds to intrinsic material instability region in TCSR experiments. Finally, the differences between the moduli obtained from the linear theory and the moduli calculated from the whole frequency spectrum are shown.

[1] L. Heymann, N. Aksel, Transition pathways between solid and liquid states in suspensions Phys. Rev. E **75**, 021505 (2007).

SC-6. Suspension Hydrodynamics I

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Nina C. Shapley and Chongyoup Kim

Wednesday 9:45 Portola SC37

Microrheological origins of the irreversible flow of suspensions

Shihai Feng[1], Alan Graham[1], Cynthia Heath[1], Patrick Reardon[1], and Marc Ingber[2]

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The hydrodynamic behavior observed for a sphere released under gravity in a Newtonian liquid is not consistent with that predicted by classical continuum theory when the sphere is near a solid wall. An irreversibility arises in the velocity of the sphere as it approaches and recedes from the plane that cannot be accounted for using continuum hydrodynamic equations alone. Earlier experiments on spheres falling from a plane were conducted under conditions such that this irreversibility could be attributed to the surface roughness of the spheres In this investigation, we extend these studies to situations where the pressure field between the receding sphere and the plane drops to the vapor pressure of the fluid and cavitation occurs. Experimental data support the theoretical prediction for a sphere's motion based on the irreversible effect of cavitation and physical roughness in different flow regimes. The effects of these near-contact irreversibilities on particle trajectories, shear-induced self diffusion, and particle migration in concentrated suspensions are discussed.

Wednesday 10:05 Portola SC38

The effect of shear on the size distribution in concentrated suspensions of non-neutrally buoyant vesicles

Arun Ramachandran and Gary Leal

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It is well known that when a suspension of vesicles of size 100 nm or smaller is synthesized, the size distribution of the vesicles does not remain steady with time; rather, it changes over a time scale that can vary from days to several months. This change in the size distribution has a special implication for non-neutrally buoyant vesicle systems in that a shift towards larger vesicle sizes leads to a greater propensity for vesicles to phase separate from the suspending fluid on account of gravity. This is highly undesirable for most vesicle related applications since these require spatially homogeneous suspensions. There are two hypotheses in the literature to explain this phenomenon. The first suggests that the evolution of the size distribution follows a thermodynamic route, presumably involving the exchange of surfactant between vesicles and the surrounding aqueous medium. Most processes for synthesizing vesicles such as lipid film hydration, ethanolic lipid injection in aqueous buffer and reverse phase evaporation result in vesicles that are in kinetically trapped states and tend to shift towards the equilibrium distribution. The second pathway is based on collisions between the vesicles. By the term collision here, we imply an encounter that brings vesicles into the range of non-hydrodynamic attractive (or repulsive) forces. For a non-neutrally buoyant vesicle suspension, such collisions may result from Brownian motion, relative gravitational motion between different sized particles, and any imposed shear in the system. These "collisions" between the vesicles may lead to an evolution in the size distribution due to the formation of larger structures such as fused systems or aggregated clusters, which depends on the rate and efficiency of these collisions in bringing about aggregation or fusion.

In this paper, we investigate this aging of vesicle suspensions with and without shear, as a function of the initial vesicle size, the levels of salt and non-adsorbing polymer, and the surfactants that constitute the bilayer. The basic objective of adding shear is to provide a basis for a controlled collision rate that can be enhanced significantly relative to that due to differential sedimentation and diffusion. If we hypothesize that the coarsening of a vesicle suspension to vesicles of larger sizes via fusion or cluster formation is a crucial component of their ultimate instability, these experiments will allow us to speed up the process, thus shrinking a long-term aging event to a shorter time-scale. The system that we have initially pursued to perform the shear cell studies is the Couette cell geometry designed with sampling ports along its height. The samples extracted at regular intervals of time are analyzed using differential interference contrast microscopy and light scattering, thus providing data on both the spatial and temporal evolution of the size distribution. These results will be discussed during the talk.

Wednesday 10:25 Portola SC39

Dimensionnal effect on viscosity of a confined suspension

Philippe Peyla, Yohann Davit, and Claude Verdier

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In this work, we study experimentally and numerically the viscosity of non-brownian confined suspensions of hard spherical particles confined between two walls in a shear flow. By varying the wall-to-wall distance (gap), we show that the viscosity presents a remarkable behavior as a function of the confinement. A transition occurs from a 3D configuration (no confinement) to a quasi2D (Q2D) one when the wall-to-wall distance becomes smaller than twice the spheres diameter. We find, as expected, that the effective viscosity increases when the gap decreases. This is due to dissipation which is enhanced for smaller gaps. But, more precisely, when the wall-to-wall distance decreases, the linear term in volumic fraction (diluted case) increases while the quadratic term decreases to zero when the suspension reaches a Q2D regime and becomes negative for smaller gaps. In a Q2D suspension, it is proven that an anti-drag effect holds between two particles which move perpendicularly to their connecting line. Experimental measurements on diffusion coefficients have been achieved for colloidal Q2D suspensions by Cui et al [1] which shows this behavior without any ambiguity. We suspect that such anti-drag interactions can affect the viscosity of Q2D semi-diluted suspensions. Especially, it could explain the fact that the quadratic term becomes negative for strong confinements.

[1] B. Cui, H. Diamant, B. Lin and S. Rice, Phys. Rev. Lett., vol. 92, 258301 (2004)

Wednesday 10:45 Portola SC40

The coagulated behavior of latex particles in a seed coagulation

Masatsugu Fukui, Takashi Ueda, Yoshiyuki Komoda, Hiroshi Suzuki, and Hiromoto Usui

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In manufacturing process of submicron order latex particles, the collection procedure is one of the most important technologies, since the coagulate of latex particle containing much water requires a severe drying condition. When applying a seed coagulation technology to this process, latex particles are coagulated on the surface of the seed particle, which is much larger than a latex particle, and form a shell on its surface. As a result, the large seed coagulate with low water content is produced and it can improve the efficiency of the dehydration and drying processes. In this coagulate process, however, a homo-coagulation of latex particles and a hetero-coagulation between latex and seed particles progress simultaneously, and thus the detail of the coagulation mechanism has not been well clarified yet. It has recently found that the extent of homo-coagulation of latex particle may have a significant relationship with the seed coagulation. In this study, we investigated the effect of the liquid temperature and flow intensity on a behavior of homo-coagulation of latex particles, and the same time we proposed the procedure to predict the size of latex coagulate by the use of viscosity of latex particle suspension. We also discuss the relationship between the size of latex cluster and seed coagulate. Latex particles with the size of 0.2um in diameter formed a primary coagulate with the addition of coagulant and PVA, and they had a relatively narrow size distribution around 10um. And in a suspension of water and latex particles, the higher order coagulate (cluster) was constructed by primary coagulates and their size significantly depended on the liquid temperature and mixing speed. The size of the cluster increased when the liquid temperature was more than 60C probably because the surface of the latex particle may be soften at that temperature. On the other hand, at a high mixing speed the cluster was not increased so much in spite of high temperature. It suggested that the effect of shear break-up of cluster surpassed that of shear coagulation under a turbulent fluid flow. Then we have estimated an inter-particle bonding energy by applying the suspension viscosity to the thixotropy model proposed by Usui. It was found that the particle interaction had a strong relationship with the liquid temperature and it increased drastically at a higher temperature than 60C as well as the size of cluster. Furthermore, the size of cluster corresponding to apparent shear rate in a mixing vessel calculated by inter-particle bonding energy showed good agreement with the experimental results at a moderate mixing condition. At the condition of a high mixing speed, however, at a turbulent flow region, the actual cluster size was a little smaller than prediction probably due to the effect of cluster break-up by turbulence.

Wednesday 11:05 Portola SC41

Fundamental pair interactions and applications for colloidal silica particles by coarse-grained simulations

Cheng K. Lee and Chi C. Hua

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In the first part of this presentation, we introduce how the fundamental pair interactions for colloidal silica particles may be constructed from a self-consistent mapping procedures and coarse-grained simulations without introducing any adjustable parameter. Force fields for silica particles with diameter ranging from 1 nm to 100 nm are reported and tabulated in a simple analytical form. In the second part, we describe how the previously obtained force fields may be utilized for modeling rod-like colloidal systems. Focus is on exploring the effects of force field and particulate aspect ratio on the thermodynamic and rheological properties.

Wednesday 11:25 Portola SC42

Rheology of semi-dilute suspensions of rigid ellipsoids at high Peclet numbers

Joontaek Park, Hyun-Ok Park, Jonathan M. Bricker, and Jason E. Butler

Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

The rheology of semi-dilute suspensions of rigid particles with high aspect ratios have classically shown shear thinning behavior in the limit of large Peclet numbers. Experiments reported here on the rheology of polystyrene ellipsoids of moderate aspect ratios and at semi-dilute concentrations also exhibit significant shear thinning. However, rationales typically used to explain the shear thinning behavior are eliminated in these experiments. The ellipsoids are rigid, with no effects of flexibility as expected for even very stiff materials with high aspect ratios. The ratio of the rheometer gap to the ellipsoid length is also relatively large. Most importantly, the shear thinning probably does not occur due to adhesion between particles, as demonstrated by direct comparison between ellipsoids of different aspect ratios and spheres using identical materials. Recent theoretical and computational findings which may elucidate the origins of the observed shear thinning are also presented and discussed.

CF-7. Computational and Multiscale Modeling 2

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Antony N. Beris

Wednesday 9:45 Steinbeck CF46

Studies on contraction flows and pressure-drops: Extensional viscosity and dissipative stress effects

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One of the specific features of interest in contraction flows is the study of pressure-drops, covering various geometric configurations and fluid rheology. Provocatively, experimental observation on 'excess pressure-drop' for severe strain-hardening Boger fluids of practically constant shear-viscosity, has revealed significant enhancement above Newtonian fluids in axisymmetric but not planar configurations geometries. Yet, this discrepancy has eluded prediction in contraction flows, for all relevant viscoelastic models and numerical schemes. Hence, in this paper, we explore the ability of network-type models (Phan-Thien/Tanner PTT) and kinetic-based models (pom-pom) to reflect enhanced pressure-drops in contraction/expansion flows (ratio 4:1:4). This is contrasted against counterpart contraction flows. Severe strain hardening is captured through suitable parametric control, whilst ensuring strong suppression of shear-thinning properties, to approximate those of typical solvent-dominated Boger fluids. This advances upon our prior work with Oldroyd models. In this fashion, a rising trend for enhanced pressure-drop versus Weisenberg number is identified. The position in further contrasted against that for dissipative stress models, where both inelastic and viscoelastic models are introduced with uprising outcome. The numerical techniques adopted follow a hybrid finite element/volume algorithm of incremental pressure-correction time-stepping structure. Novel features are posed with respect to discrete treatment of pressure terms, time discretisation and handling of velocity-gradient data.

Wednesday 10:05 Steinbeck CF47

Viscoelastic flow through gradual contractions: Experiments and simulations

Fiona L. Keegan[1], Marcel P. Escudier[1], Manuel A. Alves[2], and Robert J. Poole[1]

[1]Department of Engineering, University of Liverpool, Liverpool, UK; [2]Dep. Chemical Eng., Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal

In this paper we present a combined experimental and numerical study of the flow of polymer solutions through smooth planar gradual contractions. Although viscoelastic flows through sudden contractions have been widely studied, and are one of the classic benchmark problems in computational rheology, flows through gradual contractions, with cross-sectional shapes similar to a wind-tunnel contraction for example, have received very little attention. Our motivation for the current work stems from our earlier work on flow through gradual-contraction/sudden-expansion geometries (Poole et al [1,2]) where extremely large, and unexpected, velocity overshoots were observed close to the sidewalls in the contraction section. The shape of the velocity profiles was such that we called the effect "cat's ears". Although we have had limited success simulating the phenomena [2] using the linear form of the Phan-Thien and Tanner model [3], the calculated overshoots were always much smaller than those observed experimentally. In the current paper we discuss a simplified version of the problem, removing the sudden expansion and the resulting geometric singularity, with the aim of clarifying the mechanism responsible for the cat's ears effect. We report new experimental results, primarily velocity profiles obtained using laser Doppler anemometry, for a range of aqueous solutions of a polyacrylamide solution ($c/c^* \sim 1$, 1.7 and 10) flowing through a planar gradual contraction of area contraction ratio eight. Our results once again exhibit large velocity overshoots confirming that the expansion is not responsible for their appearance.

In addition to the new experimental results, we report on the results of a systematic three-dimensional numerical investigation to provide complementary insight into the flow. We make use of a finite-volume technique, together with the high resolution 'CUBISTA' scheme for the convective terms in the constitutive equations [4], to study the flow of the UCM and Oldroyd-B models and the linear form of the PTT model in the geometry. We are able to show that the modified geometry enables higher Deborah numbers to be obtained than in our previous study and significant velocity overshoots to be predicted.

R J Poole, M P Escudier and P J Oliveira, Laminar flow of a viscoelastic shear-thinning liquid through a plane sudden expansion preceded by a gradual contraction. Proc Roy Soc London Series A. 461 (2005) 3827; R J Poole, M P Escudier, A Afonso and F T Pinho, Laminar flow of a viscoelastic shear-thinning liquid over a backward-facing step preceded by a gradual contraction. Physics of Fluids 19, 093101 (2007; N Phan-Thien, R I Tanner, A new constitutive equation derived from network theory, J Non-Newt Fluid Mech 2 (1977) 353; M A Alves, P J Oliveira and F T Pinho, A Convergent and Universally Bounded Interpolation Scheme for the Treatment of Advection, Int J Num Meth Fluids 41 (2003) 47.

Wednesday 10:25 Steinbeck CF48

Experimental and computational evaluation of polymer flow for increasing aspect ratio geometries in two complex flows

David G. Hassell, T D. Lord, and Malcolm R. Mackley
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The ability to predict the three dimensional behaviour of polymer melts when subjected to both shear and extensional flow is important for the design and scale up of industrial processes. In this work, an extensive study is presented outlining experimental observations of Principal Stress Difference (PSD) in increasingly three-dimensional flow and the subsequent comparison to both two and three-dimensional simulations. Three different polymers were used, a monodisperse polystyrene, polydisperse polystyrene and a high density long chain branched polyethyelene, which exhibit different characteristics during flow. Using a Multi-Pass Rheometer, small quantities of polymer were subjected to flow through a Cross-Slot and contraction-expansion slit geometry, which exhibit regions of both high shear and high extensional flow. Three optical depths were used for each geometry, which provided slit width/cross-slot entrance width to depth aspect ratios of approximately 7:1, 5:1 and 1:1. The observed PSD for the polymers in both geometries illustrated a progressive development from three-dimensional to increasingly two-dimensional flow as the aspect ratio was increased. The effect of this increasing three-dimensionality of the flow on such features as stress fangs in the contraction-expansion slit and W cusps along the outlet centreline in the cross-slot was also quantified. Subsequent comparisons were made between the experimental results and two finite element solvers, a Langrangian 2D and Eulerian 3D code. Due to the diverse range of materials interrogated, both the POM-POM and ROLIE-POLY constitutive models were used to compare against experimental data for the branched and linear materials respectively. A qualitative and quantitative analysis was carried out to evaluate the success of the two codes in accurately capturing the stress development in both linear and branched materials, and identify the differences between the two and three dimensional flow results. This work provides a robust set of experiments in both two and three dimensional flow using well characterised linear and branched materials for the comparison with predictive software.

Wednesday 10:45 Steinbeck ⊛ CF49

Measurement and modelling of high density polyethylene melt extrudate swell

Timothy M. Nicholson[1], Michael T. Martyn[2], and Tom C. McLeish[3]
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The extrudate swell behaviour in two grades of high density polyethylene, one with long chain branching and one linear, and for comparison, a low-density polyethylene melt were measured and the results compared with finite element modelling using the Pom-Pom and Roliepoly constitutive equations implemented in a Lagrangrian solver. The simulations throw into sharp focus the delicate nature of the final extrudate swell observed in a given experiment. The four physical processes of deformation-induced elasticity, downstream convection, surface tension and skin-formation on cooling play against each other in different ways as the extrusion rate changes.

The Pom-Pom model, devised for branched polymers showed a remarkably good quantitative prediction of extrudate swell for the LDPE and branched HDPE over an order of magnitude in shear rate with increasing deviations at the highest rates occurring as the information-content on correspondingly high-rate processes within the models reduces.

The Pom-Pom model also was quite successful in modelling the linear HDPE. This suggests that decoupling of orientation and stretch degrees of freedom, true of all entangled polymers, branched and linear, is the really essential step in creating a good viscoelastic model for polymer melts. Once q is set to 1 in the Pom-Pom model, we have a reasonable (if over shear-thinning) model for a linear melt. The Roliepoly model, developed for linear polymers should do a better job at predicting the behaviour of these polymers; however this is dependent on obtaining good parameters. The polydisperse nature of these polymers may also mean that the Roliepoly model, derived for a monodisperse melt, may not be any more accurate that a multi-mode Pom-Pom model for commercially polydisperse melts.

Wednesday 11:05 Steinbeck ⊛ CF50

Numerical and experimental studies on extrudate swell of linear and branched polyethylenes

Vivek Ganvir[1], B P. Gautham[1], Rochish M. Thaokar[2], and Ashish Lele[3]
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Accurate prediction of extrudate swell is important for several polymer melt processing unit operations since this helps in cutting down manufacturing costs of complicated dies such as those required in a profile extrusion process. Extrudate swell prediction has shown significant difficulties due to two key reasons. The first is the appropriate representation of the constitutive behavior of the polymer melt. The second is regarding the simulation of the free surface, which requires special techniques in the traditionally used Eulerian framework. We have simulated extrudate swell using an Arbitrary Lagrangian Eulerian (ALE) technique based finite element formulation.[1] In the present work we compare our ALE simulations with experimental data on the extrudate swell of commercial grade HDPE, LLDPE and LDPE resins. The resins were characterized for their rheological behavior in both shear and uniaxial extension. The polymers were extruded from a capillary under isothermal conditions and the extrudates were observed on-line using a video camera. ALE simulations were performed using phenomenological constitutive models (PTT) and molecular constitutive models like eXtended Pom-Pom (XPP) for branched (LDPE) and Rolie-Poly for linear (HDPE) polymer melts.

[1] Ganvir et al, Presented at XV IWNMNNF 2007 at Rhodes, Greece

Wednesday 11:25 Steinbeck CF51

Dynamics of branched polymer melts in complex kinematics flows: A computational/experimental study

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In this study large scale numerical simulations are coupled with flow visualization and flow induced birefringence measurements to evaluate the performances of the multi-mode Giesekus model in predicting the flow behavior of a rheologically well characterized branched polymer melt in a prototypical processing geometry. Specifically, we have performed extensive finite element flow simulations of a low density polyethylene (LDPE) melt in a cross-slot channel. The simulation results have in turn been compared with experimental measurements of the kinematics and flow induced birefringence in a novel cross-slot channel rheometer, whose front and back viewing windows are lubricated to eliminate end effects as well as undesirable temperature gradients. A detailed comparison of computational and experimental results has revealed that the multimode Giesekus model can accurately capture the flow characteristics at low to moderate Weissenberg numbers (Wi). However, simulation results at high Wi are at best qualitative. The failure of the simulations in quantitatively predicting the flow behavior close to the stagnation point at high Wi is partly attributed to the inaccuracy of the experimental data resulting from multiple orders of retardation occurring within the measurement volume as well as lack of precise control over the lubrication film dynamics. Based on these observations various avenues for improving the lubricated cross-slot channel rheometer are outlined.

GA-1. Collisional Flows and Inelastic Gases

Organizers: V Kumaran and Melany Hunt
Session Chair: James T. Jenkins

Wednesday 9:45 Bonsai III GA1

Extended kinetic theory for dense inclined flows

James T. Jenkins[1] and Diego Berzi[2]

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We adopt an extension of the kinetic theory for dense shearing flows that involves a length scale in the rate of collisional dissipation that is associated with particle clusters [1,2] and apply it to dense flows down inclines. We compare the predictions of the theory for inclined flows over rigid, bumpy boundaries and the surface of erodible heaps with the results of physical experiments [3,4] and numerical simulations [5].

[1] J.T. Jenkins, Phys. Fluids. 18, 103307 (2006); [2] J.T. Jenkins, Gran. Matt. 10, 47 (2007); [3] O. Pouliquen, Phys. Fluids 11, 542 (1999); [4] P. Jop, et al., J. Fluid Mech. 541, 167 (2005); [5] Silbert, et al., Phys. Rev. E 64, 051302 (2001).

Wednesday 10:05 Bonsai III GA2

Fluctuations and response in granular gases: Validity and failure of Einstein relation

Andrea Baldassarri, Andrea Puglisi, and Angelo Vulpiani

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The linear response in different models of driven granular gases is studied. In some situations, even if the the velocity statistics can be strongly non-Gaussian, we do not observe appreciable violations of the Einstein formula for diffusion versus mobility. The situation changes when strong correlations between velocities and density are present: in this case, although a form of fluctuation-dissipation relation holds, the differential velocity response of a particle and its velocity self-correlation are no more proportional. This happens at high densities and strong inelasticities, but still in the fluid-like (and ergodic) regime.

A. Puglisi, A. Baldassarri and A. Vulpiani. Violation of the Einstein relation in Granular Fluids: the role of correlations. Journal of Statistical Mechanics: Theory and Experiment, P08016, 2007

Wednesday 10:25 Bonsai III GA3

Does the Chapman-Enskog expansion for viscous granular flows converge?

Andres Santos

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The fundamental question addressed in this work is whether the partial Chapman-Enskog expansions $P_{xy}=-\Sigma_k \eta_k (du_x/dy)^{2k+1}$ and $P_{xx}-p=-\Sigma_k \eta_k' (du_x/dx)^{k+1}$ of the shear stress P_{xy} and the normal stress difference $P_{xx}-p$ converge or not for a gas of inelastic hard spheres. By using a solvable kinetic model it is shown that, in contrast to the elastic case, the above series do converge, the corresponding radii of convergence increasing with inelasticity. It is argued that this paradoxical conclusion is not an artifact of the kinetic model and can be understood in terms of the time evolution of the scaled velocity gradients in the simple shear and longitudinal flows, respectively.

Wednesday 10:45 Bonsai III GA4

Segregation in moderately dense granular binary mixtures

Vicente Garzo

Departamento de Fisica, Universidad de Extremadura, Badajoz, Spain

Segregation and mixing of dissimilar grains is perhaps one of the most interesting problems in agitated granular mixtures. Although several mechanisms have been proposed, the problem is not completely understood. Among the different competing mechanisms, thermal diffusion becomes one of the most relevant mechanisms at large shaking amplitudes. In this presentation, the thermal diffusion factor of a granular mixture in a gravitational field is determined from a recent hydrodynamic solution [1] of the Enskog kinetic theory that applies for strong dissipation and moderate densities. The knowledge of thermal diffusion allows us to find a criterion for segregation that involves all the parameters of the granular mixture: composition, masses, sizes, and coefficients of restitution. The intruder limit case is considered here in detail, showing both the Brazil-nut effect and the reverse Brazil-nut effect by varying the diameter and mass ratios, the density and the inelasticity. The present results extend previous attempts derived in the intruder limit case in the absence of thermal gradients and are also consistent with recent experimental results.

[1] V. Garzó, J. W. Dufty and C. M. Hrenya, Phys. Rev. E 76, 031303 (2007); V. Garzó, C. M. Hrenya and J. W. Dufty, Phys. Rev. E 76, 031304 (2007).

Wednesday 11:05 Bonsai III GA5

Rheology of dense sheared granular flows

V Kumaran

Department of Chemical Engineering, Indian Institute of Science, Bangalore, India

Rapid granular flows are defined as flows in which the time scales for the particle interactions are small compared to the inverse of the strain rate, so that the particle interactions can be treated as instantaneous collisions. We first show, using Discrete Element simulations, that even very dense flows of sand or glass beads with volume fraction between 0.5 and 0.6 are rapid granular flows. Since collisions are instantaneous, a kinetic theory approach for the constitutive relations is most appropriate, and we present kinetic theory results for different microscopic models for particle interaction. The significant difference between granular flows and normal fluids is that energy is not conserved in a granular flow. The differences in the hydrodynamic modes caused by the non-conserved nature of energy are discussed. Going beyond the Boltzmann equation, the effect of correlations is studied using the ring kinetic approximation, and it is shown that the divergences in the viscometric coefficients, which are present for elastic fluids, are not present for granular flows because energy is not conserved. The hydrodynamic model is applied to the flow down an inclined plane. Since energy is not a conserved variable, the hydrodynamic fields in the bulk of a granular flow are obtained from the mass and momentum conservation equations alone. Energy becomes a relevant variable only in thin 'boundary layers' at the boundaries of the flow where there is a balance between the rates of conduction and dissipation. We show that such a hydrodynamic model can predict the salient features of a chute flow, including the flow initiation when the angle of inclination is increased above the 'friction angle', the striking lack of observable variation of the volume fraction with height, the observation of a steady flow only for certain restitution coefficients, and the density variations in the boundary layers.

Wednesday 11:25 Bonsai III GA6

Experimental study of the freely evolving granular gas under microgravity condition

Soichi Tatsumi, Yoshihiro Murayama, and Masaki Sano

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In spite of many theoretical and numerical studies, there are few experimental works on freely evolving granular gas. We made an ideal state for freely evolving granular gas in experiments[1]. Key feature of our experiment is microgravity condition produced by parabolic flight (by Diamond Air Service Co. Ltd.), which allows us to reduce the effect of frictional force, and we can realize an ideal granular gas state governed by only inelastic collisions between working granules. Zirconium beads (d = 1 mm) were confined in a quasi-2D cell, which was vertically vibrated. After stopping the vibration, we observed freely evolving processes.

We focused on three physical quantities, **1)** energy decay which corresponds to the evolution of the granular temperature defined by mean square velocity, **2)** velocity distribution function (VDF), and **3)** cluster formation which is related with the inhomogeneity of the system. In early stage of the evolution the energy decay obeys Haff's law[2], and the obtained VDF agrees with the theoretical predictions (Poschel and Brilliantov[3]). In the later stage, however, both the energy decay and the VDF differ from those theories since a cluster formation cannot be ignored. These results provide us new insights into further understanding of freely evolving granular gas.

[1] Experimental Study of the Kinetics of the Granular Gas under Microgravity, Soichi Tatsumi, Yoshihiro Murayama, Masaki Sano, *to be submitted,* 2007; [2] Grain flow as a fluid-mechanical phenomenon, P. K. Haff, *J. Fluid Mech.*, **134**, 401-430, 1983; [3] Kinetics of The Granular Gas, N. V. Brilliantov and T. Poschel, *Oxford University Press*, 2003.

EM-4. RheoOptics/NMR

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: Norbert Willenbacher

Wednesday 9:45 De Anza I EM22

Rheo-NMR of rapidly evolving fluid systems

Michael L. Johns

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Rheo-NMR techniques have been extensively applied to a range of rheologically interesting materials and typically provide unique information by combining NMR's ability to produce spatially resolved velocity maps with structural quantification at a range of length-scales ranging from the molecular to the meso-scale. Typically however, due to acquisition time constraints, such measurements are limited to flow structures and systems at equilibrium, or that are evolving relatively slowly. A particular strength of our research group however is the application of both novel and rapid Magnetic Resonance (MR) techniques for imaging, velocimetry and self-diffusion measurement; here we apply these to Rheo-NMR. In particular we will show how rapid MR measurements are able to accurately image droplet deformation, rupture and coalescence in opaque sheared samples by compensating for any image distortion due to object rotation. We will also show how the rapid measurement of droplet size distributions (based on self-diffusion measurement) is possible for emulsions/dispersion being sheared (this requires the inclusion of velocity compensation into the measurement protocol), and the subsequent quantification of droplet migration in such shear fields for emulsions/dispersions at a range of dispersed phase concentrations (1). With respect to rapid measurement of velocity fields, various results will be presented for the time resolved measurement of velocity fields during start-up, shut down and oscillatory shear for a range of Rheo-NMR geometries and materials, including emulsions, shear banding fluids and particle dispersions. A temporal resolution of 5 ms will be demonstrated and potential for further improvement discussed. The presentation will conclude with some examples of extrapolation of these techniques to typically process geometries including screw extruders and mixing cells.

(1) Hollingsworth, K.G. and Johns, M.L. (2006), Droplet migration in emulsion systems measured using MR methods, Journal of Colloid and Interface Science, 296(2) 700-709.

Wednesday 10:05 De Anza I EM23

Simultaneous oscillatory rheology with dynamic light scattering-echo

George Petekidis
IESL, FORTH, Heraklion, Crete, Greece

The understanding of the behavior of several concentrated soft matter systems such as glasses, gels and pastes under shear would significantly benefit by simultaneous measurements of their macroscopic mechanical properties and their microscopic structure and dynamics. To this end we have constructed a novel set-up that combines a strain controlled rheometer (ARES-Rheometrics) with dynamic light scattering (utilizing both single and multispeckle detection), implementing the technique of LS-echo, utilized so far with home made shear cells [1], on a conventional rheometer. We use this set-up in order to get simultaneous measurements of the visco-elastic properties of turbid colloidal systems under oscillatory shear in the linear and non-linear regime and of the scattered intensity correlation function in the backscattering geometry. In this way their viscolelastic properties during shear induced melting (yielding) may be measured simultaneously with shear induced particle rearrangements on the scale of a particle radius or less. Microscopic dynamics of the sample under oscillatory shear is followed through the correlation function formed by the peaks of the echoes, subtracting in this way the trivial effects of affine motion that would otherwise complicate the analysis. Hence, shear induced irreversible particle rearrangements can be quantitatively measured and average shear induced diffusion coefficients can be determined as a function of strain amplitude and frequency. These microscopic quantities are then discussed in relevance with macroscopic viscoelastic properties for glasses of hard and soft sphere particles.

[1] G. Petekidis, A. Moussaïd, P.N. Pusey, Phys. Rev. E, 66, 051402, (2002).

Wednesday 10:25 De Anza I EM24

Simultaneous light scattering-rheology measurements for studying stress induced phase transitions

Aadil Elmoumni[1], Aloyse J. Franck[1], Matthew E. Helgeson[2], Matthew Reichert[2], Jason M. McMullan[2], and Norman J. Wagner[2]
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There are a growing number of simultaneous rheological techniques that are of great interest for many applications. Simultaneous rheometry and small angle light scattering (SALS) is of particular interest for obtaining information on material structure orientation, particle size and shape. A compact SALS setup for simultaneous measurements has been developed and integrated into a combined motor and transducer (or stress-controlled) rheometer. The laser source is positioned below a lower Peltier platen, which incorporates a small quartz window. The light beam is perpendicular to the surface of the Peltier platen. The beam passes through the quartz window, the sample and an upper quartz plate. As the beam is scattered by interactions with the electrons of objects within the sample, the pattern formed is collected by an optical assembly with collimator, redirected with a mirror away from the upper test fixture, and projected onto a 2D camera array. Quantitative measurements are possible by calibrating the setup with monodisperse micron size polystyrene beads. Two case studies are presented. The first study tracks the kinetics of shear-induced colloidal crystallization by large amplitude oscillatory rheology and simultaneous SALS measurement of the crystal order parameter. We report the kinetics of crystallization from a shear-melted state to an hcp ordered crystal and their dependence on oscillation frequency, amplitude and temperature. The second study involves the use of light scattering simultaneous with rheology to measure the onset of shear banding in a worm-like micellar solution as a function of concentration and temperature. A butterfly light scattering pattern that is a signature of shear banding is obtained. The ability to easily control stress and temperature enables studying the shear banding transition as a function of the proximity to the isotropic-nematic phase transition.

Wednesday 10:45 De Anza I EM25

Exploration of new transient amphiphilic structures by a microfluidic chip-CryoTEM integrated system

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We present new transient nanostructures of amphiphilic solutions by imaging of aggregate structures as soon as they leave the microfluidic chip. By integrating microfluidic chip to a controlled environment vitrification system (CEVS), artifact-free visualization of a vast number samples with different chemical conditions, dispensing and mixing times is made possible. The integration allows a rapid characterization of macromolecular conformations using cryogenic transmission electron microscopy. A capillary connecting microchannels is passed through the side of the CEVS box and the mixed samples are injected directly on to a holey carbon grid and blotted to remove excess liquid. Subsequently, the grid bearing the sample is plunged into a liquid ethane reservoir and ready to be analyzed by TEM. We use the self-assembling dilute aqueous cetyl trimethyl ammonium bromide (CTAB) and dodecyl benzene sulfonic acid (HDBS) system to show the effect of evolution timescale and the transient status of aggregate nanostructures. Results show a time transition of long cylindrical shaped vesicles to wavy tubular shaped vesicles to spherical shaped vesicles structures. Flow rate and diffusion times were varied to probe the evolution of transient vesicle structures. The creation of the tubular structures is discussed using energy principles. Finally, the nanosturtures observed using other amphiphilic systems will be presented.

Wednesday 11:05 De Anza I EM26

Linear to branched micelles transition: A rheometry and diffusive wave spectroscopy (DWS) study

Claude Oelschlaeger and Norbert Willenbacher
Institute of Mechanical Process Engineering and Mechanics, University, Karlsruhe 76131, Germany

The frequency-dependent shear modulus of aqueous wormlike micellar solutions of cetylpyridinium chloride (CPyCl) in the presence of a strongly binding counterion sodium salicylate (NaSal) has been measured as a function of temperature, surfactant and salt concentrations by using DWS based tracer microrheology as well as mechanical techniques including rotational rheometry, oscillatory squeeze flow and torsional resonance. Good agreement between mechanical and optical techniques has been found in the frequency range from 10^{-1} to 10^5 rad/s. Upon increasing the salt concentration, at fixed surfactant concentration, we observed 2 maxima for the zero shear viscosity [1] as well as for the terminal relaxation time. The initial viscosity increase in the region of the first maxima has been explained by linear micellar growth but the decrease is still not really clear. Recently Danino and coworkers [2] have performed a cryo-TEM study on the same system and have shown formation of branching points after the maximum corroborating some preliminary theoretical models. From the dynamic shear moduli at low and intermediate frequencies and their change with temperature we obtain the mesh size and the scission energy. The scission energy passes through a maximum upon the transition from linear to branched micelles. In the frequency range above 10^4 rad/s a $\omega^{3/4}$ scaling is observed for the loss modulus G'' as expected for semiflexible objects like wormlike micelles. The persistence length l_p can be determined either from the highest Rouse-Zimm frequency ω_0 marking the transition from the $\omega^{5/9}$ to the $\omega^{3/4}$ scaling or from the absolute value of the shear modulus according to the statistical mechanical theory of Gittes and MacKintosh. For the linear micelles the persistence length decreases with increasing salt content as expected, but increases significantly upon the transition to the branched structure. Concerning the existence of the second peak there is no clear theoretical explanation. In the region of the second viscosity increase, the TEM pictures showed a decrease of the branching density accompanied by an elongation of the micelles. After the second maximum a shortening of the micelles and an increase of the branching density is observed but also formation of micellar rings. The variation of the scission energy and the persistence length upon this second maximum will also be discussed.

[1] Hoffmann, H. In Structure and Flow in Surfactant Solutions; Herb, C. A., Prud'homme,R., Eds.; ACS Symposium Series 578; American Chemical Society: Washington, D.C., 1994; p 2; [2] Ludmila Abezgauz, Ory Ramon and Dganit Danino. Department of Biotechnology and Food Engineering, Technion, Haifa, Israel. European Colloid and Interface Society, Geneva 2007.

Wednesday 11:25 De Anza I EM27

Non-contact method for measurement of surface/interfacial liquid properties with laser manipulation technique

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We are introducing a new measurement method for the surface or interface properties of liquids, such as the surface tension, viscosity or elasticity. In this method, we use only two lasers, one for deforming the liquid surface slightly and the other for sensing the deformation of the surface. The principle of the surface deformation by laser is the following. The momentum of the light depends on the refractive index of the medium, and the light momentum changes at the liquid surface when the light penetrates the surface. This change of the light momentum generates the weak pressure on the surface with the direction toward the lower-index medium. As a result, laser beam through the liquid surface makes a nano-scopic deformation, ~10 nm, on the surface. The magnitude of this deformation is inversely proportional to the surface tension and the quickness of the deformation is inversely proportional to the viscosity. Based on this principle, we developed a non-contact measurement method in which the surface displacement excited by the pump laser is measured with another probe laser. The frequency response of the surface to the modulated pump laser brings us the accurate value of the surface tension and viscosity. The advantages of this method are that we can treat the materials without touching it in measuring, and that the pump laser deforms only a quite small amount of liquid and the deformation is quite quick. Utilizing these advantages, we applied this method to measurements of the properties of liquids in extraordinary conditions. One is to observe the liquid-liquid interface with the ultra-low tension. In heptane and water system containing AOT as a surfactant, the interfacial tension changes with NaCl concentration and with the temperature. We succeeded to observe that the interfacial tension had a minimum value, ~ 1 μN/m, for a certain concentration of NaCl. The interfacial tension minimum was also observed at the characteristic temperature and the micro-emulsion phase appeared at that time. The other one is to measure the surface properties of high-viscous liquids. We made a series of experiments measuring the viscosities of silicone oils, and the results showed that this method had ability to measure the viscosity from 1 to 10^6 cSt on the time scale of below 10 s accurately. These experiments show that this method would be a new tool for the studies of various interfacial phenomena. Using this method, we can also observe the surfaces of the gels or the colloidal liquids.

SE-4. Surfactant Solutions

Organizers: Denis Weaire and Lynn M. Walker
Session Chair: Srinivasa Raghavan

Wednesday 9:45 De Anza II SE25

Multi-mode relaxation behavior of drag-reducing surfactants with excess addition of counter-ions

Hirofumi Watanabe, Hiroshi Suzuki, Yoshiyuki Komoda, and Hiromoto Usui
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Experimental studies on the relaxation characteristics of drag-reducing surfactants have been performed. The relaxation time after shear addition was measured by a cone-plate type rheometer in order to investigate the effect of the concentration of surfactants and counter-ions in the aqueous solution. The concentration of surfactants, oleylbishydroxyethylmethylanmonium chloride: Ethoquad O/12, was changed from 1,000 to 4,000 ppm, while the molar ratio of counter ions, sodium salicylate, to surfactants ranged from 1.5 to 100. From the results, it was found that the relaxation behavior of surfactant solution causing drag reduction shows multi-mode relaxation with several relaxation times and that the major relaxation time decreases with the molar ratio of counter-ions and by the concentration of surfactants. The number of relaxation times was also found to decrease with the molar ratio of the counter-ions and concentration of surfactants.

Wednesday 10:05 De Anza II SE26

Rheology, microstructure and drag reduction of cationic surfactant solutions with mixed counterions

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Counterions added to dilute cationic surfactant aqueous solutions are effective at inducing and stabilizing threadlike micelle formation which often leads to unique flow phenomena such as viscoelasticity, flow birefringence and turbulent drag reduction (DR). DR effectiveness of cationic surfactant/counterion systems, as indicated by the effective temperature range and critical shear stress for loss of DR, depends on the chemical structures of the cationic surfactant and the counterion, their concentrations and their molar ratios. Previous cryo-TEM, NMR, rheology and

DR results showed that some aromatic counterions, due to their ability to penetrate into the micellar core, can induce morphological micelle change (spherical to threadlike and further to vesicles) and greatly promote micelle growth at low surfactant concentrations. In this study, the DR effectiveness of two quaternary ammonium surfactant solutions (cetyltrimethylammonium chloride or CTAC, and Ethoquad O12, an unsaturated C18 and C16 alkyl mixture of cis- hydroxyethyl methyl ammonium chloride from Azko Nobel, Inc.) with different pairs of mixed aromatic counterions (sodium salicylate, sodium 4-ethylbenzenesulfonate, sodium 3,4-dichlorobenzoate and sodium 3-hydroxy-2-naphthoate) was investigated along with their micellar nanostructures and rheological properties. We found that certain combinations of counterion mixtures can dramatically change the rheological properties and improve DR effectiveness over either single counterion. With mixed counterions, the effective DR temperature range can be expanded and higher shear stress stability can be achieved. Cryo-TEM imaging carried out on these systems reveals the micelle nanostructures of the mixed counterion systems. NMR measurements on CTAC systems illustrate the penetration binding patterns of the competing mixed counterions such as insertion depth and orientation. The Cryo-TEM and NMR information help explain the unexpected temperature "gap" phenomenon observed for the CTAC-sodium salicylate and sodium 3,2-hydroxynaphthoate system, a non-continuity of effective DR temperature range for a system containing two counterions with very different binding affinities.

Wednesday 10:25 De Anza II SE27

Cooperative networks: Viscoelastic synergy in solutions of wormlike micelles and non-ionic polymers

Matthew W. Liberatore and Timothy Shenk
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Mixtures of polymers and surfactants in solution are important in a wide range of applications including detergents, personal care products and oil recovery fluids impacting the chemical, pharmaceutical and petroleum industries. Here, synergy is created between non-ionic polymers and wormlike micelles allowing the properties of the solution, especially the rheology, to be tuned. Maintaining the wormlike micelle state of surfactant aggregation in the presence of an entangled polymer network is a viable challenge. Experimental protocols for studying the polymer-micelle mixtures include flow and oscillatory rheology, rheo-optics, scattering using light and neutrons, and phase mapping. Using theoretical models from surfactant and polymer science, this experimental characterization allows tremendous insight into important length scales (from the nanoscale to macroscopic) and time scales of the co-entangled network. Preliminary studies mix wormlike micelles of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) with the polysaccharide hydroxyethyl cellulose (HEC). By tuning the concentration of NaSal the overall length of the wormlike micelles increases creating either entangled or branched networks, which changes the viscosity of the solution. Upon the addition of the polymer, changes to the viscosity and shear thinning nature of the mixtures are observed. Polymer concentrations up to the entanglement concentration of the polymer increase the zero shear viscosity of the solutions. In one case, the zero shear rate viscosity increases 1000 fold compared to the wormlike micelles alone. However, the zero shear rate viscosity of the mixtures decreases upon the addition of polymer at concentrations above the entanglement concentration. Overall, experimental control of temperature and macromolecule concentration allows the development of structure-property relations of wormlike micelle-polymer cooperative networks.

Wednesday 10:45 De Anza II SE28

Linear and non-linear rheology of soft composite transient networks

Laurence Ramos[1], Kaori Nakaya[2], Hervé Tabuteau[1], and Christian Ligoure[1]
[1]CNRS-University Montpellier 2, LCVN, Montpellier 34095, France; [2]Department of Physics, Ochanomizu University, Tokyo 112-0012, Japan

We investigate the rheological behavior of a new type of transient network: bridged wormlike micelles, whose structure has been recently characterized by us. This composite material is obtained by adding telechelic copolymers (water-soluble chains with hydrophobic stickers at each extremity) to a solution of entangled wormlike micelles (WM). For comparison, naked WM and hairy WM decorated by amphiphilic copolymers are also investigated. While these latter systems exhibit almost a same single ideal Maxwell behavior, bridged WM solutions are well described, in the linear regime, as two Maxwell fluids components blends, characterized by two markedly different characteristic times, Tfast and Tslow, and two elastic moduli, Gfast and Gslow, with Gfast >> Gslow. The slow mode is mainly related to the the transient network of entangled WM, and the fast mode to the network of telechelic active chains (i.e. chains that do not form loops but bridge two micelles). The dependence of the linear viscoelasticity with the surfactant concentration, C, and the sticker-to-surfactant molar ratio, R, is discussed. In particular, Gfast is found to be proportional to the number of active chains in the material, CxR. Simple theoretical expectations allow then an evaluation of the bridges/loops ratio for the telechelic polymers. On the other hand, these novel composite networks are found to stiffen, due to polymer stretching, in the weakly non-linear regime, and to exhibit shear-banding in the highly non linear regime.

Wednesday 11:05 De Anza II SE29

Extensional rheology Of branched wormlike micelle solutions

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Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA, USA

Wormlike micelle solutions are used in a wide range of applications including detergents, personal care products as well as rheological modifiers. In this talk, we present the results of our extensional rheology of a series of wormlike micelle solutions. The experiments are performed using a series of linear and branched wormlike micelle solutions consisting of sodium oleate (NaOA) and octyl trimethyl ammonium bromide (C_8TAB). The ratio of NaOA to C_8TAB is fixed at 70/30 while the total surfactant concentration is varied. The shear rheology of wormlike micelle solutions is found to demonstrate a maximum in shear viscosity at 4wt% followed by a sharp decrease in viscosity with increasing surfactant concentration. It has been shown through Cryo-TEM imaging that the maximum in the shear viscosity corresponds to the transition from linear entangled to branched micelles. The steady-state value of the extensional viscosity of the wormlike micelle solution is found to decrease monotonically with increasing total surfactant concentration and increasing degree of micelle branching. Additionally, the steady-state value of the Trouton ratio is found to decay rapidly with increasing micelle concentration, approaching an asymptote close to Newtonian limit for concentrations of 4wt% and above. Additionally, preconditioning the wormlike micelles through an initial pre-shear prior to stretch is found to have a significant effect on the extensional rheology. These results are most likely due to the additional stress relief mechanisms available to branched micelles which appear to be extremely efficient in extensional flows; namely the fast and fluid sliding of branch points along the length of the micelle and the increased occurrence of 'ghost-like' crossing of micelles at entanglement points with increasing surfactant concentration. These observations demonstrate how sensitive the extensional rheology of wormlike micelles is to branching.

Wednesday 11:25 De Anza II SE30

Photorheological fluids made easy: Light-sensitive wormlike micelles based on common, inexpensive surfactants

Srinivasa R. Raghavan, Aimee M. Ketner, and Rakesh Kumar

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Photorheological fluids, i.e., those with light-tunable rheological properties can be useful in a variety of applications, such as in sensors, dampers, and valves for microfluidic or MEMS devices. Currently, such fluid formulations are available only to a few research groups since they tend to be based on specialized photosensitive molecules (e.g. a photoresponsive surfactant or polymer). Here, we describe formulations based on common, inexpensive, surfactants, with the light-sensitivity coming from added organic moieties that is also commercially available. A first example of such fluids was reported recently (JACS 129, 1553 (2007)) and displayed a 1000-fold drop in viscosity upon irradiation with UV light. Here, we describe two new systems being studied in our lab. One is a photogelling system, in which the fluid exhibits a rapid and controllable increase in viscosity (photogelling) upon exposure to UV radiation. The second is a reversible fluid that can be switched from high to low viscosity and back by irradiation with different wavelengths of light. The microstructural origins for these effects are based on changes in the sizes and shapes of wormlike micelles formed by the molecules in water. The interplay between light-induced changes in molecular geometry and micellar structure will be a consistent theme in this work. We will present results from a variety of spectroscopic, analytical and scattering techniques to elucidate the molecular and microstructural mechanisms for our results.

Thursday Morning – 7 August 2008

KL-9. Keynote Lecture 9

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Antony N. Beris

Thursday 8:30 Serra I KL9

Elastic turbulence: A random flow without inertia

Victor Steinberg
Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel

Recent advances in elastic turbulence will be discussed. The role of elastic stress in the statistical properties of elastic turbulence, realized by the flow of a polymer solution between two disks is investigated experimentally. The dynamics of the elastic stress are analogous to those of a small scale fast dynamo in magneto-hydrodynamics, and to those of the turbulent advection of a passive scalar in the Batchelor regime. Both systems are theoretically studied in literature, and this analogy is exploited to explain the statistical properties, the flow structure, and the scaling observed experimentally. The following features of elastic turbulence are confirmed experimentally: (i) the rms of the vorticity (and that of velocity gradients) saturates in the bulk of the elastic turbulent flow, leading to the saturation of the elastic stress. (ii) the rms of the velocity gradients (and thus the elastic stress) grows linearly with Wi in the boundary layer, near the driving disk. The rms of the velocity gradients in the boundary layer is one to two orders of magnitude larger than in the bulk. (iii) the PDFs of the injected power at either constant angular speed or torque show skewness and exponential tails, which both indicate intermittent statistical behavior. Also the PDFs of the normalized accelerations, which can be related to the statistics of velocity gradients via the Taylor hypothesis, exhibit well-pronounced exponential tails. (iv) a new length scale, i.e. the thickness of the boundary layer, as measured from the profile of the rms of the velocity gradient, is found to be relevant for the boundary layer of the elastic stresses. The velocity boundary layer just reflects some of the features of the boundary layer of the elastic stress (rms of the velocity gradients). This measured length scale is much smaller than the vessel size. (v) the scaling of the structure functions of the vorticity, velocity gradients, and injected power is found to be the same as that of a passive scalar advected by an elastic turbulent velocity field. Besides influence of polymer concentration in dilute, semi-dilute, and concentrated regimes are studied.

KL-10. Keynote Lecture 10

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Paulo Roberto de Souza Mendes

Thursday 8:30 Steinbeck KL10

Residual stresses and viscoelastic deformation of injection molded parts

Jae R. Youn
Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea

Injection molding is one of the most common polymer processing operations because good quality products are usually obtained and major post-processing treatment is not required. However, residual stresses generated during molding affect the final shape and durability of the finished part. Residual stresses are caused by polymer melt flow, molecular orientation, non-uniform temperature field, pressure distribution, and density distribution. Residual stresses were predicted by numerical methods using both commercially available softwares and in-house codes. Cavity filling, packing, and cooling stages were analyzed to predict residual stress fields right after ejection. Residual stress distribution predicted by the thermal stress analysis was compared with the measurement results. Residual stresses of molded polymeric parts were measured by the layer removal method and the hole drilling method. Thermo-viscoelastic stress analysis was carried out to predict deformation and residual stress variation after annealing of the part. Viscoelastic deformation of the part was predicted during annealing and the deformed geometry was compared with that measured by a three dimensional scanner. The viscoelastic stress analysis with a thermal cycle will enable us to predict long term behavior of the injection molded polymeric part. As practical illustrations, complex automotive parts and film insert molded (FIM) specimens were produced and examined to evaluate residual stress variation and long term viscoelastic deformation. Viscoelastic deformation of the automotive part was predicted by performing viscoelastic stress analysis in order to understand long term behavior of the part when exposed to room temperature or higher temperature. Thermal history of the FIM part was calculated in the cavity by using a finite difference method for the residual stress analysis. Residual stresses and bending moment of the FIM parts were predicted and compared with the experimental results. Warpage reversal phenomenon of the FIM part, which was caused by the thermal shrinkage of the inserted film and relaxation of residual stresses, was observed after the part was annealed at elevated temperature.

HS-5. Block Copolymers

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chair: Julia A. Kornfield

Thursday 9:45 San Carlos IV HS31

Deformation of inclusions and lamellae during melt elongation of blends of a styrene-butadiene block copolymer with polystyrene

Ulrich A. Handge[1], Matthias Buschnakowski[2], and Goerg H. Michler[2]
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The end-use properties of block copolymers are determined by their chemical composition, their molecular architecture and their microstructure. A well-known example are styrene-butadiene (SB) block copolymers. Blending SB block copolymers with a general purpose polystyrene can lead to materials with tailored end-use properties while maintaining reasonable costs. Consequently, the mechanical and rheological properties of such blends are presently intensively investigated. In this work, we studied the melt rheology of blends of a styrene-butadiene block copolymer (LN3) and a commercial polystyrene (PS 158K) in shear and elongation. Both materials were supplied by BASF AG. Three different blends of LN3 and PS 158K were prepared by melt blending. The weight fraction of PS 158K was 20, 40 and 80 wt.%. Linear viscoelastic shear oscillations and melt elongation and subsequently recovery experiments were performed at temperature T = 170°C. In addition, the development of the blend morphology with applied strain was investigated using transmission electron microscopy. PS 158K and LN3 formed a two-phase blend with a PS 158K or a LN3 matrix, respectively. The block copolymer chains of LN3 were arranged in a lamellar phase. Our rheological experiments revealed that the complex modulus, the transient elongational viscosity and the recoverable stretch of the PS 158K/LN3 blends mainly resulted from a superposition of the properties of pure PS 158K and pure LN3. In melt elongation, the inclusions in the PS 158K resp. LN3 matrix were deformed into an extended shape. The alignment of the lamellae of the LN3 matrix for 20wt.% and 40wt.% PS 158K was more pronounced with increasing Hencky strain.

Thursday 10:05 San Carlos IV HS32

Using external fields to control the location of nanoparticles in block copolymers: Simulations and experiments

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The importance of spatial location of nanoparticles in polymer nanocomposite materials has fueled interest in using block copolymers (BCP) as particle guiding scaffolds. Researchers have tailored the surface chemistry of functional nanoparticles (NPs) to prevent aggregates and selectively place them in desired BCP domains. However, magnetite NPs, having numerous potential applications in electrical and biomedical fields, tend to aggregate and phase separate from BCP matrix due to strong magnetic dipole attractions. To control the distribution and location of magnetic nanoparticles in a polymer matrix, we have combined electrospinning (a process that draws polymer solution jets to submicron scale fibers by electric field) and confined assembly of polystyrene-b-polyisoprene (PS-b-PI) block copolymer [1,2]. When monodisperse 4 wt% magnetite NPs (~ 4 nm) are added to symmetric PS-b-PI, transmission electron microscopy (TEM) images of microtomed, electrospun fibers show that NPs are uniformly dispersed only in the PI domain, while the confined assembly of well-ordered alternate concentric rings of PS and PI domains is preserved in electrospun fibers. For 10 wt% NPs, a transition of morphology is seen from concentric rings to a bicontinuous phase with NPs again uniformly dispersed in the PI domain. To further understand the effect of flow conditions on the nanoparticle location in block copolymers, we have performed coarse grained molecular dynamics simulations using dissipative particle dynamics (DPD) thermostat under simple shear flow. First, we study the effect of shear on location of nanoparticles in block copolymers mimicking experimental systems where model metal particles are coated with the desired block. Then we model the system, such that particle-particle interactions exceed those of particle-polymer, qualitatively resembling the PS-b-PI system with self-attracting, magnetite nanoparticles. Our results reveal that shear can play an important role in controlling the location of nanoparticles in block copolymer matrices.

[1] V. Kalra, P. A. Kakad, S. Mendez, T. Ivannikov, M. Kamperman, and Y. L. Joo, "Self Assembled Structures in Electrospun Poly (styrene-block-isoprene) Fibers", Macromolecules, 2006, 39, 5453; [2] V. Kalra, S. Mendez, J. H. Lee, H. Nguyen, M. Marquez, and Y.L. Joo, "Confined Assembly in Coaxially Electrospun Block Copolymer Fibers" Advanced Materials, 2006, 18, 3299.

Thursday 10:25 San Carlos IV HS33

Hidden dynamics in nanophase segregated triblock and pentablock copolymer melts

Frederico I. Roschzttardtz, John Embery, and Tom C. McLeish
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The rheological properties of CEC triblock and CECEC pentablock copolymers (where C and E refer to poly(cyclohexylethylene) and poly(ethylene) respectively) have been evaluated. It was found, as expected, that their terminal behavior diverges strongly from the terminal relaxations of single homopolymers. Their behavior reflects a long-time relaxation process which is beyond the time-scale of experimental observation. Nevertheless, new relaxation processes have been found which fit within the experimental time-scale. The “new transitions” observed in the dynamic behavior, were identified by plotting phase angle (d) versus dynamic complex modulus (G*). The process observed is temperature dependent and seems to be correlated with the content of PCHE (poly(cyclohexylethylene) in the block copolymer. This relaxation has been observed only in lamellar triblock and pentablock copolymers. Shear alignment does not affect the relaxation behavior. In the non-linear rheology of the block copolymers, however, significant differences are observed between the behavior of perpendicular oriented and unoriented lamellar morphologies. For example, with the evidence of a strong overshoot on the stress when block copolymers are not oriented. Here we will summarize these new dynamic rheological transitions and correlate to structural changes.

Thursday 10:45 San Carlos IV HS34

Flow behavior of cubic and cylindrical block copolymer gels

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Block copolymers in a solvent that is selective for one of the blocks will self-assemble to form micellar aggregates with 10-100nm dimensions. Solvent changes with temperature can be utilized to drive a thermoreversible micellization. Here, we discuss this transition in a system driven by the dehydration of the central block of a triblock copolymer at higher temperatures in water; at concentration that lead to close-packed micellar gels. Within these gels, a further transition from cubically-packed spherical micelles to hexagonally-packed cylindrical micelles is seen in systems of the appropriate relative block size. Transitions between the two different polymorphic states are complex and we have tracked this mechanically and with structural probes (small-angle scattering and optical birefringence). The time scales and directionality of the transitions will be discussed. In addition, we will provide mechanical and structural results on the impact of adding nanoparticulate matter to the solvent phase in these systems. In this case, the micellar gel acts as a template for the spatial position of the nanoparticulate material. Use of this approach to manipulate nanoparticles does require improved understanding of the impact of the particles on the template and our studies of this in the case of hexagonally-packed cylinders will be outlined.

Thursday 11:05 San Carlos IV HS35

Rheological and dielectric behavior of dipole-inverted $(SIS)_p$-type multiblock copolymers: Estimates of bridge/loop fractions for respective I blocks and effect of loops on high extensibility of bridges

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A series of symmetric styrene (S)-*cis*-isoprene (I) multiblock copolymers of $(SIS)_p$-type (p = 1, 2, 3, and 5 corresponding to tri-, penta-, hepta-, and undecablock) was synthesized with an anion-coupling method and their rheological and dielectric behavior was examined in *n*-tetradecane (C14), a solvent dissolving the I block and precipitating the S block. The molecular weights of the constituent blocks were almost identical for these copolymers, and a particular I block(s) of respective copolymers had symmetrically once-inverted type-A dipole while the remaining I blocks had non-inverted dipoles. At 20°C, the $(SIS)_p$/C14 systems with the $(SIS)_p$ concentration of 40 wt% formed a bcc lattice of glassy, spherical S domains (as confirmed from SAXS) and exhibited the gel-like elasticity. This elasticity was sustained mainly by the bridge-type I blocks connecting the S domains and partly by the coexisting loop-type I blocks. The dielectric loss (ε") data exclusively detected the fluctuation of the midpoint of the dipole-inverted I block having either bridge or loop conformation. (Since the ends of the I blocks were immobilized on the surface of the glassy S domains, the motion of the I blocks having non-inverted dipoles was dielectrically inert.) A moderate difference was noted for the ε" data of the $(SIS)_p$ copolymers normalized by the volume fractions of respective dipole-inverted I blocks. This difference unequivocally indicated that the bridge- and loop-type I blocks exhibited different dielectric responses and that the bridge fraction ?bridge moderately changed with the location of the dipole-inverted I block in the $(SIS)_p$ copolymer backbone as well as the number of repeating SIS units, p. On the basis of a hypothesis of dielectric similarity between the loop and its half-fragment tail under an osmotic constraint, ϕ_{bridge} was estimated from the ε" data of the $(SIS)_p$ copolymers and their precursor SI diblock copolymer (having the tail-type I block). ϕ_{bridge} was a little larger for the I block located at the center of the copolymer backbone than for the off-center I block and ϕ_{bridge} of the center I block decreased slightly with increasing p. The $(SIS)_5$ undecablock system was extensible up to the stretch ratio of $\lambda = 30$, and the loops therein appeared to osmotically stretch the bridges thereby helping the bridges bear such a high extensibility.

SG-6. Numerical Simulations

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Jorg Baschnagel

Thursday 9:45 San Carlos II SG37

Relaxation dynamics of chain fluids during the approach to the glass transition

Joanne Budzien[1], Taylor C. Dotson[2], Julieanne V. Heffernan[3], Douglas B. Adolf[4], and John D. McCoy[2]

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Our recent work has been using chain molecules to investigate the approach to the glass transition through molecular dynamics simulations. We have chosen to analyze the data by constructing master curves that correlate dynamic quantities with thermostatic quantities. This enables us to collapse data from different state points (PVT data) taken along various cooling paths onto a single curve. The benefit of using this procedure is that the underlying physics can be observed without the complication of chemical details or path dependence.

We have studied a few simple systems using variations on the standard bead-spring model. We have added attractions and varied the angle constraint from freely jointed to freely rotating. This enables us to keep with the spirit of simple models and yet have the possibility of observing different physics. Our systems also have a few single site penetrants to help gauge the effect of length scale on dynamics.

With just these simple systems, we have seen some interesting dynamics. The Stokes-Einstein relation is observed to break down for the freely rotating system, but not the freely jointed system. Using the second Legendre polynomial to measure the reorientation of some vectors along the chains in the systems shows that the Debye-Stokes-Einstein relation holds, but a separation of time scales is observed as the systems approach the glass transition. This separation is more pronounced for the freely rotating systems than the freely jointed systems. The reorientation dynamics can be characterized in terms of a stretched exponential function with the exponent and time constant related to the scalar metric, which measures the position on the master curve. These quantities can be compared favorably with values obtained from experimental relaxation measurements.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Thursday 10:05 San Carlos II SG38

Linking slow dynamics and local structure in simple models of glass-forming liquids

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Establishing a relation between the dynamical features of supercooled liquids, their structural properties and, in ultimate analysis, the nature of intermolecular interactions is a key issue in the description of the glass transition. Molecular Dynamics (MD) simulations of simple model liquids are optimal tools to investigate this point, as they allow to control the preference for local structures in the bulk by tuning the interaction parameters, and to establish direct connections with the slow dynamical processes in the liquid.

We performed MD simulations for a broad set of binary Lennard-Jones mixtures displaying different types of local order, analyzed by means a Voronoi tessellation, and a varying dynamical behavior [1]. We show that the super-Arrhenius dependence of structural relaxation times (Angell's fragility) in Lennard-Jones mixtures is strictly related to the growth, upon supercooling, of slow domains characterized by distinct microstructural features. The more fragile is the mixture, the more rapid is the increase of particles forming locally preferred structures. Such microstructural heterogeneities provide a natural basis for understanding the existence of localized regions of mobility and immobility in supercooled liquids (dynamic heterogeneities).

The connection between structure and dynamics in the models studied has signatures in the properties of stationary points of the Potential Energy Surface (PES) [2]. We relate the formation of slow domains in the liquid to the increase, upon supercooling, of average energy barriers in the PES, as obtained from the relation between the energy and the fraction of unstable modes of saddles. Upon supercooling, the unstable modes of saddles in the PES become more and more localized in real-space and influence the dynamics of the liquid within the beta-relaxation timescale [3]. Interestingly, particles at the center of locally preferred structures are stabilized and are not involved in the unstable modes. We also discuss the extension of such arguments to simple models of network glass-formers and polymer melts.

[1] D. Coslovich and G. Pastore, J. Chem. Phys. 127, 124504 (2007); [2] D. Coslovich and G. Pastore, J. Chem. Phys. 127, 124505 (2007); [3] D. Coslovich and G. Pastore, Europhys. Lett. 75, 784 (2006)

Thursday 10:25 San Carlos II SG39

MD simulation of structure and dynamics of glass-forming polymer films

Jorg Baschnagel, Simone Peter, and Hendrik Meyer
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We present results from molecular-dynamics simulations for a bead-spring model of a polymer melt in free-standing and supported film geometries. We investigate the influence of confinement on static and dynamic properties when cooling the melt towards its glass transition. We find that the relaxation at the free surface is faster not only in comparison to the bulk, but also with respect to the slightly accelerated dynamics at the supported, smooth surface. We perform a layer-resolved analysis of the dynamics and also determine the glass transition temperature Tg of the polymer film. We find that Tg decreases with film thickness, in qualitative agreement with some experimental results. We also show results for supported and capped films, i.e., films embedded between two substrates. Both substrates are identical; they are either smooth or rough. For smooth substrates we find that the film dynamics is faster than the bulk, whereas it is slower for rough substrates. The simulations thus suggest that the complex relaxation behavior found in our model polymer films has the following causes: (i) the bulk-like slowing down of the dynamics on cooling; (ii) a smooth transition of faster (or slower) relaxation relative to the bulk at the surface or substrate to bulk-like behavior in the interior of the film; (iii) a stronger penetration of the surface-induced perturbations into the film at low temperature. These effects may also be present in experimental systems and could cause a shift of Tg.

Thursday 10:45 San Carlos II SG40

Molecular dynamics simulations and neutron scattering of melts of poly(ethylene propylene): Bridging the gap between fully atomistic and coarse-grained models

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The combination of atomistic molecular dynamics (MD) simulations with neutron scattering has proven to be a powerful tool for investigating the structure and dynamics of polymer melts at local and inter-macromolecular scales, i.e., where these systems display universal features of glass-forming liquids. At larger scales, polymer melts show unique dynamic processes that are controlled by the chain-connectivity and molecular weight of macromolecules. These processes ultimately determine the rheological properties of polymer melts. Unfortunately, the study of these dynamic processes by means of fully atomistic simulations is impossible with current-day computer power, being necessary the development of coarse-grained models. In this work we have used a bottom-up approach to construct an appropriate coarse-grained model of poly(ethylene propylene) (PEP) melts starting from fully atomistic MD-simulations of PEP validated by extensive neutron scattering measurements.

Fully atomistic MD-simulations were carried out on a system of 12 chains of PEP of 80 monomers each, being in total 14424 atoms in a cubic cell, subjected to periodic boundary conditions. After appropriate equilibration, simulations at NVT conditions were done until 100 ns. The temperature range was from 300K to 500K, well above the glass transition temperature of PEP (213K). The static and dynamic structure factors, which can be measured by neutron scattering, were calculated from the atomic trajectories obtained during the simulation runs. The obtained results were directly compared with neutron scattering measurements carried out on both protonated and deuterated PEP samples, in particular, diffraction with polarization analysis and neutron spin echo (NSE) measurements. The good agreement found allows concluding that the atomistic simulations were good mimic of the real structural and dynamic properties of PEP, at least at the length/time scale simulated. Once the atomistic simulations were validated we have used the microscopic configurations obtained to construct a coarse-grained model of PEP appropriate for investigating the large-scale dynamics. To do that, each atomistic chain is replaced by a set of 8 blobs, each of them containing 10 monomers. The relevant parameter is now the center of mass of each blob. The rest of the coordinates per blob of the atomistic system are treated as bath variables, i.e., by means of random forces. In these conditions, the dynamics of blob-chains can be described in terms of a Langevin equation, involving a potential of mean force and a friction coefficient related to the random forces. These are deduced from the atomistic simulation results. Once they are fixed we can run Brownian dynamics simulations at longer times of coarse-grained chains of different lengths. In this way we can investigate large-scale dynamics (Rouse regime, crossover to reptation, etc,) of PEP. We will present the results obtained by these procedure at 492K.

Thursday 11:05 San Carlos II SG41

Visco-hyperelastic modelling for amorphous polymers close to their α transition

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Near their α transition amorphous polymers exhibit a specific type of behaviour combining hyper elasticity and anelasticity. Experimental observations during loading - unloading -reloading tensile tests performed over a wide range of temperatures and strain rate cleary enlighten such kind of behaviour. A novel route, based on revisited hyperelatic Edawrds Vilgis' model, will be presented that enable modelling of *the huge and combined evolution upon strain rates and temperature, *the occurence of anelasticity and hysteresis effect, *strain hardening due to crystallisation. This model is written within a thermodynamlical frame work. It is a 3D approach that could be easily implemented. Viscous effect is introduce using physical concept and does not rely, as often, on analogic 1D models. Potentially such model should allow modelling thermal recovery during heating above glass transition. Validation in non monotonic tension will be discussed using experiments on PMMA, HIPS and PET.

Thursday 11:25 San Carlos II SG42

Diffusion and structural relaxation in sheared glassy systems

Fathollah Varnik

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Diffusion in melts undergoing strong shear is investigated via large scale molecular dynamics simulations of a well established glass forming model system, namely the 80:20 binary Lennard-Jones system first introduced by Kob and Andersen [W. Kob and H.C. Andersen, PRL **73**, 1376 (1994)]. In previous works [F. Varnik JCP **125**, 164514 (2006) and F. Varnik and O. Henrich PRB **73**, 174209 (2006)], the interplay between the dynamics of structural relaxation on the length scale of the average interparticle distance and the stress response of the model was studied. Here we focus on the large scale dynamics under homogeneous shear by evaluating the time dependence of the mean square displacements for temperatures ranging from the supercooled state to far below the mode coupling critical temperature of the model. Particularly long simulations are performed allowing an accurate determination of the diffusion constant. For low temperatures and at not too high shear rates, the mean square displacements exhibit the well known two step relaxation behavior with a long time diffusive motion along the spatial directions perpendicular to the flow. In the flow direction, on the other hand, a third regime follows the diffusive motion, where Taylor dispersion with the typical t^3 time dependence clearly dominates the long time behavior of the particle displacements. At the lowest studied temperatures, the cross over from the diffusive regime to the regime where the contribution of Taylor dispersion becomes significant, occurs at length scales of the order of a particle diameter but is shifted towards progressively larger displacements as temperature increases. Moreover, once the contribution of Taylor dispersion is subtracted from particle displacements, diffusive motion is recovered also along the flow direction. Interestingly, a comparison of diffusive motion along the flow, the shear gradient and the vorticity directions shows small but systematic anisotropic effects.

HP-9. Entangled Polymers II

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Christian M. Bailly and Jay D. Schieber

Thursday 9:45 San Carlos III 💿 HP58

A critical analysis of using step-strain and extensional rheology to obtain the multi-mode "pom-pom" model parameters for branched high-density polyethylenes

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A critical analysis of the combination of step-strain and uniaxial extension to obtain the model parameters for the McLeish-Larson multi-mode pom-pom model for a series of well-defined commercial polyethylene resins is presented. These metallocene catalyzed resins have a branching content ranging from linear to 0.79 LCB/10^4 C and have been well characterized in previous studies. The structural makeup of these materials across the molecular weight distribution is believed to be well understood providing a set of materials for which the theory can be adequately compared to the fitted model parameters for consistency as well as examined to ensure the fitted model parameters qualitatively make sense. The information available on these materials offers an excellent opportunity to compare our predictions to and aid in the possible determination of a more unique set of parameters. Incorporated in this study is an analysis of a novel encapsulation technique designed to overcome material failures in extensional flow seen at strains higher than two units using a LLDPE stabilizer sheath.

Thursday 10:05 San Carlos III 💿 HP59

Verification of branch point withdrawal in elongational flow of pom-pom polystyrene melt

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According to tube model ideas, chain stretch at deformation rates below the inverse Rouse time of the chain, is only possible for polymer topologies with two or more branch points. The basic topologies which embody this idea are the H-molecule with two side chains, and the pom-pom molecule with q > 2 side chains at each end of the backbone. According to the pom-pom hypothesis, maximum chain stretch of the backbone is limited by branch point withdrawal, i.e. the side chains are drawn into the tube of the backbone as soon as the relative tension in the backbone reaches a value of q. This hypothesis, which has never been verified before, can now be tested by considering recent elongational experiments by Nielsen et al. [Macromolecules 39, 8844-8853 (2006)] on a nearly monodisperse polystyrene pom-pom melt with $q = 2.5$. The analysis presented is based on the original integral version of the Pom-Pom model, and on the Molecular Stress Function (MSF) model with strain-dependent tube diameter. The material strain measure determined from the experiments is found to be consistent with a constant maximum stretch, independent of the elongation rate, which is, however, significantly larger than q. To achieve quantitative agreement between experiment and modelling, (1) dynamic dilution of the backbone, which increases the tube diameter of the backbone and reduces equilibrium tension, (2) finite extensibility effects, (3) transition from chain stretch to tube squeeze at lower strain rates, and (4) the dynamics of branch point withdrawal need to be considered. Integrating all of these features in a MSF stretch evolution equation with multiple time scales, the fundamental pom-pom hypothesis is confirmed.

Thursday 10:25 San Carlos III HP60

Elongational dynamics of narrow molar mass distribution linear and branched polystyrene melts

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The understanding of nonlinear flow properties of polymer melts requires reliable experimental stress-strain measurements on well-characterized polymers. Especially well defined narrow molar mass distribution (NMMD) polymer melts contribute to the understanding of the complex flow physics of polymer melts, as reptation based constitutive theories do have the monodisperse polymer as the model molecule. The startup of uni-axial elongational flow followed by stress relaxation or reversed bi-axial flow, as well as large amplitude oscillatory elongational flow, has been measured for NMMD linear and branched multi-arm polystyrene melts, using the filament stretching rheometer (FSR). The used FSR (Bach, Rasmussen , Hassager (2003) Journal of Rheology 47, 429 - 441) allows measurements on polymeric fluids, including polymeric melts, from room temperature until 200°C. The branched polystyrene melt was a multiarm A_n-C-C-A_n pom-pom polystyrene with an estimated average number of arms of n=2.5. The molar mass of each arm is about 28 kg/mole with an overall molar mass of Mw=280 kg/mole. The principle of time-strain separability fails completely to describe the dynamic elongation data. Similarly the Doi-Edwards model with any 'stretch evolution' equation is not capable of capturing the reversed dynamic of NMMD melts. An integral molecular stress function constitutive formulation within the 'interchain pressure' concept (Wagner, Kheirandish, Hassager (2005) Journal of Rheology 49, 1317-1327) seem to agree with all experiments for linear melts.

Thursday 10:45 San Carlos III HP61

Decoding the viscoelastic response of polydisperse star/linear polymer blends

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It is well known that polydispersity and branching have important and, at the same time, hardly predictable effects on rheological and processing properties of industrial polymers. In the literature, many studies have been done to predict the rheology of polydisperse linear polymers and monodisperse, well-defined, branched polymers. Industrial polymers are instead, in many case, simultaneously polydisperse and branched, exhibiting a much more complex viscoelastic behaviour. When polydispersity and branching are both present, many different relaxation processes are indeed active at the same time and their corresponding kinetics are expected to reciprocally influence each other.

In order to understand the viscoelastic behaviour of such a class of complex materials, we investigated the rheology of several blends of polydisperse linear and stars polymers with the help of a coarse grained - tube model. Set of polydisperse star/linear polybutadiene blends characterized by different composition and arm average molecular weight was prepared. Linear “parent” polymers were synthesized via anionic polymerization. A coupling agent was introduced in a second stage in order to obtain the blends. In order to characterize the composition of the blends, light scattering data were performed for determining their molar mass distributions (MMD). Then, using an adequate statistical approach, MMD were divided into different categories of architectures. We obtained a full set of linear and non-linear rheological data. Then, we extended our tube-based model* to predict their linear viscoelasticity. This requires several modifications of the initial model in order to deal with a very large number of different particles and star molecules having arms of different lengths. The non-linear rheological response was analyzed with special attention to the time-strain separability and to the damping function at short and long times, whereas the response to uniaxial extension were also investigated.

* E. van Ruymbeke, C. Bailly, R. Keunings, D. Vlassopoulos: "A general methodology to predict the linear rheology of branched polymers", Macromolecules, 39, 6248-6259 (2006)

Thursday 11:05 San Carlos III HP62

Rheology of short-chain branched polyethylene melts under shear: Results from NEMD simulations and comparison with linear and H-shaped analogues

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Considering the growing experimental and theoretical interest in the rheology of branched polymers [1-4], we have undertaken a systematic study of the role of chain branching on the structural and dynamical behavior of model polyethylene (PE) melts using nonequilibrium molecular dynamics (NEMD) simulations for shear flow. Three different model PE systems (all characterized by the same total chain length, equal to 178 carbon atoms) have been considered: short chain branched (SCB) chains consisting of short (up to 6 carbon atoms) branches frequently spaced along the main chain backbone, H-shaped chains, and linear chains. In order to avoid system-size effects, rather large simulation boxes have been used especially at high shear rates (containing up to 35,000 total atoms), since chains are likely to be significantly oriented and deformed to the flow direction. Also, in all cases, the simulations were carried out for sufficiently long (especially, at low shear rates) in order to obtain reliable statistics. Results will be presented for a number of structural and dynamical properties (such as the center-of-mass self-diffusion coefficient, the shear viscosity, the 1st and 2nd normal stress coefficients, and the conformation tensor), and will be discussed as a function of molecular architecture.

[1] Lewis, J.F. et al., Macromolecules 1993, 26, 647-654; [2] McLeish, T.C.B.; Larson, R.G., J. Rheol. 1998, 42, 81-110; [3] Öttinger, H.C., Rheol. Acta 2001, 40, 317-321; [4] Karayiannis, N.Ch.; Giannousaki, A.E.; Mavrantzas, V.G., J. Chem. Phys. 2003, 118, 2451-2454; Karayiannis, N.Ch.; Mavrantzas, V.G., Macromolecules 2005, 38, 8583-8596.

Thursday 11:25 San Carlos III HP63

Effect of multiple branch points on non-linear rheology

Keith M. Kirkwood[1], Dimitris Vlassopoulos[2], and Gary Leal[1]
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We report on experimental studies of entangled linear comb polymer melts and solutions (polyisoprene in squalene). The comb systems that we consider have approximately 5-18 arms with lightly entangled arms relative to the backbone. The arms are relatively low MW so that the number of entanglements per arm ranges from approximately 3-10. In these systems, the backbone MW is such that that they are well entangled after the dynamic dilution effect of arm relaxation. The low number of branches on the backbone (relative to the number of entanglements) allows us to understand the backbone as a discrete system with the branch points representing friction points restricting the motion of the backbone. The effects of the branch points on the stress relaxation mechanisms are illuminated with the high entanglement of the backbone. We study the effect of the branch point on the behavior of the backbone in linear and non-linear flows by comparing results with blends of linear chains. Rheo-optical measurements for comb solutions are used to understand the effect of mechanisms such as convective constraint release on the comb architecture. The contributions of the branch points to the relaxation of the backbone in both step-strain and steady shear flows are reported.

BR-4. Physiological Fluids II

Organizers: James L. Harden and Christoph F. Schmidt
Session Chair: Victor Breedveld

Thursday 9:45 Redwood BR22

Viscosity and lubricity of hyaluronan and synovial fluid

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Synovial fluid is the fluid that lines our freely moving (synovial) joints and is vital to joint lubrication. The polyelectrolyte hyaluronan is an important component of synovial fluid and its presence results in highly viscoelastic solutions. Normal synovial joints exhibit an extremely low coefficient of friction-similar to an ice skate on ice. This is not the case for arthritic joints. An experimental model of synovial fluid has been developed and characterized. Our relatively simple model is actually a weak, reversible gel, as indicated by the model's complex, nonlinear, shear-history-dependent rheological behavior. In our rheological studies of the synovial fluid model and bovine synovial fluid, we observe three regions of behavior: (1) rheopexy at low shear rates (< 1 s^{-1}), (2) a transition region at moderate shear rates (*ca.* 1 s^{-1}), and (3) shear thinning at higher shear rates (> 10 s^{-1}). We hypothesize that these different regions of fluid behavior may correspond to different lubrication mechanisms in the joint. We are utilizing nanoindenter to investigate the lubricating ability of our model through wear studies and coefficient of friction measurements as a function of load, scan and scratch speed, probe geometry, surface roughness, and composition of the model.

Thursday 10:05 Redwood BR23

Stress analysis of shear-thinning synovial fluid flow

Nariman Ashrafi
School of Mechanical Engineering, University of Kwazulu-Natal, Durban, South Africa

Stress analysis is carried out for normal (shear thinning) and pathological (Newtonian) synovial fluid in joint articulation in general. The fluid is assumed to follow the Carreau-Bird model in the concentric-cylinder flow. The effect of shear thinning phenomena on velocities and consequently stresses is then explored. Obtained from the conservation of mass and momentum equations, the dynamical system includes additional nonlinear terms in the velocity and stress components through the shear-dependent viscosity otherwise non existent in Newtonian systems. The analysis shows that change of stability picture of base flow due to the nonlinearity actually causes stress regularization. Clinical data show rapid increase of both shear and normal stresses for pathological synovial fluid (inflammatory or degenerative) during certain angles of articulation which corresponds to the evaluated stresses in this study as the fluid approaches Newtonian range.

KEY WORDS: Pathological Synovial fluid, Shear thinning, nonlinear Stress Analysis

Thursday 10:25 Redwood BR24

Stress communication and filtering in biological layers

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We focus on mucus layers in human lung pathways and how stress is communicated from oscillatory driving conditions such as coordinated cilia and cough. Experimental evidence from cell cultures is presented that relates stress signaling to biochemical release rates of ATP and water volume regulation. We then model and simulate a mucus layer in large amplitude oscillatory strain, and show how certain frequency signals are communicated through the layer while others are filtered.

Thursday 10:45 Redwood 💿 BR25

A numerical model of viscoelastic layer entrainment by airflow in cough

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Coughing is an alternative mode of ensuring mucus clearance in the lung when normal cilia induced flow breaks down. A numerical model of this process is presented with the following aspects. (1) A portion of the airway comprising the first three bronchus generations is modeled as radially reinforced elastic tubes. Elasticity equations are solved to predict airway deformation under effect of airway pressure. (2) The compressible, turbulent flow induced by rapid lung contraction is modeled by direct numerical simulation for Reynolds numbers in the range 5,000-10,000 and by Large Eddy Simulation for Reynolds numbers in the range 5,000 - 40,000. (3) A two-layer model of the airway surface liquid (ASL) covering the airway epithelial layer is used. The periciliary liquid (PCL) in direct contact with the epithelial layer is considered to be a Newtonian fluid. Forces modeling cilia beating can act upon this layer. The mucus layer between the PCL and the interior airflow is modeled as an Oldroyd-B fluid. The overall computation is a fluid-structure interaction simulation that tracks changes in ASL thickness and airway diameters that result from impulsive airflow boundary conditions imposed at bronchi ends. In particular, the amount of mucus that is evacuated from the system is computed as a function of cough intensity and mucus rheological properties.

Thursday 11:05 Redwood BR26

Development of an interfacial extensional rheometer with applications in model tear films

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Extensional flow is a fundamental flow with many industrial and research applications. While much effort has been put forth to develop extensional rheometers for bulk fluids, thus far no one has applied this type of deformation to two dimensional problems such as complex interfaces. We have developed such an instrument, an interfacial extensional rheometer. Based on a tensiometer designed by Jones and Middelberg (Chemical Engineering Science, 2002), we have made several improvements that will allow us to measure two-dimensional extensional viscosity. In this device, two rods are floated in parallel at the air-water interface. One is connected to a motor and the second is attached to a force transducer to measure how interfacial films respond when subjected to extensional strains. A camera is mounted above the instrument to directly observe flow fields on the surface. It also allows us to measure the width of the "necking" region, which is necessary to calculate two-dimensional extensional viscosity. Before application to complex systems, the rheometer was used to measure the stress-strain response of silicone oil viscosity standards to confirm that Trouton's rule can be measured accurately with this system. Once this correlation was established, the rheometer was applied to model tear film systems. The tear film is a complex structure consisting of several distinct layers that aid in lubricating and protecting the eye. Some of the most prominent components in this film include both polar and non-polar lipids, proteins and triglycerides. During a blink the film is rapidly compressed and expanded on the surface of the eye, so spreadability and film continuity are vital to a functional tear film. We are investigating the rheological properties of model tear films and potential dry eye formulation additives in hopes of developing a more successful treatment. In particular, the response of these materials under extensional flow will help to identify which compounds are responsible for establishing continuity of the tear film and how this can be improved.

MP-7. Particulates

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: Marie-Claude Heuzey

Thursday 9:45 Colton I-III 💿 MP46

Influence of cellulosic nanofillers on the rheological properties of polymer electrolytes

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New polymer electrolytes are needed to improve the performances and safety of lithium and polymer batteries, the aim being to ensure both high ionic conductivity and high enough mechanical properties to lower the internal resistance while preventing shorts. Due (i) to their high solvating ability vs lithium cation and (ii) to their high segmental mobility, poly(oxyethylene) (POE) based polymer electrolytes are the most studied. They however exhibit poor mechanical properties at their operating temperature i.e. above their melting temperature. In this study, nanocomposite polymer electrolytes, based on high molecular weight POE were prepared from high aspect ratio natural cellulosic nanofillers. The thermomechanical behaviour of the resulting nanocomposites was investigated using differential scanning calorimetry, dynamic mechanical analysis and rheometrical measurements. The influence of entanglements versus percolation mechanism on the determination of the mechanical properties of the composite was also investigated. For the different cellulosic fillers considered in the POE matrix, a decrease of the melting temperature and a restricted cristallinity of POE were observed in the presence of a large amount of fillers. This result may be explained by the affinity between POE and cellulose, resulting in strong interactions between the two components thus affecting the mobility of the chains. Moreover, the presence of cellulosic fillers was found to significantly enhance the mechanical properties of the nanocomposite. In addition, the storage modulus stabilizes above the melting temperature of POE. This stabilization may be explained by the formation of a rigid percolating cellulose network resulting from strong interactions between the nanoparticles through strong hydrogen bonds. Shear rheometry of the unfilled POE and related nanocomposites shows that the shear viscosity first decreases when the concentration in cellulose increases. Then typical suspension behaviour is obtained and the viscosity increases with the concentration. This observation is in agreement with DSC and DMA results and may be explained in terms of polymer-filler interactions: below a critical concentration, the leading phenomenon is the interactions between POE ether functions and cellulose hydroxyl groups. In this low concentration regime, increasing cellulose content leads to an increase in the specific area that decreases the polymer available in the solution and results in a viscosity drop. When all the POE is adsorbed on the cellulose surface, a critical concentration is reached and a typical suspension behaviour, namely a viscosity increasing with the concentration is then observed. Interactions between cellulose fillers, leading to the reinforcing effect, are again possible. The formation of a rigid network between cellulose fillers leading to the reinforcing effect above the melting temperature of the matrix is well predicted by a percolation concept.

Thursday 10:05 Colton I-III MP47

Shear rheology of suspensions of porous zeolite particles in concentrated polymer solutions

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Membrane-based gas separations are environmentally benign and energy efficient. However, the drive towards higher gas membrane selectivity and better productivity continue to stretch the currently available membrane capabilities. Mixed matrix hollow fiber membranes were recently conceived as a tool to meet these challenges. Crucial to the success of this membrane type is the processability of suspensions of zeolites in polymer solutions into a defect-free hollow fiber membrane configuration. Much work remains to be done to elucidate the rheology of these porous particle suspensions, especially with regards to their behavior under elongational deformations, which are characteristic during fiber spinning. We will present experimental data on the shear and extensional rheology of Ultem/NMP solutions with and without suspended surface-modified porous/nonporous zeolite (ZSM-5) particles.

We found that the zeolite suspensions had relative viscosities that significantly exceeded the Krieger-Dougherty predictions for hard sphere suspensions at particle loadings as high as 30 weight percent. We will show that the major origin of this discrepancy is the selective absorption of the NMP solvent into the zeolite nanopores. Solvent absorption raises the particle and polymer concentrations, and thus enhances both the viscosity of the Ultem/NMP continuous phase and the particle contribution to suspension viscosity. Other factors, such as particles non-sphericity and interactions of particles with Ultem polymer, increase the suspension viscosity to a lesser extent.

We propose a predictive model for the viscosity of porous zeolite suspensions by incorporating an absorption parameter, α, into the Krieger-Dougherty model. We also propose three independent approaches to determine α. The first one is indirect and based on zeolite density/porosity data, assuming that all pores will be filled with solvent. The other two methods are based on our experimental data, 1) by comparing the viscosity data of porous versus non-porous zeolite suspensions and 2) by carefully measuring the suspension rheology as a function of polymer concentration. The different approaches will be compared and evaluated.

Using a capillary-breakup extensional rheometer (CaBER) we also measured the transient extensional viscosities of Ultem/NMP solutions and zeolite/Ultem/NMP suspensions in order to determine the effect of the suspended zeolite particles on the break-up dynamics of thin filaments, which is highly relevant for fiber-spinning. We determined mean relaxation times and a quasi-steady apparent extensional viscosity for Ultem/NMP solutions. The Trouton ratio for several concentrations of polymer and zeolite was determined and evaluated. The relaxation times of Ultem/NMP solutions increases significantly when doped with porous zeolite.

Thursday 10:25 Colton I-III MP48

The squeeze flow of yield stress fluids

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A systematic study of pastes undergoing squeeze flow (SF) was performed. The validity of the method for determining the yield stress is explored under lubrication conditions as well as elongational (perfect wall slip) conditions. Additionally, the rheological behavior of the pastes was measured independently, using precise rheometrical tests. Several different concentrations of Carbopol were examined, with varying yield stress. Tests were performed with a specified volume of fluid between the two parallel plates and constant force was applied. The yield stress could then be determined from the resultant fluid height. It is shown that the results depend significantly on the initial shape of the sample. By carefully controlling the experimental conditions of the squeeze test, however, the yield stress can be efficiently determined. Additionally, a specific experiment was devised in which the SF takes place within an MRI device, enabling the radial velocity profile to be measured. The results are then compared with theoretical predictions for the case of the lubrication assumption as well as that of pure elongation.

Thursday 10:45 Colton I-III MP49

Extrusion criterion for firm cement-based materials

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Extrudible materials exhibit a mainly plastic rheological behaviour. It clearly appears that the yield stress level governs the material extrusion ability according to the flow geometry. Recent advances in pre-cast concrete technologies show that extrudible cement-based materials such as mortar are likely to undergo liquid filtration during extrusion forming process. Such filtration changes the flowing material rheology (increasing of plastic yield value) and may induce material heterogeneities inside the extruder and strongly affects the extrudates surface quality. Such a paste evolution in the extruder is a key parameter for the extrusion achievement: the paste has to remain homogeneous. In the case of firm cement based material, the paste heterogeneity and the high solid volume fraction enhance the drainage phenomenon and the liquid filtration. The flow is then governed by the competition between the velocity of the fluid phase flowing through the granular media and the process time required to form the material. The aim of the study is to define a criterion for the extrusion velocity in order to avoid flow induced heterogeneities. We propose an analysis based on the understanding of the fluid filtration mechanisms through a static granular skeleton. Soils mechanics concepts such as Cam-Clay modelling, Terzaghi principle and consolidation theory are used in order to describe the links between granular skeleton permeability and plastic yield value evolution. A critical time ratio (extrusion time - required time to assure a significant change of yield value) is calculated and used as extrusion criterion. Experimental tests validate the proposed criterion. An extrudible mortar is formulated according to bibliography and experiments are performed varying extrusion velocity.

Thursday 11:05 Colton I-III MP50

Rheology of carbon black suspensions: Effect of carbon black structure

Yuji Aoki

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We have studied the dynamic viscoelastic properties of carbon black (CB) suspensions. We found that the rheological behavior of the CB suspensions changes with the affinity of suspending medium toward the CB particles and is classified into three different types of the behavior. CB is constituted of carbon primary particles fused by covalent bonds into aggregates that generally unbreakable during the normal processing of the materials. The CB aggregates exist in a variety of shape types from the higher-structure CB grades consisting of more branched structures to lower structure grades containing more compact structures. In this paper, we report the effects of CB aggregates on the rheological properties for the CB suspensions. The relationship between three types of rheological behavior and the structure of CB aggregates is discussed.

CG-2. Induced Gels and Attractive Glasses

Organizers: Dimitris Vlassopoulos and Wilson C. Poon
Session Chairs: Rut Besseling and Guillaume Ovarlez

Thursday 9:45 San Carlos I CG7

Flow-enhanced heterogeneity in model colloidal gels

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Colloidal gels are of great importance in various area of both classical technology and emerging fields. The structure formation in colloidal gels and the mechanisms of yielding and flow however remain to a large extent elusive. Here we use tailored 2D suspensions by pinning particles at a liquid-liquid or liquid-air interfaces. For such particle monolayers, structural information in a single plane suffices to provide a complete description of the interparticle structure [1]. The interparticle interactions are tailored in such manner that weak aggregation is induced; this has been verified and the interactions have been quantified previously using optical tweezers [2]. Such systems can hence be used as model systems to study the dynamics, structure and rheology of weakly aggregated suspensions in general. Here we indicate how model experiments on 2D suspensions can be used to understand fundamental flow phenomena such as yielding and restructuring in aggregated suspensions. Well characterized suspensions are generated by destabilizing a colloidal crystal. A DLCA structure is obtained under quiescent conditions. It is fractal at low surface coverage and heterogeneous with voids and clusters at higher surface coverages. When a shear flow is started, these experiments enable the analysis of the bonds that break, a real space analysis of the restructuring of the materials and identification of the mechanisms that lead to shear densification and enhanced heterogeneity on the gel structure. The real space results obtained on the 2D systems will be compared to scattering data on both model depletion gels and sticky sphere systems in 3D, as obtained by synchrotron X-ray scattering studies. We hope to prove that flow enhancement of heterogeneity is a generic feature of colloidal gels and discuss the underlying mechanisms that control it.

[1] Reynaert S, Moldenaers P, Vermant J, Langmuir, 22 (11): 4936-4945 (2006); [2] Park. BJ. Pantina J. Reynaert S, Furst E, Vermant J, Langmuir, accepted for publication.

Thursday 10:05 San Carlos I CG8

Rheology of carbon nanotube suspensions and networks

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The structure and rheology of carbon nanotube suspensions and networks is measured using a variety of optical and rheological methods. Birefringence, dichroism, depolarized light scattering and video microscopy measurements under shear flow are combined with strain-rate and stress-controlled rheometry to characterize the transient and steady-state non-equilibrium structure of the suspensions as a function of confinement, concentration, shear stress and shear rate. Based on these measurements, we construct a non-equilibrium phase diagram that maps the flow-induced evolution from solid-like nanotube gels to flowing nematics at varied nanotube concentration and confinement. Although the carbon nanotubes are strongly non-Brownian, we find features characteristic of first-order phase transitions, including a discontinuity in the nematic order parameter at the isotropic-(para)nematic phase boundary. Using simple physical arguments, we account for the shape of the coexistence curves, as well as the dependence of the order parameter on concentration and stress. Simple scaling arguments are also used to relate the morphology of the quiescent nanotube network to the measured shear modulus and yield stress. Practical implications for the flow processing of nanotube suspensions and melt carbon-nanotube polymer composites are discussed, and comparisons are made with broadly analogous behavior exhibited by a variety of other sheared complex fluids.

Thursday 10:25 San Carlos I CG9

Flow of attractive colloidal suspensions in microchannels

Jacinta C. Conrad and Jennifer A. Lewis
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We use confocal microscopy to investigate the behavior of suspensions of attractive colloids during flow. We characterize the bulk rheological properties of attractive colloidal suspensions, and then directly image them during flow in microchannels. We investigate both the gel structure and the flow properties as a function of applied pressure and the colloid volume fraction. While quiescent, the gel structure is nearly homogeneous and isotropic, whereas flow leads to the formation of dense clusters separated by large voids. When the applied pressure or displacement is relatively small, the particle velocity is nearly constant in the center of the channel; near the walls the gel yields via breaking of clusters. When the applied pressure or displacement is large, the gel structure is disrupted and the flow velocity changes across the channel width.

Thursday 10:45 San Carlos I 💿 CG10

Rheological properties and structure of gels generated from stable polymer colloids through high shear in a microchannel

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It is well known that for a fully or partially destabilized colloidal system, gelation may occur under stagnant conditions when the particle volume fraction reaches a certain value. Structure of the obtained gels depends on the extent of the destabilization and can be characterized through measuring their rheological properties (Wu and Morbidelli, Langmuir, 17, 1030, 2001). In this work, we study the gelation behavior in high turbulent shear induced in a microchannel, for the colloidal systems that are fully stable under stagnant conditions. In particular, the colloidal system is composed of styrene-acrylate copolymer particles stabilized by both the surface charges from the polymer chain end groups and adsorbed aliphatic sulfonate surfactant. The aggregation behavior of the system in the microchannel is investigated by tuning the surfactant surface coverage of the particles. It is found that there is a clear correlation between the surfactant surface coverage and the gelation behavior. When the particle surface is fully covered by the surfactant or the surface coverage is larger than 80%, aggregation and gelation do not occur even at the largest shear rate (~2E+6 1/s) of the device. When the surface coverage is smaller than 80%, partial aggregation of the system can be observed. Moreover, when the surface coverage is smaller than ~65% and the particle volume fraction is larger than 15%, the system is fully aggregated, forming a gel. It should be noted that without adsorbing the surfactant, the colloidal system is fully stable under stagnant conditions with only the surface charges coming from the polymer chain end groups. The above results clearly indicates that the adsorbed surfactant layer has a strong depression effect on the turbulent aggregation, and the aggregation between two particles in the turbulent flow becomes effective only when their collision occurs at the surfactant-free patches on the particle surface. Storage modulus and limit of linear of the gels formed at different particle volume fraction have been measured using a strain-controlled rheometer in order to characterize the gel structure. It is found that at high surfactant surface coverage, strong-link gels are formed and the mass fractal dimension of the clusters constructing the gels is around 2.1, while with progressively decreasing the surfactant surface coverage, weak-link gels are formed with the mass fractal dimension between 2.6 and 2.8. Similar depression effect of the adsorbed surfactant layer on the turbulent aggregation has been observed also for the other surfactants.

Thursday 11:05 San Carlos I CG11

Microstructure, phase behavior and rheology for colloidal suspensions with attractive/repulsive interparticle potentials

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Large scale dynamic simulations with hydrodynamic interactions are presented to study the phase behavior, microstructure and rheology of concentrated colloidal suspensions with varying strengths of short range attractive potentials. We document the transitions from fluid like states to crystals to gels and investigate the effects of adding varying strengths of long range repulsive potentials on the phase behavior and microstructure. Dynamic simulations confirm equilibrium predictions on the disappearance of crystalline phases with increasing repulsive forces and show significant changes in the microstructure for gel phases. The strength of the repulsive force affects both the strength and connectedness of the gel (as manifest in number of bonds per particle) as well as characteristic length scales and morphology of the gel microstructure. Comparison is made with experimental results from confocal microscopy and scattering experiments. Simulation results include direct visualizations of suspension microstructure, structure factors and statistical measures of gel morphology. Simulations for for sheared suspensions document the shear thinning behavior, yield stress, elastic moduli and normal stresses in the suspensions. Dynamic recovery of gel states from periods of rapid shear is investigated.

Thursday 11:25 San Carlos I 💿 CG12

Rheology of frustrated colloidal states: Transition from a colloidal gel to an attractive glass

Nick Koumakis[1] and George Petekidis[2]
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The addition of short-range attractions between colloids in hard sphere glasses result in a distinct modification of their linear and non-linear rheology. While pure hard-sphere glasses exhibit a single step yielding at a yield strain that corresponds to breaking of the cage of nearest neighbors, attraction-dominated glasses show a two-step yielding where the first step corresponds to the breaking of attractive bonds between particles and the second one to the cage breaking process [1]. On the other hand at low particle volume fractions attractions eventually lead to gels consisting of inter-connected particle networks that exhibit a much different rheological response with a rather brittle character. Here we present a systematic study of the linear and nonlinear rheology of a series of colloid-polymer mixtures at a constant inter-particle depletion attraction and particle volume fractions spanning the region from highly concentrated attractive glasses to low volume fraction gels. Dynamic frequency sweeps were used to measure the linear viscoelastic properties while dynamic strain sweeps and step rate tests probe the yielding process under oscillatory and steady shear conditions. The transition from a highly concentrated attractive glass to a low volume fraction colloid-polymer gel appears to take place gradually with the cage breaking process being substituted by a cluster dominated process as the volume fraction is decreased.

[1] K. Pham et al. Europhys. Lett. 75, 624, (2006).

SC-7. Yielding and Thixotropy III

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chair: Roger T. Bonnecaze

Thursday 9:45 De Anza III 💿 SC43

Influence of thixotropy on pressures required during pumping of concrete

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Concrete is world wide applied material number two (after water) and pumping of it is one of the most easy and reliable placement methods. Concrete can be regarded as an extreme case of a suspension. This material contains less than 10 % (by mass) water, meaning more than 90 % is solid, with dimensions varying between 1 µm and 4 dm. From a rheological point of view, this material behaves as a Bingham fluid, having a yield stress, but also having varying rheological properties in time due to thixotropy and loss of workability.

In this paper, the influence of thixotropy on the pumping pressures will be described. Increasing pumping speed decreases the thixotropy, giving the material an apparent lower yield stress and lower viscosity. This increase in fluidity requires less pumping pressure, but on the other hand, it can lead to segregation and inhomogeneity of the material. Further research will show whether the pipe length is also influencing the rate of structural breakdown, and whether pressure losses will no longer be linearly dependent on the pipe length. On the other hand, these phenomena cannot have a full quantitative description, because this is too complicated due to the large variations in the shear rate history of the concrete: mixing, transport, remixing in the truck, start of pumping, ..., which are important in order to know the starting thixotropical state.

Thursday 10:05 De Anza III SC44

Transition from a simple yield stress fluid to a thixotropic material

Philippe Coussot[1], Alexandre Ragouilliaux[1], Guillaume Ovarlez[1], and Benjamin Herzhaft[2]
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From Magnetic Resonance Velocimetry we determine the local constitutive equation of different model emulsions. We show that a pure emulsion can be turned from a simple yield stress fluid to a thixotropic material by adding a small fraction of colloidal particles. The two fluids have the same behavior in the liquid regime but the loaded emulsion exhibits a critical shear rate below which no steady flows can be observed. For a stress below the yield stress, the pure emulsion abruptly stops flowing, whereas the viscosity of the loaded emulsion continuously increases in time, which leads to an apparent flow stoppage. This phenomenon (viscosity bifurcation), which leads to a strong localization of the flow in steady-state at low shear rates, can be very well represented by a model assuming a progressive increase of the number of droplet links via colloidal particles.

Thursday 10:25 De Anza III SC45

Comparative study of particle interaction between PMMA particles by Usui's thixotropy model and AFM

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The temperature dependence of the particle interaction between mono-modal spherical PMMA particles with different particle sizes in aqueous media was evaluated by both Usui's thixotropy model and AFM measurement. Usui has recently proposed the thixotropy model in which the number of primary particles contained in an aggregated cluster was adopted as the thixotropic model parameter. This model was mainly developed for silica-water slurries which showed typical non-Newtonian and thixotropic characteristics. In his model, inter-particle bonding energy between primary particles is easily determined when the steady state viscosity data are given experimentally. On the other hand, the adhesive force between two particles was tried to measure directly by an atomic force microscope (AFM) in liquid recently. It is known that both the pull off force and repulsive force between two particles were obtained through the force curve measurement by AFM. In this presentation, we discuss the physical meaning of the inter-particle bonding energy between PMMA mono-modal spherical particles in aqueous media, whereby it is not only calculated by Usui's thixotropy model from the rheology data, but also the direct measurement by AFM. In addition, we also describe the influence of the temperature and particle size on the inter-particle bonding energy between PMMA particles which is essential for understanding of the viscosity of polymer slurries.

Thursday 10:45 De Anza III SC46

Effect of latex particles addition on the rheological behavior of concentrated silica suspensions used as cement pastes model systems

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The quality of a cementitious material depends of course on its composition and may be improved by the addition of a polymer powder. But, the quality of cement pastes also depends on the control of their rheological properties.So, the objective of this work is to study the effect of the addition of solid latex particles on the rheological behavior of cement pastes. To be sure that the observed behavior is not due to the chemical evolution of the cement pastes, we have studied concentrated silica suspensions in lime saturated water as model systems.The redispersible powder, obtained by drying a polystyrene acrylate latex, is constituted by partially hydrophobic particles. In the first part of this work, we have characterized the linear and non linear behavior of silica suspensions in absence of polymer. A sharp transition between a gel state and a liquid state is observed when the shear stress amplitude is increased during oscillary tests. An apparent yield stress and a shear thinning regime followed by a shear thickening regime are also displayed. The observed behaviors are explained by the formation of aggregates in the suspensions: the percolation of these aggregates induces the gelation at rest or at low shear stresses and the crumbling of the aggregates is responsible for the shear thinning behavior. Moreover, the use of a viscosity model, in which liquid is trapped within the aggregates, allows to determine, for the liquid state, a solid volume fraction in the aggregates or the amount of liquid entrapped. In the second part of this work, we have studied the effect of the composite suspension composition (polymer/silica ratio up to 0.25 in weight) on the different rheological parameters determined in the first part. The addition of polymer does not qualitatively modify the rheological behavior. But, replacing silica particles by polymer particles induces a decrease of the storage modulus in the gel state , a decrease of the yield stress and a decrease of the viscosity in the liquid state. The decrease of the storage modulus might be due to the lower interactions between polymer and silica particles than those between silica particles. The decrease of the viscosity might be related to the smaller amount of water entrapped within the aggregates, due to the lower hydrophilicity of polymer particles compared to that of silica particles.We have also shown that the polymer contribution to the storage modulus and to the solid volume fraction in the aggregates is proportionnal to the added polymer volume fraction. Moreover, scanning electron microscope observations on cryofracturated surfaces show that the polymer particles are very well dispersed. All these features suggest that there are no separate polymer aggregates but rather composite silica/polymer aggregates.

SC-8. Suspension Hydrodynamics II

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Chongyoup Kim and Nina C. Shapley

Thursday 9:45 Portola SC49

Dynamic simulation of colloidal rod suspensions with application to nano-barcodes

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Many dispersions of colloidal particles with application in materials processing, biological assays, or medicine, contain elongated or rod-like particles, such as suspensions of carbon nanotube, nanobarcodes or drug delivery vehicles. Much recent literature has demonstrated that the dynamics of these suspensions at non-dilute concentrations involves physical principles which are unlike those operating in suspensions of spheres. In this work, we examine, via numerical simulation, three problems which exemplify these differences. First, we examine the effect of rotational Brownian motion on the stability and wavenumber selection of sedimenting fiber suspensions. Note in this context, that the instability in sedimenting rod like particles is associated with the particle orientation evolution and therefore, Brownian motion can have a qualitative effect on the instability in finite vessels. Next, we then describe the dynamics of dilute suspensions of polarizable particles in electric fields, with specific comparison to the experiments on 'nano-barcodes' by Rose and Santiago. This work extends the initial simulations of Saintillan et al. 2007 to direct comparison to new experimental data. Finally, since processing of these barcodes often involves a driven mean flow in microfluidic devices, we examine the shear rheology of dilute and concentrated nano-rod solutions to understand the effects of particle anisotropy on shear induced migration and suspension microstructure.

Thursday 10:05 Portola SC50

The dynamic behavior of a concentrated non-Brownian glass fiber suspension in simple shear flow

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In this paper we investigate the relationship between the non-linear viscoelastic rheology, in start-up of shear flow, and the microstructure of a concentrated short glass fiber-filled composite fluid. Specifically, we compare the experimentally determined fiber orientation distribution to that predicted using the generalized Jeffery's equation, modified to include inter-particle interaction. Stress growth experiments in start-up of flow are performed on a Rheometrics Mechanical Spectrometer (RMS-800) using cone and plate geometry (cone angle = 0.1 rad, diameter = 50 mm). Samples at rest and in equilibrium are deformed at a constant rate for a specific time (i.e. strain) that correlates to various points of interest and then the flow is stopped. The sample temperature is then lowered below the melt temperature (Tm) of the suspension to "freeze" the fiber orientation. After which the sample is collected. The 3D fiber orientation distribution within the sample is then determined using a confocal laser microscope. The experimentally determined orientation is then compared to predictions for the evolving orientation based on the generalized Jeffery's equation, modified to include inter-particle interaction. Experimental data was found to be in good agreement with model predictions.

Thursday 10:25 Portola SC51

Rheology of semi-flexible fiber suspensions

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The rheological behavior of model suspensions consisting of a Newtonian silicone oil and fibers with different flexibilities has been studied in steady and transient shear flows. Various fiber suspensions have been prepared to investigate the effect of flexibility, stiffness, length, diameter of fiber as well as the role of interactions in semi-concentrated and concentrated regimes. In order to avoid variations of the fiber density and flexibility simultaneously when comparing suspensions with different fiber aspect ratios, the fiber volume fraction used was adjusted to have the same average distance between fibers in each concentration regime for the various suspensions. The experimental results show that the viscous and elastic properties of the fiber suspensions are strongly influenced by the fiber flexibility. The viscosity and the first normal stress differences increase as the fibers become more flexible and the suspensions exhibit more noticable shearthining behavior. It has been shown that fiber flexibility can influence the relaxation time dramatically, specially at low shear rates. The effect of fiber flexibilty on the rheological properties becomes more pronounced in the concentrated regime, which can be attributed to enhanced fiber-fiber interactions with semi-flexible fibers.

Most available models for predicting the rheological properties of fiber suspensions consider the fibers as rigid bodies, while as fibers stiffness decreases or fiber aspect ratio increases, the fiber tends to bend and is not a rigid body anymore. Experimental data on suspensions with flexible fibers are quite scarce in the literature, which makes our data quite unique. Our experimental observations suggest that fiber flexibility must be taken into account when developing a rheological model for such systems. Results from our measurements are qualitatively compared with direct simulation predictions of the Switzer-Klingenberg model developed for the rheology of flexible fiber suspensions [1], and quantitatively with predictions using the mesoscopic level model of Rajabian-Dubois-Grmela for semi-flexible fiber suspensions [2].

[1] Switzer III, L.H., Klingenberg, D.J., 2003. "Rheology of shear flexible fiber suspensions via fiber level simulations". J.Rheol. 47:3. 759-778; [2] Rajabian, M., Dubois, C., Grmela, M., 2005. "Suspensions of Semiflexible Fibers in Polymeric Fluids: Rheology and Thermodynamics". Rheol Acta 44: 521-535.

Keywords: rheology, fiber suspension, flexibility, shear flow, model.

Thursday 10:45 Portola SC52

Polyamide fibre model system for exploration of the effect of anisotropy on aggregated rod rheology

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Systems of aggregated colloidal rods are common in many industries, including consumer products and paper production, as well as in new materials such as carbon nanotube and shear thickening suspensions. The rheology of these systems is a complex function of colloidal rod aspect ratio, concentration and interaction potential. To understand the effect of these parameters on linear and non-linear rheology, we seek a model system that is easily prepared and can fully span in a single material the range of aspect ratios, concentrations and interactions relevant to applications. In this study, we consider a new model system consisting of self-assembled polyamide anisotropic colloids suspended in aqueous surfactant dispersions. The colloidal particles are formed via a crystallization process from an amorphous polyamide powder. When this powder is dispersed in the aqueous surfactant phase at temperatures from 65 to 100 °C colloidal particles form. At low temperatures, the polyamide material forms low aspect ratio rods ($r \sim 4$). Rope-like structures with aspect ratios up to $r \sim 400$ are formed at high temperatures. We use confocal laser scanning microscopy (CLSM) and static light scattering to characterize the microstructure of the rod-like suspensions in solution at quiescent conditions. Atomic force microscopy (AFM) is applied to study the morphology of thin films of the polyamide structures. Pair interactions between the rods are varied by manipulating the surfactant concentration or by the addition of salt. By means of dynamic light scattering and linear rheology we report how aspect ratio, interaction potential and concentration control the Brownian dynamics and flow properties of the polyamide fibre dispersions. We report in particular the complex relationship between aspect ratio and concentration on rheological behavior.

Thursday 11:05 Portola SC53

Effects of matrix viscoelasticity on rheology of dilute and semi-dilute suspensions of non-Brownian rigid spheres

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The rheological behaviour of suspensions has received considerable attention. However, while most part of the experimental literature deals with highly filled systems, mainly composed of colloidal particles of irregular shape, relatively few studies investigated the rheology of dilute or semi-dilute rigid sphere suspensions. Such systems, however, are of interest for at least for two reasons: on the one hand, low concentration sphere suspensions find applications in several fields. On the other hand, the rheological response of semi-dilute suspensions of this type is a good test for theories that explore concentrations beyond the well known Einstein's infinite dilution limit. Furthermore, even less is known about the role of matrix viscoelasticity. In this work, the rheology of non-Brownian, inertialess rigid sphere suspensions in both Newtonian and viscoelastic fluids has been investigated. Volume fractions up to 10% were used, thus crossing the border between the dilute regime and the semi-dilute regime, where interparticle interactions become increasingly relevant. PMMA spherical particles (mean diameter 14 micron) were suspended in one Newtonian fluid (Polyisobutilene, PIB) and two viscoelastic fluids (Polydimethylsiloxane, PDMS) of different molecular weight. The rheological response of suspensions was studied both in steady and linear oscillatory shear flow. As expected, both viscosity and viscoelastic moduli showed an increase with increasing volume fraction of the suspended particles. In the limit of sufficiently slow flows, however, the rheological parameters showed a simple scaling behaviour that resulted in the independence of the relative viscosity and moduli (i.e., the ratio between the value measured for the suspension to that measured for the pure matrix) upon shear rate and frequency, respectively. Following Batchelor's approach for non-dilute Newtonian suspensions, a second order polynomial dependency for the rheological properties was assumed. A robust regression procedure to the experimental data showed the following, relevant features: - The first order polynomial coefficient was found to be equal to 2.5 (the Einstein's dilute prediction) for the viscosity and the viscoelastic moduli. This result was found to hold true for both Newtonian and viscoelastic fluids; - The second order polynomial coefficient for the Newtonian PIB suspensions was found to be in excellent agreement with Batchelor's predictions. The coefficient value was essentially the same for both steady shear viscosity and oscillatory loss modulus. - In the case of viscoelastic, PDMS suspensions, the second order coefficient was found to be substantially larger than that measured for the Newtonian case. Furthermore, the same value of this coefficient was found for both viscous and elastic moduli.

Thursday 11:25 Portola SC54

Particle-wall interaction in a viscoelastic fluid

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Understanding of the mechanics of a single collision is an essential input in modeling natural or industrial processes such as, among others, agglomeration, granular flows, sediment transport and, in general, any multi-phase flow problems where solid particles are involved. In this work, particle-wall interaction in viscoelastic fluids is experimentally studied. The effect of Stokes number, Weissenberg number and surface roughness on the rebound velocity of a colliding spherical particle on a wall is considered. Different Nickel-steel spherical particles are released in viscoelastic solution of different high-molecular-weight polymers in water with different concentration and the coefficient of restitution is calculated for particle-wall collision. The critical Stokes number at which no rebound occurs is studied for different Weissenberg number.

CF-8. Computational and Multiscale Modeling 3

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Patrick D. Anderson

Thursday 9:45 Steinbeck CF52

Design of a cross-slot flow channel for extensional viscosity measurements

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An automatic procedure for optimal shape design studies of viscoelastic fluid flow is presented. The proposed methodology couples our finite-volume viscoelastic code [1] with the CONDOR optimizer [2] together with a fully automated mesh generation and adaptation procedure. The optimal shape design methodology allows the automatic search for the ideal shape of a given flow geometry that achieves optimal performance, according to a specified objective function. Although the computation of the objective function is expensive, since it corresponds to a full viscoelastic fluid flow simulation, we demonstrate that it is nowadays possible to undertake viscoelastic fluid flow optimization studies using a simple desktop computer. The proposed optimization methodology is general, fully automated, and applicable to laminar flows of Newtonian and viscoelastic fluids.

In this study we design a cross-slot flow channel in which the extensional flow along the centerline occurs at a constant strain rate in a wide region near the stagnation point, a requirement to carry out meaningful extensional viscosity measurements. Contrary to previous studies (e.g. [3,4]), we demonstrate that it is not necessary to artificially promote slip at the walls in order to achieve a constant strain rate, therefore avoiding the use of lubricating fluids.

The proposed design of the cross-slot geometry generates a velocity field in which the measurements are practically insensitive to inertial and elastic effects, since the predicted strain rates are nearly constant in a wide region near the stagnation point. This feature was found for a broad range of operating flow conditions and for the constitutive equations tested, namely the upper-convected Maxwell, Oldroyd-B and Phan-Thien-Tanner models. In particular, the optimized device is shown to operate efficiently under creeping flow conditions, thus making the proposed design suitable for microfluidic applications, for which the elastic effects are enhanced due to the small dimensions and high strain-rates typically observed.

[1] M. A. Alves, P. J. Oliveira and F. T. Pinho. Int. J. Num. Meth. Fluids, Vol. 41, pp. 47 (2003); [2] F. V. Berghen and H. Bersini. J. Comp. Appl. Math., Vol. 181, pp. 157 (2005); [3] A. V. Pendse and J. R. Collier. J. Appl. Pol. Sci., Vol. 59, pp. 1305 (1996); [4] J. Soulages, T. Schweizer, D. C. Venerus, J. Hostettler, F. Mettler, M. Kroger and H. C. Ottinger. J. Non-Newt. Fluid Mech., In Press (2007). DOI:10.1016/j.jnnfm.2007.10.006.

Thursday 10:05 Steinbeck CF53

Shear history effects on extensional flow of non-Newtonian fluids in filament stretching rheometers

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Modifications to filament stretching rheometers have been used by several researchers in recent years to study the effect of preshear on the transient evolution of the microstructure and viscoelastic tensile stresses for moderately viscous polymer solutions. A typical preshear/extensional experiment usually includes three well-defined stages, namely a preshearing step, followed by exponential axial stretching and then stress relaxation and filament thinning. Measurements collected from these three stages provide a complete quantitative characterization of the effect of preshear history on the extensional rheological properties of the test fluid. In the present work, we simulate all the three stages of the preshearing/filament-stretching experiment using a transient free surface finite element approach. The 'swirl' velocity component due to the preshear is efficiently handled by a 2.5-dimensional axisymmetric finite element formulation, which incorporates the effects of viscoelasticity, surface tension, fluid inertia and a deformable free surface. The rheology of the Boger fluid used in the experiments is simulated by a single-mode FENE-P model with strong strain-hardening corresponding to large values of the extensibility parameter L. During the filament stretching stage, we consider the simplest 'type II' kinematics, with a simple exponential separation of the two plates. The simulation results demonstrate the strong effect of preshear on the evolution of the filament profile and the resulting extensional viscosity (Trouton ratio). The predicted effect of pre-shear on the transient extensional viscosity agrees qualitatively well with the available experimental data.

Thursday 10:25 Steinbeck CF54

Boundary layer approximation applied to capillary entry flow of mobile viscoelastic solutions

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In this study, the boundary layer approximation developed for high Reynolds number Newtonian fluid flow is applied to the capillary entry flow of non-Newtonian viscoelastic fluid, and an analytical method to predict the development of the inflow region length or the elongation viscosity is proposed. Experiments are also carried out to verify the applicability of the method. When the contraction ratio is large, the fluid in the vortex surrounding the inflow region is essentially at rest. Therefore, the pressure is uniform and the forces exerting on a fluid element in the inflow region are the elongation stress force and the shear stress force. They are considered to be in balance since the inertia force is taken to be negligible because the Reynolds number Re is not so high, say less than the order of 10. The equality between the elongation and shear stress forces leads to the principle that the ratio of the radius R_{inf} to the length L_{inf} is inversely proportional to the square root of the Trouton ratio Tr. This corresponds to the case of high Reynolds number Newtonian flows where the non-dimensional boundary layer thickness is inversely proportional to the square root of Re. Thus the boundary layer approximation is shown to be applicable to fluids with high Tr value to simplify the Cauchy's equation. Then, a momentum equation is obtained by integrating the simplified equation over the inflow region in order to obtain an equation for the flow rate Q and L_{inf}. Another equation is derived for Q and L_{inf} from the momentum balance of the capillary flow. Thus start-up behavior of Q and L_{inf} can be calculated under a given driving pressure P_d, if the material functions in steady shear flow and the elongation viscosity are known, or, the elongation viscosity is calculated from the measured Q and L_{inf}. Experiments on an aqueous solution of polyacrylamide with a concentration of 0.2wt% (PAA/W) show that the relationship between Q and L_{inf} in the terminal steady state is well predicted by this analysis. The uni-axial elongation viscosity of PAA/W estimated from the measured values of Q and L_{inf} in the steady flow is much higher than the shear viscosity resulting in values of Tr as high as one thousand. However, the transient behavior accompanied with the overshoot of Q and gradual growth of L_{inf} are not reproduced by this analysis when the elongation viscosity is constant. Hence, improvement of the method will be necessary by taking the time or strain dependence of elongation viscosity into consideration.

Thursday 10:45 Steinbeck CF55

Effect of viscoelasticity on moving contact-line dynamics

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In the continuum physical framework, the moving interface on a no-slip solid substrate constitutes a stress singularity at the contact-line. This singularity has to be accommodated by some artificial slip boundary conditions in the continuum models. As an alternative, we propose a phase-field model that uses molecular diffusion to remove the singularity without introducing ad hoc slip conditions. In this talk, we first discuss simulations of the moving contact-line in Newtonian systems. Quantitative comparisons with experimental data are made to show the capacity of the theoretical model and numerical algorithm. Then we demonstrate that viscoelasticity affects the viscous bending of interface near contact-line, and therefore the overall behavior of the contact-line such as dynamic and apparent contact angles. The viscoelastic results will be compared with previous analysis and spin-coating experiments of Homsy and coworkers.

EM-5. Microscopic and Microfluidic Rheometry

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: Anubhav Tripathi

Thursday 9:45 De Anza I EM28

Multi-sample micro-fluidic rheometry

Kalman B. Migler, Doyoung Moon, and Anthony J. Bur
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We have developed a multi-sample micro-fluidic rheometer (MMR) which is capable of measurements over a broad range of temperatures, viscosities and shear rates. The instrument is inherently simple as the flow is generated by external gas pressure and the shear rate is measured through optical tracking of the flow front. In the current implementation, the required volume of each sample is approximately 20 micro-liter and we measure four samples simultaneously. We test the MMR using two NIST Standard Reference Materials (a PDMS melt and a PIB solution), a polystyrene and several lower viscosity standards - we report a high level of accuracy and precision. We demonstrate procedures for correcting data for shear-thinning and entry/exit flows. This instrument will be particularly useful in cases of multiple samples, limited material quantity, when flow heating is unacceptable and when optical access is useful. More generally, the techniques employed here pave the way for the development of polymer melt microfluidics.

Thursday 10:05 De Anza I EM29

Microfluidic device with coupled confocal imaging to probe viscoelastic properties of soft biological solids such as bacterial biofilms

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We present a technique to characterize the material properties of soft biological solids such as bacterial biofilms in a microfluidic device. The device uses the response of a flexible, deforming membrane to characterize the viscoelasticity of the test material. Attributes of the device are its simple fabrication and operation as well as its ability to probe rheological properties at the length scale of known heterogeneities in these materials. Thus, the device helps to resolve issues with the application of standard mechanical rheology measurements for biological materials such as sample volume requirements, time scales for film growth and material heterogeneity. The device uses a flexible membrane fabricated in poly(dimethyl siloxane) (PDMS) according to the methods of Studer and co-workers (Studer et al., J. Appl. Physics 95(1), 393-398, 2004) to deform bacterial aggregates which can be grown at biologically relevant shear rates in the microfluidic environment. We find that the static and temporal response of the valve membrane correlates well with the viscoelastic properties of a model gellan gum when convoluted with the overall elastic response of the device, as simulated by finite element modeling. We demonstrate the application of the device to characterize the viscoelastic properties of bacterial biofilms comprised of Staphylococcus epidermidis and Klebsiella pneumoniae. Measurement of steady-state deformation yields the linear elastic response of the biofilms as well as their yield strains. We also study the transient response of the PDMS membrane coupled to the biofilm when the system is subjected to a step stress of varying magnitude. By means of time-resolved confocal laser scanning microscopy we track the membrane deformation and thereby extract the viscoelastic relaxation time of the soft biological solid.

Thursday 10:25 De Anza I 💿 EM30

Direct observation of phase transition dynamics in suspensions of soft colloidal hydrogel particles

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Synthetic mono-disperse colloids are widely used as model systems for the study of phase behavior. Depending on particle volume fraction, colloidal suspensions undergo phase transitions between liquid, glassy and crystalline states. The glassy state, often referred to as out-of-equilibrium state, is usually defined as having internal relaxation times that exceed readily accessible experimental time scales. Relaxation of structure and dynamic heterogeneity of the glassy state has been the subject of various theoretical and experimental studies.

The majority of research to date has focused on hard spheres, but the attention of the community is shifting towards soft particles. Due to the tunability of their softness and volume via temperature changes, colloidal microgel particles of crosslinked poly(N-isopropylacrylamide) have emerged as model system for soft spheres. By introducing acrylic acid (AAc) moieties in the polymer network (pNIPAm-co-AAc), one can further enhance control over particle volume through pH. At low pH, the acid groups remain protonated, while deprotonation at high pH leads to electrostatic repulsion within the polymer network and results in particle swelling.

We have investigated the dynamics and phase behavior of suspensions of stimuli-responsive pNIPAm-co-AAc hydrogel colloidal suspensions. Particle Tracking Microrheology (PTmR) was used in combination with a microfluidic dialysis cell to directly observe dynamics of these particles in concentrated suspensions. Our PDMS-based microfluidic device allows us to manipulate the composition of the solvent in the sample, in particular the pH, which controls the volume fraction of the particles. The effect of such pH-induced changes in volume fraction on the phase behavior has been investigated. A major advantage of the dialysis cell is that changes in pH can easily be reversed, so that it is possible to step through the phase diagram at will; this in contrast to hard sphere suspensions in which in-situ changes in volume fraction are impossible. PTmR also provides spatio-temporally resolved data by monitoring individual particles, in comparison with conventional light scattering, which yields ensemble-averaged quantities.

We will present the phase diagram of concentrated hydrogel suspensions as a function of pH and particle concentration, as well as quantitative information on the dynamics of the phase transitions. We found, for example, that in response to the particle mobility (quantified via mean-squared displacement (MSD)) drops instantaneously, while the sample heterogeneity (non-Gaussian parameter) and crystallinity continue to evolve during further microstructural rearrangements. In particular, we show that the glassy system departs from Gaussian behavior over time, supporting observations for hard sphere systems. A unique result for the soft spheres is their ability to undergo glass to crystal transitions even in jammed configurations due to the deformability of the particles.

Thursday 10:45 De Anza I EM31

Vibrating microcantilevers: Tools for microrheology

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The microbeam dynamic analysis shows that vibrating microcantilevers can be used to measure fluid mechanical properties such as density and viscosity. Contrary to classical rheological measurements using microcantilever sensors, the development of the proposed microrheometer is based on the measurement of fluid properties at each vibration frequency, without necessarily being bound to resonance phenomenon. For this approach an analytical model is implemented; the corresponding measurements, which enable the determination of viscosity as a function of frequency, are encouraging for the development of a useful microrheometer on a silicium chip for microfluidic applications. Simultaneous measurements of both phase and amplitude lead to the rapid determination of both unknown fluid parameters (viscosity and density). The rheological behaviours of several Newtonian fluids over a wide frequency range (10-1000 Hz), resulting in a viscosity range of up to 30Pa.s, were verified. The concept is extended to the realm of viscoelastic fluids in order to observe the real and imaginary parts of the complex shear modulus $G = G' + jG''$ of a complex fluid as a function of the frequency. The preliminary measurements performed in binary mixtures made of EHDT silicon-gel confirm the fact that the elastic plateau and terminal relaxation frequency for Maxwellian fluids can be deduced from vibration spectra. These results represent a new method for rheological measurements and an improvement in microrheology.

Thursday 11:05 De Anza I EM32

Micro-cantilever based rheology

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The vibrational characteristics of a micro-cantilever are highly dependant on the properties of the surrounding medium. This principle can be used in the measurement of fluid properties as was demonstrated by Boscovic et al in 2002. They developed a technique for characterizing low viscosity, simple fluids in which the vibration of a microcantilever due to the Brownian motion of the surrounding fluid is measured with the optics of an atomic force microscope (AFM). The fluid properties are then determined using the frequency response of the microcantilever assuming simple harmonic behavior. This method is limited to fluids with low viscosity because in highly viscous fluids, the vibrations due to Brownian motion of the fluid are difficult to detect and the simple harmonic oscillator assumption is not valid. We are modifying this technique for higher viscosity and complex fluids. For this purpose, the fixed end of the cantilever is moved using a piezoelectric material, and the response of the cantilever immersed in the fluid is observed by the AFM optics. In order to study the performance of this technique two series of solutions were studied. First, solutions of glycerol in water at varying concentrations providing a wide range of viscosity without elasticity were studied. Then lightly entangled solutions of polystyrene in diethyl phthalate were studied. With this experimental study we are able to observe the different effects of a viscoelasticitic medium as compared to a Newtonian medium on the vibrational characteristics of microcantilevers in response to two different forcing functions. Using the results we hope to be able to measure the rheological properties of fluids on the micrometer scales with tiny amounts of liquid.

Boscovic S, JWN Chon, P Mulvaney, JE Sader, J. Rheol. 46(4), 891-899 (2002)

Thursday 11:25 De Anza I EM33

Detachment and attachment mechanisms of viscoelastic fluids

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Using a Surface Forces Apparatus coupled to various optical visualization techniques, we have been conducting adhesion measurements of polymer and other material surfaces and films to investigate the transition between pure liquid-like and solid-like flow and especially failure. The transient deformations and flows during both detachment and coalescence were investigated. Thus, in the case of **detachment**, liquid columns thin then snap, while solids crack. The first is determined by the surface tension and viscous forces of liquids; the second is determined by the elastic and tensile strengths of solids. The question is: is there a gradual transition between these two apparently very different failure regimes? By studying the way liquids, viscoelastic polymers, glassy and brittle solids detach when pulled apart over a large range of pulling forces, pulling rates, temperatures, and material properties, we find that there is a continuous transition between these two very different modes of failure, and we are still characterizing the nature of this transition. To this end, we have employed viscoelastic fluids such as polymers of different molecular weights, and solids such as sugars, at different temperatures, thereby modulating the viscosities of the materials by more than 10 orders of magnitude. Detachment rates are being varied from the pm/sec (creep) regime to the m/sec (crack propagation) regime, a range of 12 orders of magnitude. We find that the deformations of the columns or necks of materials as they come or break apart are very complex, exhibiting irregular transient fingering patterns as well as internal cavities; but that the transition nevertheless seems to vary in a continuous way from simple neck thinning, to inward liquid-like fingering, to sharp solid-like cracking. Videos demonstrating all of these effects will be shown.

We have also studied the dynamics of **adhesion** or **coalescence** of polymer melt surfaces and films. As in the case of detaching junctions, transient fingers appear at the bifurcating circle, but these are much more ordered, i.e., periodic, than in the case of detaching surfaces. These fingers grow then disappear as coalescence proceeds, eventually leaving a smooth and continuous polymer-air interface.

The above effects, including the fingering geometries and their life-times depend on the viscosities and film thicknesses of the polymers, as well as on the pulling rates (in the case of detaching surfaces). The glass transition temperatures of the fluids and the Deborah Numbers appear to play important roles in the transitions between different modes of detachment and coalescence, and many of the phenomena observed appear to be describable in terms of the Saffman-Taylor equations for fingering instabilities.

SE-5. Emulsions

Organizers: Denis Weaire and Lynn M. Walker
Session Chair: Matthew Libertore

Thursday 9:45 De Anza II SE31

Irreversible shear-induced elastification of “nanonaise”

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While most materials weaken through fracturing when subjected to large stresses, we show that a viscous, anionically stabilized, microscale emulsion can be irreversibly transformed into a highly elastic “nanoemulsion” by extreme mechanical shear. As the repulsive droplet size approaches the Debye screening length, the nanoemulsion vitrifies. As a result, the onset of elasticity for disordered uniform nanoemulsions can occur at droplet volume fractions far below maximal random jamming of spheres.

Thursday 10:05 De Anza II SE32

Microfluidics velocimetry reveals spatial cooperativity in the flow of emulsions

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Amorphous glassy materials of diverse nature-molecular glasses, concentrated emulsions, pastes, granular materials-display complex flow properties, intermediate between solid and liquid, which are at the root of their use in many applications. Using a microfluidic velocimetry technique, we characterize the flow of oil in water concentrated emulsion, confined in gaps of different thicknesses by surfaces of different roughness, under pressure drop. The section of our microchannel is rectangular, with high aspect ratio. In a planar pressure-driven flow, the local shear stress S(z) is imposed by momentum conservation: S(z) = DP.z/L with DP the applied pressure drop between the two ends of the channel (of length L) and z the position from the center of the channel. The shear stress is the local slope of the velocity profile. We can construct the local flow curve. We study the influence of the confinement (i.e. the width of the microchannel), the oil fraction, the diameter of the oil droplets, the polydispersity of the emulsion, the wall roughness (smooth or rough) on the velocity profiles and the local rheological curves. Beyond the classical non-linearities of the rheological behaviour, we evidence a finite size effect and the absence of an intrinsic local flow rule. For a given oil fraction, but different confinements and/or wall properties, no overlap of the local flow curves is observed. In contrast, a rather simple non-local flow rule is shown to account for all the velocity profiles. The non locality in the dynamics is quantified by a length, characteristic of the cooperativity of the flow at these scales, which is unobservable for an oil fraction below the jamming oil fraction and increases with the concentration of the glassy phase. This length measures the influence of the plastics events. This length is typically a few oil droplet diameters.

Thursday 10:25 De Anza II SE33

Observing Ostwald ripening in a concentrated emulsion using MRI techniques

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Ostwald Ripening occurs in emulsions when oil drops of different sizes are present. There is a greater solubility of oil in the aqueous phase around smaller oil drops than larger oil drops. This difference leads to a concentration gradient where oil is transferred from the small oil drop to the bigger oil drops. This phenomena has usually been observed experimentally in dilute solutions due to the limitations of optical drop size measuring techniques. By applying the Restricted Diffusion Theory to an MRI diffusion experiment, we are able to back out the drop size of the emulsions. Using an MRI to take drop size measurements allows us to use a highly concentrated emulsion (70 vol% oil) to show that Ostwald Ripening also occurs in this system. We are able to show Ostwald Ripening occurring for octane, but not for any higher carbon chain oils such as decane, dodecane, and tetradecane. Also, we are able to show that different surfactants (anionic and nonionic) have a minimal effect on Ostwald Ripening.

Thursday 10:45 De Anza II SE34

Effect of surfactant monolayer concentration on the measurement of the surface tension of emulsion droplets

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The effect of insoluble surfactant monolayer concentration on the measurement of interfacial surface tension using drop relaxation methods is studied using the Boundary Integral Method. Emulsion droplets with a surfactant monolayer modeled with the Langmuir equation of state are

subjected to axisymmetric extensional flows until a steady-state deformation is reached. The external flow is then removed and the retraction of the drops to a spherical equilibrium shape in a quiescent fluid is simulated. Neglecting the initial and final stages, the retraction process can be closely approximated by an exponential decay with a characteristic time, t_r. The strength of the external flow on each model drop is increased in order to investigate the coupled effect of deformation and surfactant distribution on the characteristic relaxation time. Different model drops are considered by varying the internal viscosity and the equilibrium surfactant concentrations from a surfactant free state (clean) to high concentrations approaching the maximum packing limit. It is shown that the characteristic retraction time t_r depends non monotonically on the surfactant concentration. The magnitude of deviation from the retraction time increases with the deformation of the drop. The characteristic relaxation times obtained from the simulated drop dynamics are used to determine surface tension and internal viscosity by employing linear theory. Errors as large as 30% are found at intermediate surface concentrations.

Thursday 11:05 De Anza II SE35

Relating viscosity changes to phase inversion during the synthesis of tackifier emulsions

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Water-based pressure-sensitive adhesives, used in labels, tapes and self-adhesive postage stamps, are made by combining a tackifier emulsion with a latex dispersion. Here we focus on the tackifier emulsion that is synthesized by progressively adding water to a significantly more viscous molten resin with continuous agitation. A water-in-oil emulsion that is initially formed undergoes phase inversion, at some point, producing an oil-in-water emulsion. After phase inversion, water is normally continuously added to dilute the emulsion. The final product has a dispersed phase size that is of the order of one micrometer. In this talk, we describe the construction of an instrumented mixer fitted with multi-stage inner and outer impellers which rotate in opposite directions. Experiments were conducted at constant impeller speeds, different constant temperatures and with the use of varying amounts of additives. In each case, the torque was measured as a function of time and the amount of water added. The point of phase inversion was identified with the help of torque and electrical resistance measurements. It was found that the torque increased monotonically before phase inversion, but it decreased monotonically after phase inversion. The increase can be attributed to increasing dispersed phase concentration and increasing emulsion amount. Similarly, the decrease in torque after phase inversion is mainly due to the low viscosity of water, which is the continuous phase, and a progressively decreasing dispersed phase concentration; the total emulsion amount still increases, and this tends to temper the reduction in torque. The measured torque was used to compute the emulsion viscosity. This exercise employed the use of torque data obtained during the mixing of corn syrup, a viscous Newtonian liquid, and this allowed us to separate the effect of changing liquid volume from the effect of changing emulsion concentration. Emulsion viscosity was interpreted using models available in the literature, and the viscosity versus time behavior was utilized for developing a criterion for phase inversion.

Thursday 11:25 De Anza II SE36

In situ formation and evolution of gas hydrates in water-in-oil emulsions using pressure rheometry

Patrick J. Rensing[1], Matthew W. Liberatore[1], Peng Tonmukayakul[2], Carolyn A. Koh[1], and E. Dendy Sloan[1]
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In oil and gas production and transportation a major concern is the formation of gas hydrates (gas-water inclusion compounds that are stable at high pressures and low temperatures). Gas hydrates have a tenacious ability to plug pipelines, and may lead to unscheduled shut downs. The successful operation of pipeline transport with gas hydrates particles will depend on the ability to control gas hydrate agglomerations and depositions. Gas hydrates can be thermodynamically inhibited but this is proving cost ineffective and environmentally unfriendly. For this reason the oil/gas industry is moving to hydrate management rather than traditional methods of thermodynamic inhibition. One intriguing possibility would be to convert the water in the pipelines to non-agglomerating gas hydrates and then flow the slurry. However, this cannot be reliably achieved until basic understanding of hydrate slurry rheology is gained.

To develop this fundamental understanding, *in situ* pressurized gas hydrate formation and rheological measurements from a water-in-oil emulsion have been conducted. In addition *in situ* ice formation and rheological measurements, from a water-in-oil emulsion, have also been investigated as an analogous system. In this work, small amplitude oscillatory and steady shear techniques have been used to characterize the rheolgical properties of these systems where the effect of water volume fraction (10 – 50%), temperature (–10 to 1°C), pressure (14.5 – 1500 psia), and shear rate (10 – 500 s^{-1}) on the sample have been investigated. The results demonstrate that hydrate and ice formation can be detected in steady shear and oscillatory measurements, where a large viscosity (and elastic modulus) increase coincides with ice/hydrate formation. Since temperature and pressure affect the thermodynamic stability of hydrates these are particular key variables that need to be tuned for this system. One intriguing result from this work is that the formation and dissociation of both ice and gas hydrates appear to destabilize previously stable emulsions.

Thursday Afternoon – 7 August 2008

KL-11. Keynote Lecture 11

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Lynn M. Walker

Thursday 1:15 Steinbeck KL11

Recent progress in shear banding in complex fluids

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When subjected to shear flow, many complex fluids attain a heterogeneous state in which two different microstructures, flowing at different shear rates or suffering different shear stresses, coexist heterogeneously in "shear bands". Such systems include surfactant systems (wormlike micelles, lamellar systems, spherical colloidal-like micelles), block copolymer solutions, colloidal suspensions, and liquid crystals, among others. Although these phenomenae have been studied for decades now, the development of new methods of observing and measuring complex fluid microstructure and velocities in shear flow (microscopy, NMR, ultrasound, particle velocimetry, etc) is rapidly revising our knowledge of shear banding. In this talk I will review the basics of shear banding and discuss current issues, including dynamics and instabilities, boundary effects, and the intriguing possibility of shear banding in conventional polymer solutions.

KL-12. Keynote Lecture 12

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Norm Wagner

Thursday 1:15 Serra I KL12

Anomalous rheology of polymer-nanoparticle suspensions

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Einstein predicted that addition of nanoparticles to a liquid produces a viscosity increase according to his famous relation. We have shown that addition of nanoparticles, of order 10 nm in diameter, to a polymeric liquid produces a viscosity decrease in both the terminal and high shear regions under certain conditions. Of course Einstein is not wrong, the nanoparticles' size is such that they disturb the liquid's structure so its viscosity decreases. This solid solvent behavior will only occur when the nanoparticles are well dispersed since an agglomerate will function as a super-particle to generate continuum expectations. Thus, mixing conditions and an understanding of the thermodynamics are critical which we have detailed in previous publications. Here we will discuss a variety of systems to demonstrate the generality of the non-Einstein effect such as: magnetite dispersed in polystyrene and polystyrene nanoparticles dispersed in poly(methyl methacrylate), which both show a large viscosity decrease. Since the nanoparticles do not adversely affect the materials' physical properties, and indeed do impart multifunctional properties, these suspensions offer unique materials with reduced viscosity to allow enhanced processing.

HS-6. Telechelic/Associative Polymers

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chairs: Florian J. Stadler and Robert A. Weiss

Thursday 2:30 San Carlos IV HS37

Micro and macrorheology of Pluronic aqueous solutions at the sol-gel transition: Evidence of a phase separation on the micro-scale

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In aqueous solutions, triblock copolymers of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO-Pluronic) self-assemble into a number of known aggregation states depending on concentration. In dilute concentration regimes, they form independent core-shell micelles, whereas highly concentrated PEO-PPO-PEO solutions instantaneously form a thermo-setting gel upon heating. The strong viscoelastic response observed at temperatures above the sol-gel transition suggests these systems form 'hard' gels, consisting of a dense network of interconnecting micelles. Previous works revealed anomalous rheological behaviours, suggesting the formation of polydisperse aggregates in the gel. We present the outcomes of a study of the evolving properties of Pluronic F68 and F127 aqueous solutions during the temperature-induced sol-gel transition, employing both conventional macrorheology and particle tracking microrheology. At high heating rates (2 °C per minute), using shear rheometry to monitor the elastic and storage moduli as a function of temperature, the instant of the formation of a network was detected as a single, sharp transition. We confirmed this so-called gel point to be dependent on the nature and the concentration of the pluronic copolymer. All solutions were found to be highly sensitive to shear, and moreover, the gel temperature was shown to be highly dependent on the shear imposed upon the solution prior to the test. Also, when sufficiently decreasing the heating rate, we observed the appearance of at least one secondary transition for a number of solutions, revealing the occurrence of a more intricate gelation process and suggesting the existence of distinct dynamic processes with different time scales. Microrheology was thereafter employed to identify the nature of all association processes and determine both the length-scale and the time-scale of the change in the properties before a network is ultimately formed. At low heating rate, the same secondary transitions during the gelation process were observed and their nature was revealed. Optical video-microscopy also evidenced strong heterogeneity on the macro-scale and on the micro-scale.

Thursday 2:50 San Carlos IV HS38

Inter- and intramolecular interactions of associative polymers in solution

Ralph L. David, Ming-Hsin Wei, and Julia A. Kornfield
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Model polymers with matched backbone length are used to examine the effects of degree of functionalization and type of interaction (self-associating or donor-acceptor) on shear and extensional rheology of associative polymer solutions. A series of polymers with pair-wise, hydrogen bonding stickers were made by functionalization of 500 kg/mol 1,2-polybutadiene (1,2-PB) with carboxylic acid groups (0 to 2%). We examined the shear viscosity of 0 to 30% wt solutions in chlorododecane (giving c*=0.4% wt for the unmodified polymer) and found that the self-associating stickers had very little effect on the zero shear viscosity until concentration exceeded 3-4c*. Instead of increasing the viscosity, stickers reduced the viscosity even at concentrations up to 2-3c*. Intramolecular association and the consequent reduction of coil size, thus, have a dominant effect even at c*, overlooked in prior literature. To favor interpolymer association, we used donor-acceptor pairs: the acid functionalized chains (A-chains) served as donors and polymers bearing tertiary amines (N-chains, 1 to 12% functionalization) were used as acceptor chains. We examined solutions as a function of degrees of functionalization (fA and fN), the molar ratio of acid to amine groups, and overall concentration. Depending on fA and fN, many donor-acceptor pairings resulted in phase separation into gel and sol phases. Those pairs that provided homogeneous solutions were examined further. Dynamic light scattering showed that large aggregates formed in dilute solution, and the zero-shear viscosity increased sharply with concentration even below c*, crossing the viscosity-concentration curve of the unfunctionalized polymer solutions below c*. Study of elastic effects under extentional flow required the use of longer chains; 1300 kg/mol 1,4-PB polymer molecules of low polydispersity were also prepared by functionalization with carboxylic acid and tertiary amine groups. Solution elasticity and extentional viscosity were studied via both capillary thinning experiments (i.e. capillary breakup rheometry using a Thermo Haake CaBER1) and drop breakup experiments (i.e. by high-speed imaging of the splashing and breakup of individual droplets impacting a solid surface). The increase in elasticity and extentional viscosity attributable to stickers seemed to parallel that of the shear viscosity for semi-dilute solutions. On the other hand,in dilute solution stickers seemed to cause a decrease in polymer elasticity as inter and intramolecular associations inhibit stretching of the chains and drive chain collapse.

Thursday 3:10 San Carlos IV HS39

Aqueous formulations of associating polymers: Thermothinning versus thermothickening

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Hydrophobically Modified Polymers [HP] have attracted increasing attention in the last two decades, because of their unusual rheological properties such as enhanced viscosification efficiency, shear thickening property, self-healing ability... They actually find a large number of applications in various technological areas such as enhanced oil recovery, cosmetic lotions, paints and coatings, food additives and pharmaceuticals. These systems typically consist of a water-soluble backbone bearing a small number of hydrophobic stickers either dispersed along the macromolecular structure or specifically located at the ends of the chain. Their thickening ability in aqueous solution arises through reversible intermolecular associations caused by the unfavourable solvent conditions for the hydrophobic groups. The transient character of the physical network is nevertheless very sensitive to the temperature and a strong weakening of the viscoelastic properties is generally observed upon heating (thermothinning behaviour). Conversely, thermothickening or thermoassociating polymers [TP] were developed more recently on the basis of a reversible aggregation process underwent by macromolecular stickers characterized in water by a Lower Critical Solution Temperature (LCST). Such responsive systems are able to gel aqueous formulations above a critical temperature that is strongly related to the primary structure of the copolymer. In the present work, we will describe the structure and the properties of thermothinning and thermothickening polymers based on a grafted poly(sodium acrylate) architecture. We will focus more specifically on the nanostructure of these copolymers in semi-dilute aqueous solutions (SANS studies) and on the resulting viscoelastic properties. By combining the chatacteristiics of hydrophobic and LCST stickers, either grafted on different polymer chains (copolymer mixtures) or incorporated into the same macromolecule (double grafted copolymers : HTP), we will show that it is possible to get a large variety of temperature dependence for aqueous based formulations.

Thursday 3:30 San Carlos IV HS40

Shear and elongational flow behavior of inhomogeneous, acrylic thickener solutions

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Alkali-swellable acrylate thickeners are widely used in different applications like coatings, adhe-sives or personal care products. Here we have used the commercial thickener Sterocoll FD as a model system for investigation of the molecular mechanisms controlling the thickening properties of this class of polymers. This polyelectrolyte is a statistical copolymer of methacrylic acid (MAA) and ethylacrylate (EA). These copolymers are known to form intermolecular aggregates in aqueous solution due to the hydrophobic nature of statistically occurring EA-sequences. Neu-tralized aqueous solutions of this type of polymer are highly viscous, but weakly elastic at con-centrations (0.5-5 wt%) typically used in commercial products. We have investigated shear as well as elongational flow properties of solutions in this range of polymer concentrations to gain deeper insight into the dominating thickening mechanisms. Linear viscoelastic moduli G' and G" have been determined in a broad frequency range up to 10^4 rad/s employing oscillatory squeeze flow. Extensional flow behavior has been characterized using the CaBER-technique including high speed imaging for control of the homogeneity of deformation and the limits of filament stability. The linear viscoelastic relaxation is described by the classical Zimm-theory in the whole frequency range. Accordingly, no entanglements are present in these solutions even at concentrations well above those in typical applications. Zimm analysis allows for determination of an apparent aggregation number N_{app}. This number increases as the polymer concentration increases, but decreases if part of the water is replaced by ethanol as solvent. Both effects can be rationalized in terms of solvent quality, which decreases for the MAA groups as ionic strength increases and increases for the EA groups upon addition of ethanol. At polymer concentrations above 1 wt.% all solutions undergo homogeneous elongational deformation at constant strain rate up to large Hencky strains $\varepsilon > 5$. Time evolution of the filament diameter is described by a single Maxwell-model. The corresponding elongational relaxation time λ_E is always at least a factor of ten lower than the longest shear relaxation time λ_S. Thus we conclude, that the aggregates existing at rest cannot withstand strong flows and do not contribute to the elongational viscosity.

Thursday 3:50 San Carlos IV HS41

Manipulating hydrophobic interactions in associative polymer solutions via surfactant-cyclodextrin complexation

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Hydrophobically modified alkali-soluble emulsion (HASE) polymers are comb-like associative polymers with pendant hydrophobes that form a transient network in an alkaline solution consisting of both intra- and intermolecular hydrophobic junctions. These water-soluble polymers find applications in paint formulations, paper coatings and oil drilling fluids owing to their unique thickening mechanism. Depending on the application as well as processing constraints, it may be desirable to reduce/eliminate the hydrophobic associations at one stage, thereby reducing solution viscosity, and then recover them at a later stage. An effective way to remove hydrophobic associations is by use of inclusion compounds such as cyclodextrin wherein the ring-shaped sugar molecule encapsulates the polymer hydrophobe leading to deactivation of associations. In this work, we investigate the role of nonionic surfactants in recovering the rheological characteristics of HASE solutions containing cyclodextrins. Surfactants compete with the polymer hydrophobes for complexation with the cyclodextrins. The nonionic surfactants used in our study are nonylphenol ethoxylates (NPe) with different ethylene oxide (EO) chain lengths which determine the hydrophilic-lipophilic balance (HLB) of the surfactant. Our results indicate that depending on the type of cyclodextrin (α versus β) as well as the HLB of surfactant, the extent and rate of recovery of zero shear viscosity as well as plateau modulus can be vastly different. In the case of solutions containing a cyclodextrin, recovery is observed solely in the presence of low HLB surfactant (NP6). Addition of higher HLB surfactants (NP8 and NP15) to such systems does not translate into any appreciable changes in macroscopic properties. On the other hand, for HASE solutions containing ? cyclodextrin, a complete recovery of rheological properties is obtained using various surfactants. There are, however, differences in the steady shear profile and frequency spectrum of the recovered and the original solutions. The shear thinning behavior becomes more pronounced and the dynamic moduli exhibit lower frequency dependence, leading to longer characteristic relaxation times, in the presence of surfactants. Moreover, a second drop in solution viscosity as well as plateau modulus is observed at high concentrations of surfactants having high HLB values. These results are explained in terms of different mechanisms of surfactant-cyclodextrin complexation in case of a and ? cyclodextrin as well as difference in binding constants and micellar structures with changing surfactant HLB. Results from UV Spectroscopy and cloud point measurements on these systems support our hypothesis and will be discussed. These results imply that cyclodextrins and surfactants in combination can be judiciously employed to lower the viscoelasticity of HASE solutions during processing, while subsequently recovering the high viscosity and viscoelastic properties that are sought in their applications.

Thursday 4:10 San Carlos IV HS42

Tunable polymer networks based on specific hydrogen bonding motifs

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We have investigated the rheology of polymer networks in which the interpolymer crosslinks are based on controlled hydrogen bonding between polymer side groups and small-molecule crosslinking agents. Hydrogen bonds are noncovalent interactions, like metal coordination, Coulombic and dipole-dipole interactions, and therefore reversible under the appropriate environmental conditions. Hydrogen bonds are readily broken at elevated temperatures and can thus be used to form reversible, thermosensitive polymer networks.

Another unique property of hydrogen bonds as intermolecular interactions is that multiple bonds are often combined in specific molecular recognition motifs. Thymine and cyanuric acid are both well-known examples of compounds that form strong, multiple hydrogen bonds with receptor molecules that possess complementary acceptor-donor motifs. Thymine, one of the bases in DNA, forms 2-point hydrogen bonds with adenine in DNA, but can also form 3-point hydrogen bonds with diaminotriazines. Cyanuric acid forms 3-point hydrogen bonds with melamine or diaminotriazine, and even stronger 6-point hydrogen bonds with Hamilton wedge receptors.

For this study, a variety of co- and terpolymers was synthesized via ring-opening metathesis polymerization (ROMP) of three norbornene-based monomers with different functional side chains: an inert alkane (C8), cyanuric acid, and thymine. The alkane-based spacer monomers were used to dilute the functional groups and enhance solubility of the polymers in 1-chloronaphthalene. Selective ditopic crosslinking molecules were also synthesized: one with two Hamilton wedge motifs and another with two diaminotriazine groups. The objective was to create a tunable system in which the strength of the network can be manipulated by selective crosslinking different polymer side chains. As controls, we also used monotopic Hamilton wedge and diaminotriazine, which should only be able to bind to one side chain at a time and therefore not act as crosslinkers.

Shear and oscillatory rheology will be shown for solutions of spacer/cyanuric acid and spacer/thymine copolymers in the absence and presence of the small molecule hydrogen-bonding receptors. It was found that, depending on the combination of polymer and crosslinking agent a wide range of rheological properties could be obtained, from highly viscous fluid to strongly elastic gel. The variability of rheological properties reflects significant variations in the underlying molecular structure, which are currently not fully understood. The tunability of polymer networks based hydrogen bonding will be highlighted by presenting the rheology of solutions of spacer/thymine/cyanuric acid terpolymers in the presence of all cross-linking agents in varying combinations and concentrations. We were able to manipulate the rheology of the terpolymer solution by taking advantage of the competitive binding of the cyanuric acid and thymine residues with the various cross-linking agents.

Thursday 4:30 San Carlos IV HS43

Gel point determination of biopolymer-based semi-IPN hydrogels

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Semi-IPNs (Interpenetrating Polymer Networks) hydrogels were prepared by mixing two biopolymers, alginate and hydrophobically modified ethylhydroxy ethyl cellulose (HM-EHEC), followed by crosslinking the alginate by in-situ release of calcium ions. Thus by altering two different parameters, hydrophobic chain length and crosslinker concentration, we were able to tune the mechanical properties of the semi-IPNs. Previously we have shown that dynamic oscillatory studies in the linear viscoelastic region indicate storage moduli comparable to soft human tissue for hydrogels having 90wt% water. In the present work we will investigate the gel point (GP) of the evolving system by rheological techniques. Effect of % crosslinker and molecular weight (MW) on the GP will be presented. Results indicate that MW of HM-EHEC does not have significant effect on the GP but systems with lower MW HM-EHEC fails to obey Winter-Chambon criterion. Validity of Winter-Chambon criterion and alternate theories from the literature will be discussed in details. We will also present the drug release behavior of model hydrophobic drugs for our system. The mechanism of drug release and how it is related to mechanical strength and structure will be elaborated. To elucidate structure-property relationships for these materials, small angle scattering (SAXS and SANS) were performed to gain insight into the nano and micro scale structure.

Thursday 4:50 San Carlos IV HS44

Linear and nonlinear rheological characterization of temporary networks of telechelic polybutadiene

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Apolar polymers with hydrogen-bonding or ionic end-groups have a natural tendency to form temporary networks and are as such interesting systems to study the interplay between topological interactions, i.e. entanglements, and reversible supramolecular linkages. While some rheological and structural characterization of such systems has been published in the past, no systematic study on the respective influences of topological vs. supramolecular interactions has been reported. In this work, we focus on the linear and non linear rheological characterization of **telechelic polybutadienes** (PBd) with **carboxylic end groups** neutralized with various inorganic and organic bases.

A difunctional carboxylic acid terminated PBd shows only very weak associative behavior with a slightly increased temperature dependence by comparison with the neat polymer. The neutralization of the acid end-groups, however, leads to the formation of a reversible network, whose bonding strength and characteristic relaxation time depend very much on the nature of the ion, and to a much higher temperature dependence. An increase of the relaxation time by several orders of magnitude is observed together with a dramatic change of the plateau modulus by comparison with the reference polymer. This is consistent with the formation of a network with a significant reversible crosslinking density. For some samples, a very weak gel regime is observed in a *"pseudo-terminal"* region and thermorheological simplicity fails at intermediate frequencies, presumably where topological and supramolecular interactions together influence relaxation.

The extremely long terminal relaxation times are very challenging from an experimental standpoint. For some samples, an annealing of several days at elevated temperatures in the rheometer is required to obtain an equilibrium in (thermo-) rheological and structural characteristics. The equilibrium structure is destroyed by a strong mechanical treatment. Small angle X-ray scattering highlights an amorphous structure, dominated by the presence of small ionic aggregates at a repeat distance of about 10 nm for a 4 kg/mol backbone. Details of the structure are dependent on the mechanical treatment and on the chemistry.

Besides linear viscoelasticity and structural characterization, we have also studied the behavior in uniaxial elongation. Strain hardening is observed in some cases but has a complicated dependence on the neutralizing ion. Another interesting point is that the strain at rupture is highly dependent, at a given strain rate, on the characteristic relaxation time of the network (and hence on the Weissenberg number). A dramatic decrease of the elongation at break is observed when the Hencky strain rate is higher than the inverse of the reciprocal crossover frequency.

SG-7. Modeling

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Alexey V. Lyulin

Thursday 2:30 San Carlos II SG43

Microscopic theory of the relaxation and mechanical properties of polymer glasses

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A statistical mechanical theory of barriers, slow segmental relaxation and the glass transition of deeply supercooled polymer melts has been recently developed by combining and extending methods of mode coupling, dynamic density functional and activated hopping transport theories [1]. The melt is treated as a liquid of statistical segments, and the approach is built on the concept of a nanometer scale nonequilibrium free energy which quantifies local dynamical constraints and the thermally driven activated barrier hopping process. The caging force is primarily determined by the polymer-specific amplitude of longer wavelength collective density fluctuations (melt compressibility) and local chain stiffness [2]. Predictions for the kinetic glass and crossover transition temperatures, dynamic fragility, and highly non-Arrenhius temperature dependence of the segmental relaxation time are consistent with experiments on many polymer melts [1,2]. This theory has now been generalized to treat quiescent relaxation [3], physical aging [4], and nonlinear mechanical properties and the alpha relaxation process [5] below the glass transition temperature. The structural component of density fluctuations become frozen below Tg resulting in a crossover to Arrenhius relaxation. Physical aging is modeled based on a kinetic equation for the time evolution of density fluctuations. On intermediate time scales following a quench the relaxation time grows as a power law with aging time with a temperature dependent exponent. Applied stress weakens dynamical constraints thereby accelerating alpha relaxation and softening the elastic modulus. Multiple differences between our approach and the phenomenological Eyring model are identified. A constitutive equation has been constructed [6] which allows the prediction of stress-strain curves and the rate and temperature-dependence of the dynamic yielding phenomenon. Mechanical response has been studied in constant strain rate and constant stress (creep) modes. Quantitative comparisons of the theoretical results with temperature and strain rate dependent mechanical and relaxation experiments on PMMA reveal good agreement. Finally, the statistical dynamical approach can be generalized to treat large deformation-induced chain distortion which underlies the ubiquitous but poorly understood non-entropic strain hardening phenomenon, and also the coupling of mechanical deformation and aging associated with "rejuvenation" phenomena. Comparisons of the theoretical results with multiple experiments are encouraging.

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Thursday 2:50 San Carlos II SG44

Temperature dependence of relaxation time in Adam-Gibbs model for glass-forming liquids: Fluctuation effects

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Time-correlation function C(t) formalism of dynamical variables that describes slow modes in glass-forming liquids is exploited to show that, under a single assumption, the Cole-Cole plot of the time derivative of C(t) resembles the Cole-Davidson function in the entire frequency plane. Our results suggest a universal constant in supercooled liquids. The prediction is tested against dielectric relaxation data. Finally, we develop techniques to take into account fluctuation effects in Adam-Gibbs model of cooperative relaxation in supercooled liquids.

Thursday 3:10 San Carlos II SG45

An Eshelby model of the highly viscous flow

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The shear flow in highly viscous fluids is modeled in terms of local structural rearrangements which reverse a strong local shear. Using Eshelby's solution of the corresponding elasticity theory problem (J. D. Eshelby, Proc. Roy. Soc. A241, 376 (1957)), one can calculate the recoverable compliance and estimate the lifetime of the symmetric double-well potential characterizing such a structural rearrangement. A calculation of the shear relaxation spectra requires the knowledge of all possible structural rearrangements of the given glass former, at present a completely unsolved theoretical task.

Thursday 3:30 San Carlos II SG46

Solid-state constitutive modelling of glassy polymers: Coupling the Rolie-Poly equations for melts with anisotropic visco-plastic flow

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The tailoring of materials to processes, and processes to products is greatly facilitated through the use of constitutive models applicable concurrently to both melt and solid states. Such constitutive models would need to capture (1) the linear and non-linear rheology of polymer melts, (2) the process-induced deformation in the semi-solid state, and (3) the service response of the resulting oriented products in the solid state. Progress towards such models is challenging, but clearly of great scientific and practical interest. In order to achieve this ambitious goal we investigate the coupling of two existing constitutive models: the Rolie-Poly equations, developed in the Leeds laboratory as part of the µPP project, and successfully used in the modelling of complex melt flows; and a new anisotropic viscoplastic solid-state constitutive model recently developed in the Oxford laboratory.

In the present work, the melt model describes the evolution of the entanglement network through a system of simultaneous multi-mode Rolie-Poly equations with finite extensibility. The melt model parameters are obtained using standard experimental rheological techniques measuring the linear and non-linear shear response, and the elongational response. The solid-state model consists of a spectrum of anisotropic viscoplastic flow units with Eyring kinetics, representing the intrinsically anisotropic nature of the polymer chains on sub-entanglement length scales. The orientation of the flow units follows the deformation, and the fluidity of the units evolves with the stretch of the chains between entanglements. The glass structure is prescribed through equations describing the evolution of the fictive temperature of each flow unit. The interaction between the models comes through a coupling of the evolving unit fluidity to the chain stretch parameters coming from the Rolie-Poly equations. Such a combined model thus benefits from the molecular awareness of its physically-based components.

The combined model is tested by rheological and solid-state experiments using three grades of well-characterised linear monodisperse atactic polystyrene with M_w=262, 518 and 966 kg/mol. Results demonstrate that the linear and non-linear rheology, and the solid-state response can be adequately captured using a single set of material parameters applied to the constitutive model. Additionally, the applicability of the model to the prediction of solid-state properties of products with process-induced molecular orientation is explored through experiments and simulations.

Thursday 3:50 San Carlos II SG47

Case II diffusion and solvent-polymer films drying: A meso-scale model

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The presence of solvent in a polymer matrix can reduce the glass transition temperature Tg significantly. This results in a very pronounced non-linear behaviour for solvent diffusion in a glassy polymer or in a matrix close to or below the glass transition. In many instances case-II diffusion -i.e. solvent propagation with a well defined front- is observed instead of a standard Fickian diffusion profile [Thomas1982]. It is described in a phenomenological way by a non-linear diffusion equation which involves two adjustable parameters (the so-called Thomas-Windle model [Thomas1982]. Describing the reverse process, that is the drying process of e.g. a thin polymer film, is a complex issue as well [Saby-Dubreuil2001,Bornside1989].The aim of this paper is to propose a model at the nanometer scale for solvent diffusion in concentrated polymer-solvent mixtures, based on macroscopic quantities, such as the WLF parameters of the liquid, or of the Tg shift due to the presence of solvent. This model is based on the fact that dynamics in liquids close to the glass transition is spatially heterogeneous [Ediger2000,Souche2007]. The characteristic size of these dynamical heterogeneities is typically 3 to 4 nm in van der Waals liquids, which corresponds to a number of degrees of freedom (monomers or solvent molecules) of a few hundred. Before considering large scale diffusion experiments, we consider first the evolution of the dynamics of a layer of thickness 3 nm, submitted to an arbitrary time varying activity a(t). When performed systematically, this procedure allows in principle to calculate a constitutive relation for the dynamics of solvent-polymer mixtures, that can then be used for calculating the evolution of macroscopic samples in contact with a reservoir of solvent. We show how these constitutive relations allow for explaining case-II diffusion in glassy polymers and provide a physical interpretation for the parameters of the Thomas-Windle model. Regarding the process of film drying, we show that films up to 1 micrometer thick can be almost completely dried in an accessible experimental time, even at temperatures well below the polymer glass transition temperature. This is a consequence: 1- of the presence of the fast path 2- of the film being out equilibrium, and in a dynamical state which is must faster than the one it would have at equilibrium. When drying a thicker film, we show that a glassy crust may appear on the free surface, as has been shown experimentally.

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Thursday 4:10 San Carlos II 💿 SG48

Direct atomistic modelling of deformed polymer glasses

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In the macroscopic deformation of polymer glass-formers striking differences occur between polymers of similar topology. E.g., tensile-testing experiments reveal that atactic polystyrene (PS) has little plastic deformation before brittle failure, while (bis)phenol-A polycarbonate (PC) withstands significant strains. PS exibits substantial strain softening as compared to PC, but the amount of strain softening is influenced by the thermal history of the material (quenched or annealed) and/or mechanical pre-deformation. It was shown experimentally that after mechanical rejuvenation both PS and PC become very ductile and can be made to deform by shear yielding. In the present paper molecular-dynamics simulation is used to explore the influence of thermal and mechanical history of typical glassy polymers on their deformation. Polymer stress-strain and energy-strain developments have been followed for different deformation velocities, also in closed extension-recompression loops. The latter simulate for the first time the experimentally observed mechanical rejuvenation and overaging of polymers, and energy partitioning reveals essential differences between mechanical and thermal rejuvenation. All results can be qualitatively interpreted by considering the ratio's of relevant timescales: for cooling down, for deformation, and for segmental relaxation.

Thursday 4:30 San Carlos II SG49

Early stages of plastic behaviour and cavitation in glassy polymers investigated by molecular dynamics simulations

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Amorphous glassy polymers are subjected to two mechanisms of localized plasticity: shear yielding and crazing. Upon yielding, glassy polymers are prone to softening followed by progressive orientational hardening that results in the formation of shear bands with -large- localised deformation. Crazing involves also some localised plasticity [KRA83], but at a smaller scale and is preceded by the nucleation of voids that eventually formed elongated fibrils. The aim of the present study is to analyse the competition between shear yielding and crazing under impact conditions for which the characteristic time scale is of the order of a micro-second. In particular, the early stages of the cavitation process underlying craze nucleation still need to be clarified to determine whether crazing can be triggered, depending on the loading rate and conditions, and on the characteristics of the material such as the chain length and flexibility. Our study is based on coarse-grained molecular dynamics simulation [2,3] . For the analysis of various loading conditions in terms of trajectory in the deformation space, we propose a measure of the non affine displacement. It allows for distinguishing the 'uniform' non affine regime and that with the nucleation of a cavity during the deformation. This non affine displacement measure can be seen as a precursor for the process of craze initiation and subsequent fibrillation.

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Thursday 4:50 San Carlos II 💿 SG50

Finite strain viscoplastic modelling of polymer glasses

Lambert van Breemen, Leon Govaert, and Han Meijer

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Currently there are several constitutive models available that accurately capture the deformation characteristics of glassy polymers. The typical approach to describe the deformation kinetics, which is dominated by a single molecular process, is to use a single-relaxation time, i.e. thermorheological simple, with parallel strain hardening. This type of modelling proved to be successful in capturing experimentally observed phenomena such as necking, crazing and shear banding as well as life time predictions under static load.

Despite these successful applications, some problems remain. An important one being the fact that the pre-yield regime is not accurately described, leading to an incapability to capture recovery/unloading phenomena. This typically becomes a problem when looking at contact phenomena like indentation and sliding contact, i.e. friction and wear experiments, where recovery directly influences the real contact area between a single asperity and the polymer. To qualitatively give a verdict on intrinsic friction properties one needs to capture these phenomena accurately.

The cause of this problem is mainly that a single-relaxation time description is, by definition, not capable of capturing the time-dependent mechanical properties of glassy polymers, with relaxation spectra that spread out over tens of decades. Moreover, in most cases the polymers response is determined by several molecular processes, each leading to a spectrum of relaxation times with its own non-linearity and temperature dependence.

An elegant solution to the problems mentioned above is therefore the introduction of a multi-relaxation time model which captures the non-linearity of the pre-yield regime and keeps the framework of the large strain post-yield response in tact. The proposed model, which is based on a multi-mode Maxwell model including time-stress superposition, adequately describes the deformation under monotonic loading. An extension to several molecular processes is rather straightforward.

The strength of this approach will be demonstrated on PC and PMMA. A new characterization method is presented that gives a direct estimate of the required relaxation time spectrum directly from constant rate compression or tension experiments. The spectrum thus obtained can not only accurately describe the loading curves at different strain rates, but is also very successful in describing constant rate load-unload contact problems. Similar to the single relaxation time approach, the influence of thermal history can be included by introduction of an age-dependent state-parameter, leading to the definition of a reference state; the un-aged state. We will show that this method performs well for the above described transient stress states.

Thursday 5:10 San Carlos II SG51

Quantitative prediction of mechanical performance of polymer products directly from processing conditions

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Product design is currently supported by a large number of numerical tools that aid the various steps in the design process. Amongst these tools are numerical codes that allow simulation of mould filling and subsequent cooling in injection molding, and finite element packages that are able to evaluate the mechanical response of the final product under the desired loading conditions. These two examples illustrate the two design regions that can be distinguished with respect to numerical codes, i.e. the processing of the product and the use of the product. Unfortunately, there is, up till now, no real interaction between the two. The processing region focuses on the melt state and the use region focuses on the solid state, each region requiring its own numerical tools and set of material parameters. It is, however, the processing step which in part determines the behavior in the solid state. A new method is presented that directly predicts the development of yield strength distributions in injection molded products of glassy polymers. The approach is based on the results of a study on the temperature dependence of the evolution of the yield stress during annealing of polycarbonate below Tg. In combination with the process-related thermal history, derived from numerical simulations of the injection molding process, yield strength values are predicted, including their dependence on the mold temperature used. It is demonstrated that the method quantitatively predicts both short- and long-term failure of polymer products, thus making it a powerful tool for true product optimization.

HP-10. Entangled Polymers II

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Jay D. Schieber and Christian M. Bailly

Thursday 2:30 San Carlos III HP64

From reactor to rheology in LDPE modeling

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In recent years the association between molecular structure and linear rheology has been established and well-understood through the tube concept and its extensions for well-characterized materials (e.g. McLeish, Adv. Phys. 2002). However, for industrial branched polymeric material at processing conditions this piece of information is missing. A large number of phenomenological models have been developed to describe the nonlinear response of polymers. But none of these models takes into account the underlying molecular structure, leading to a fitting procedure with arbitrary fitting parameters. The goal of applied molecular rheology is a predictive scheme that runs in its entirety from the molecular structure from the reactor to the non-linear rheology of the resin.

In our approach, we use a model for the industrial reactor to explicitly generate the molecular structure ensemble of LDPE's (Tobita, J. Polym. Sci. B 2001) which are consistent with the analytical information. We calculate the linear rheology of the LDPE ensemble with the use of a tube model for branched polymers (Das et al, J. Rheol. 2006). We then, separate the contribution of the stress decay to a large number of pompom modes (McLeish et al, J. Rheol. 1998 & Inkson et al, J. Rheol. 1999) with the stretch time and the priority variables corresponding to the actual ensemble of molecules involved. This multimode pompom model allows us to predict the nonlinear properties without any fitting parameter.

We present and analyze our results in comparison with experimental data on industrial materials.

Thursday 2:50 San Carlos III HP65

Neutron flow-mapping of controlled-architecture polymer melts

Nigel Clarke[1], Pierre Chambon[2], Edoardo Deluca[1], John Embery[3], Christine Fernyhough[2], Tim D. Gough[4], Richard S. Graham[5], Isabelle Grillo[6], Lian R. Hutchings[1], Kamakshi Jagannathan[3], Harley Klein[3], and Tom C. McLeish[3]
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We report on results of a new method for probing complex flows of entangled polymer melts that is able to compare simultaneously chain configurations on different length scales and stress distribution in the flow with the predictions of molecular models. Controlled-architecture melts synthesised by anionic polymerisation and selectively deuterated are made in sufficient quantities to fill a recirculating flow device that contains a windowed processing zone. This may take the form of a constriction or a cross-slot. The whole processing rig is scanned across a narrow neu-

tron beam before a small-angle detector that reports on the structure factor of labelled chains (this sometimes requires the subtraction of two differently-labelled experiments). The same flow is probed in birefringence, measuring the independent orientation at the bond level of the chains. The polymer melt is also characterised molecularly and rheologically, and compared to predictions from the tube model in the GLaMM formulation. This model then serves to parameterise the computationally simpler RoLiEPoly model, suitable for numerical calculation of the flow by the Eulerian-Lagrangian mixed scheme flowSolve. The results of the flow computation are use in turn to compute the predicted full-chain scattering patterns by recomputing with GLaMM along the flow lines computed by flowSolve. This procedure has now been applied to polystyrene melts in the cases of: (1) monodisperse linear chains; (2) a bimodal blend of linear chains; (3) a blend of comb-architecture polymers in a linear matrix. The results indicate that entangled polymer dynamics in complex flows are relatively benign from the point of view of the chains - even sharp re-entrant corners do not initiate large chain deformations. It also clarifies the length-scale dependence of chain orientation: there are many regions of the flow in which the birefringence reports isotropy and the neutron-scattering strong anisotropy, in good agreement with the tube model. In case (3) we identify to what extent the backbones of comb polymers do and do not behave like linear chains.

Thursday 3:10 San Carlos III 💿 HP66

Effect of molecular structure on rheological behavior of nearly monodisperse H-shaped polybutadienes

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A remaining challenge in the molecular modeling of entangled polymers is the accurate prediction of the rheological behavior of polydisperse polymers with long-chain branches in which there is more than one branch point per molecule. In order to evaluate a hierarchical model for branched polymers, a several polybutadiene samples were prepared and subjected to precise and accurate rheological characterization.

Using a novel synthesis technique based on anionic polymerization, nearly monodisperse H-shaped PBDs with high 1,4 microstructure (> 90%) were synthesized. Linear viscoelastic properties of H-shaped PBDs with different arms lengths and backbones lengths were studied by frequency sweep and creep experiments. The degree of entanglement of these H-shaped PBDs ranges from 6 to 50. The effect of polydispersity was studied by means of a binary blend of two H-shaped PBDs with the same backbone length but very different arm lengths. Time-temperature superposition was used to prepare master curves using data obtained from –90 °C to 90 °C. The results were compared with the predictions of a hierarchical tube model for long-chain branched polymers. Strengths and weaknesses of the model used were revealed.

Thursday 3:30 San Carlos III 💿 HP67

Rheology and structural changes of hyperbranched polymers: Non-equilibrium molecular dynamics study

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Hyperbranched polymers are imperfectly branched or irregular tree-like structures that have special properties and potential applications in various areas such as thermoset resins, toughening agents and drug delivery. They can be synthesized economically by one-pot reaction which adapts well to large-scale production but provides a polydisperse mixture of randomly branched polymers with different size and topology. This leads to difficulties in experiments and gives simulation a valuable opportunity to shed light on getting further insight to understand the structure and rheology of hyperbranched structures. They have been simulated using bead-rod models together with Monte Carlo and Brownian dynamics techniques. In this research, hyperbranched materials were simulated using coarse-grained uniform beads and non-equilibrium molecular dynamics methods. Polymeric chains are composed of interconnected beads interacting via finitely extensible nonlinear elastic and Weeks-Chandler-Anderson potentials. Viscoelastic properties and structural changes of trifunctional hyperbranched polymers in the melt undergoing planar shear are investigated. Our results are in the range between those of dendrimers and linear analogues of equivalent molecular mass.

Thursday 3:50 San Carlos III 💿 HP68

Architecturally complex polymers: Viscoelasticity and extensional rheology

Evelyne van Ruymbeke[1], Michael Kapnistos[2], Edward Muliawan[3], Dimitris Vlassopoulos[1], Akira Hirao[4], and Nikos Hadjichristidis[5]
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We test the coarse-grained time-marching model we developed for predicting the linear viscoelastic properties of branched polymers from the knowledge of their molecular structure on several new model architectures.

Based on three viscoelastic parameters, i.e., the Rouse time of an entanglement segment, the plateau modulus and the entanglement molecular weight, this model uses the ingredients of the tube-based theories of McLeish and co-workers, and its implementation is based on a time-marching algorithm. With an new way to account for the motion of the molecular segments localized between two branching points and within the framework of dynamic tube dilation (using the extended criteria of Graessley), this conceptual approach was already successfully applied to linear, star, H and pompom polymers [1,2].

In this work, we extend our work to more complex architectures, i.e., comb polymers, tree-like polymers and telechelic architectures. A number of important issues such as the Mw or structural polydispersity effect, the role of reptation and of the different branching points in the relaxation of a comb polymer, and the limits of the Dynamic Tube Dilation – are addressed.

Based on the predictions obtained for the linear data, we extended the model for predicting the non-linear rheology, following the approach proposed by Blackwell et al. [3]. We consider in particular the case of model symmetric Cayley tree polybutadienes and poly(methyl methacrylates) having 2 and 3 generations with branches of varying degree of entanglements: the signature of each layer relaxation was evident in the linear response, both in the plateau modulus and the terminal relaxation as a distinct contribution, well-separated in time. We also performed uniaxial elongation measurements using the SER fixture. The samples tested exhibited significant strain hardening compared to the linear analogues at lower and intermediate Hencky strain rates. The extracted effective steady extensional viscosity scales with the elongational rate with a power exponent of about –0.5, in agreement with earlier findings with linear polystyrenes.

[1] E. van Ruymbeke, R. Keunings, C. Bailly, J. Non-Newtonian Fluid Mech. 128, 7-22 (2005); [2] E. van Ruymbeke, C. Bailly, R. Keunings, D. Vlassopoulos, Macromolecules, 39, 6248-6259 (2006); [3] Blackwell R. J., Harlen O. G., McLeish T. C. B., Macromolecules, 34, 2579 (2001).

Thursday 4:10 San Carlos III HP69

Tube theory for non-linear rheology of binary blends of monodisperse polymers

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We present a new tube-model theory to describe the non-linear rheology of entangled blends of long and short monodisperse polymers. For each test chain it is conceptually important to distinguish a "thin tube" (including entanglements with all other chains) and a "fat tube" (including entanglements with the slowly-moving long chains only). Our theory includes two significant advances: (i) It includes a mathematical framework for describing correlations along, and between, both the thin and fat tubes, allowing for different constraint-release rates on each; (ii) We obtain self-consistent expressions to describe reptation and stretch relaxation along both the thin and fat tubes (motion along the latter being allowed due to constraint release in the thin tube). By construction, our theory is consistent with the Viovy-Colby-Rubinstein diagram for different relaxation regimes in the linear rheology limit. We shall discuss the predictions of the theory, comparing it against simpler formulations involving pre-averaged constraint-release rates, and also comparing against experimental data for linear and non-linear rheology of model binary blends.

Thursday 4:30 San Carlos III HP70

Determination of the terminal longest relaxation time

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We analyze dynamic rheological data (G', G") for slightly polydispersed melts (Mw/Mn ~2), and show that viscosity (G*/w) scales with the power of a reduced frequency w' defined from the ratio of w and (G'/G*)2 = cos2 (theta), where theta is the stress/strain shift angle. The limit at w-->0 of w', w'o, is identified as the inverse of the longest relaxation time for the flow process in the terminal zone. Log-Log plots of (ETA*/ETA*o) versus (w'/ w'o) are linear and superpose the effect of temperature (ETAo is the Newtonian viscosity). The variation of w'o with temperature is described by an activated process. The molecular weight dependence of the exponential front factor of w'o(T), for a series of monodispersed Polystyrene, is tested for its power law dependence with M (w'oo ~ M^3.x where x varies between 0 and 0.4, to be determined). "Shear-thinning" is simply viewed as a decrease of (1/w') by the stress, and the transition zone is reached, at temperature T, when w'(T, G*) = w'o (M/Me)^3.x.

Thursday 4:50 San Carlos III HP71

Experimental studies on the relaxation behavior of commercial polymer melts

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Characteristic times for a PDMS sample with medium polydispersity were measured by using various rheological tests. Compared with the linear relaxation spectrum, the obtained characteristic times form two groups: one corresponds to the chain reptation relaxation and the other to the chain contraction relaxation (roughly the Rouse time). The crossover frequency of dynamic moduli seems belong to the latter. In step shear deformation, the relaxation behavior of the medium polydisperse PDMS and PMVS(polymethylvinylsiloxane)samples belongs to the power law type, while that of a highly polydisperse HDPE sample belongs to the kinked type. In terms of the damping function, the Doi-Edwards theory and Marrucci model overestimate the strain softening for the three commercial polymers. The occurrence of stress peaks in the step deformation experiment as the strain increases beyond a critical value is presented, implying possible strain localization or stratification in the three samples. The critical strains for the three samples are about 1.0, 2.5 and 3.0, respectively, close to the predictions of 2.1 and 2.3,respectively, by the Doi-Edwards theory and Marrucci model. Applying the viscous/elastic stress decomposition method proposed by Cho et al. to the large amplitude oscillatory shear deformation, the relationship between the generalized elastic modulus and the relaxation modulus of step deformation of the PDMS sample was examined; it is found that in the linear and initial nonlinear regimes, as the angular frequency increases, the former approaches to the latter at the corresponding time scales.

Thursday 5:10 San Carlos III HP72

Numerical investigation of effect of stirring blades on mixing efficiency of a planetary kneading mixer with non-Newtonian and viscoplastic materials

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Highly viscous mixing operation is an important procedure of many industries from food mixing to solid propellant manufacture. In the manufacturing process of solid propellant, some solid particles such as coarse and fine grained particles of oxidizer, ammonium perchlorate are mixed with an inert binding agent, which is initially a highly viscous liquid. This type of fluid is commonly classified into non-Newtonian and viscoplastic fluid. A double-blade planetary kneading mixers are usually utilized to fulfill this mixing procedure. In this work, by means of differential geometry, rheology and computational fluid dynamics (CFD), methods to visualize and analyze the mixing process happening in the planetary kneading mixers are proposed. These methods include developing three-dimensional model of the stirring blades, establishing the physical and mathematical models of the flow field in the mixing tank of the planetary kneading mixers, determining the boundary conditions of numerical simulation be virtue of rheological theory and rules, and deeply investigating the characteristics of velocity field, flow pattern, pressure distribution and viscosity distribution of the mixing field numerically simulated by means of CFD software. On the other hand, some mixing performance evaluating indexes and their calculating methods of this type of mixers, such as torque, pumping capacity, strain shear rate and shear stress, are proposed. Finally, mixing performance the planetary kneading mixers, which differ from each other in the helix angle, mounting clearance of stirring blades was evaluated via above mentioned analyzing methods. The investigating results illustrate that the preferable torque characteristic, higher pumping capacity and steady shearing rate can be achieved when the value of the helix angle and mounting clearance of the stirring blades are chosen properly.

BR-5. Rheology of Tissues and Scaffolds

Organizers: James L. Harden and Christoph F. Schmidt
Session Chair: Alex Levine

Thursday 2:30 Redwood BR28

Identifying the mechanical behavior of brain tissue in both shear and compression

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The objective of this work was to validate the non-linear viscoelastic constitutive model of brain tissue that was developed in Hrapko et al. (2006) and has shown to provide a good prediction of the shear response. The model predictions were compared to compression relaxation results up to 20% strain of porcine brain tissue samples. Compression and shear results were obtained from the same samples to reduce the effect of inter-sample variation. Compression measurement results with and without initial contact of the sample with the loading plate were compared. The influence of a fluid layer surrounding the sample and the effect of friction were examined and were found to play an important role during compression measurements. The model has been implemented in the explicit Finite Element code MADYMO. Model simulations with varying boundary conditions are used to interpret the compression results. Simulations using the non-linear constitutive model and its linearized version in a 3-D head model showed a difference in the maximum stress and strain responses of 20% and 50%, respectively.

Thursday 2:50 Redwood 💿 BR29

High resolution MR-elastography: A unique tool to study the rheological properties of tissue in vivo and the origin of its multiscale behaviour

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Background. Although the rheology of soft tissue samples is subject to extensive studies, mainly via rheometer measurements, only a few papers discuss the mechanical behaviour of living biological tissues. This is mainly due to the lack of a reliable and accurate technique to quantitatively assess the stress-strain relationship in vivo.

Aims. In this study, we show that MR-Elastography with its full 3D potential gives unique access to the frequency dependency of the complex shear modulus. In-vivo multi-frequent experiments were conducted in rat brain, fibrotic rat liver and human breast tissue. Additionally, a full physically-motivated model, in agreement with the causality principle, has been developed to explain the observed dispersion properties and finite element simulations were conducted to understand their microscopic origin.

Methods. For animal studies, experiments were conducted on a high-field MR-scanner (Bruker Pharmascan 7 Tesla). Piezoelectric plates were used to generate steady state shear waves inside the organ of interest. Monochromatic acquisitions were repeated between 200 and 1000 Hz in rat brains. For human breast experiments, a full body MRscanner was used (Philips Intera Achieva 1.5 Tesla) with a dedicated mechanical driver for breast elastography. Data were acquired between 65 and 100 Hz on healthy volunteers. All experiments were performed using a motion-sensitized MR sequence phase-locked to the mechanical excitation. This allowed recording all 3 components of the entire displacement field for each frequency. A local inversion algorithm was used to reconstruct the 3D maps of the complex shear modulus removing remnants of the compressional wave.

Results. In all experiments, both real and imaginary parts of the complex shear modulus were found to rise with frequency according to a power-law. In addition, the ratio between those 2 quantities appeared to be constant with frequency and directly linked to the exponent of the power law. Based on the hypothesis of a power-law damping, a full physical model was derived to fit the data taking into account the causality principle (Kramers-Kronig relations). This leads to a new interpretation of the viscoelastic properties in terms of intrinsic properties and architecture.

Conclusions. MR-Elastography can be efficiently used to study rheology in vivo. The frequency behaviour of the macroscopic viscoelastic parameters gives additional information about the microscopic structure of the material. The observed power-law leads to the hypothesis that an underlying self-similar network is responsible for it. Simulations show that the vascular network is a potential candidate. If proven, this could lead to a contrast provided on a macroscopic scale sensitive to changes on the level of the microscopic vascular architecture. Furthermore, at low frequency, the apparent loss modulus seems to originate more from the multiple scattering at the micro level than from the intrinsic viscosity.

Thursday 3:10 Redwood BR30

Spatial variations in the dynamic shear properties of articular cartilage

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Articular cartilage is a specialized connective tissue that covers bones in joints and transmits load across them. Its complex and inhomogeneous structure endows it with a specific mechanical response that enables it to remain effective for 6-9 decades, or most of a human lifetime. However, damage to the structure of articular cartilage gives rise to disease by compromising proper functionality. Consequently, determining the complicated relationship between structure and function in this tissue is critical to understanding the origin of cartilage diseases. Here, we measure spatial variations in the shear modulus $|G^*(\omega)|$ of bovine articular cartilage. We find that the zero frequency shear modulus $|G^*(\omega=0)|$ can vary by two orders of magnitude across a single sample and exhibits a global minimum at a depth d of 50 – 250 μm below the articular surface. Moreover, the shear modulus profile depends strongly on the applied shear and axial strains. The greatest change in $|G^*(\omega=0)|$ occurs at the global minimum where the tissue is highly nonlinear, stiffening under increased shear strain and weakening under increased compressive strain. On the other hand, the region of tissue far from the surface (d > 500 µm) is much more sensitive to the frequency of deformation, increasing in stiffness as the frequency is raised. Our results can be explained through a simple thought model describing the observed behavior in terms of known spatial variations in the structure and composition of articular cartilage.

Thursday 3:30 Redwood BR31

Morphological and mechanical characterization of reconstituted collagen networks

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Collagen is the most abundant extracellular matrix (ECM) protein and serves as a 3D culture environment for cell biology assays. Cell behavior in 3D sensitively depends on the mechanical properties of the ECM. Moreover, for computing cell tractions from the matrix deformations around invaded cells, knowledge of the matrix rheology is necessary. Confocal images of collagen gels (2.4 mg/ml) show a narrowly distributed pore size of Ø1 µm. Macrorheology using a parallel-plate rheometer revealed predominantly elastic behavior that was approximately linear for strains < 5%, with a shear modulus G' of 80 Pa, a loss modulus G" of 11 Pa, and a weak frequency dependency of both moduli according to a power-law with exponent 0.09. Microrheological behavior was measured by applying a 21 nN 'point' force to a ferrimagnetic Ø4.5 µm bead, and tracking the resulting 3D displacements of Ø1 µm fluorescent beads dispersed in the gel. Alternatively, local strain fields were determined by indenting the gel surface with a 100 µm sphere, or by shearing the gel between two parallel glass plates. Under all conditions, the microscopic gel deformations for strains < 5% closely followed those of an affine, predominantly elastic, isotropic and homogeneous continuum.

Thursday 3:50 Redwood BR32

Flow induced orientation of cholesteric collagen, a useful substrate for controlling cell orientation

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Collagen is one of the most important and abundant proteins in the human body and is present in skin, cartilage, and bone. The structure of collagen on a molecular level is that of a thin rod constructed of 3 polypeptide strands twisted together into a triple helix. When collagen is held in highly concentrated acidic solutions the solution exhibits the behavior of a liquid crystal, forming nematic and cholesteric phases. Cholesteric liquid crystal-like textures of collagen have been observed in tissues such as fish scales, human bone osteons, and pre-cholesteric ordering in tendons [1,2]. The focus of this work is to create a biocompatible substrate with the ability to control cell orientation and proliferation through the structure of collagen. These novel substrates are created by precisely depositing a solution of highly concentrated collagen with a robotic arm on a variety of materials. We have found that as a result of flow the liquid crystalline organization of the collagen can be controlled to create highly uniform morphologies. After deposition and desiccation the collagen forms structures consistent with the banding of a cholesteric liquid crystal. As a result of the flow the banding of the collagen is parallel to the direction of flow with a half pitch of 3 – 4 microns and free of defects. The response of adult human fibroblast cells to the banding structure has been shown to result in a high degree of orientation with a stretching of the cells in the direction of orientation. The organization of the collagen can be quantified using AFM and optical techniques to express the degree and uniformity of the orientation. The deposition technique allows the addition of growth factors and fillers with mechanical or structural properties to the collagen while still presenting an oriented surface. The covalent attachment of the growth factor BDNF (Brain-derived neurotrophic factor) to collagen for the culture of spiral ganglion derived stem cells is reported. The goal is developing a better understanding of the ability of cells to recognize the oriented collagen and determine how this can be used for greater control over the cellular behavior.

[1] Giraud-Guille, M.M., Journal of Biomechanics 36 (2003) 1571-1579; [2] Hulmes, D.J.S., "Building Collagen Molecules, Fibrils, and Suprafibrillar Structures" Journal of Structural Biology 137, 2-10 (2002).

Thursday 4:10 Redwood BR33

Rheology of telechelic protein hydrogels

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We present rheology and microrheology studies of regular hydrogel networks formed by reversible self-assembly of associating triblock proteins. These fibrilar, telechelic proteins consist of a hydrophilic disordered coil center domain flanked by two associating coiled-coil end domains. We will discuss a series of proteins with complimentary associating end blocks that preferentially form trimeric cross-links. The viscoelastic network structures formed by these triblock proteins behave as classical associating polymer systems. We characterize the dependence on the rheological behavior of these hydrogels on solution conditions (pH and temperature) and contrast their behavior with analogous irreversibly cross-linked protein hydrogels.

Thursday 4:30 Redwood BR34

Interfacial flow processing of biological molecules

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A new method is presented to generate ordered substrates of biological molecules for tissue culture purposes. Collagen and fibroin will be used for this purpose.

The molecules are spread at the interface of a salt solution (Phosphate Buffered Saline) and air, compressed at a high speed to induce orientation and harvested using Langmuir-Blodgett transfer. In the first part of this project, the behavior of collagen at the interface is investigated using a number of interfacial techniques. Isotherms show that collagen indeed resides at the air-fluid interface and that there is a variation in behavior dependent on the concentration of the salt and the temperature of the subphase, which is thought to be the result of a change in fiber formation. Dichroism experiments involving a dye that attaches to collagen specifically prove that the collagen fibers can be oriented at the interface and that the orientation relaxes on a time scale long enough for us to be able to transfer oriented collagen onto a glass substrate. Brewster's angle microscopy (BAM) gives us a visual picture of the interface, showing oriented collagen fibers after compression. Rheological measurements using the interfacial stress rheometer document the fibril formation of collagen at the air-fluid interface over time and may provide further insight in the dependence of the collagen behavior on salt concentration and temperature of the subphase.

After Langmuir-Blodgett transfer, primary human fibroblasts and adipose-derived stem cells are cultured on the collagen substrates. Both types of cells clearly feel the oriented collagen substrate and align upon the deposited fibers.

The same techniques will now be applied to substrates generated from fibroin, the core protein in silk. Isotherms, BAM and interfacial rheology are used to characterize the surface, and cell culture substrates are generated.

The technique presented here provides an easy method to produce substrates of well-controlled oriented collagen and fibroin that can be used in tissue culture research and/or scaffolding applications without the use of additives and/or bio-incompatible materials.

Thursday 4:50 Redwood BR35

Transient extensional rheology of an aqueous gelatin solution: Before and during gelation

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A technique for studying the extensional rheology of gelling systems is presented. The technique is based on capillary thinning extensional rheometry, and has been used to investigate the extensional rheology of an aqueous gelatin solution before and during gelation. We discuss the qualitative differences between the response prior to and soon after the gel point. In particular, we discuss the effect of gelation on the strain- and rate-dependent extensional response. We also discuss some of the methods and techniques to overcome some of the arising obstacles and limitations.

MP-8. Nanocomposites and Blends

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: O Ok Park

Thursday 2:30 Colton I-III MP52

The rheology of optically transparent polystyrene blends filled with cross-linked polystyrene beads

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In order to assist the understanding of rheological properties of polymer blends, a series of polymer blends have been made where a polystyrene matrix has been blended with spherical crosslinked polystyrene particles. The blend has sufficient transparency that optical observations can be made during processing. Different concentrations of blends were prepared by one of two routes; namely mechanical blending and blending using solvent mixing. Rheological data was obtained using standard viscoelastic rheometers and in addition processing data was obtained using a Cambridge Multipass Rhemoeter MPR [1]. Rheological data and optical observations of the blends were carried out using the MPR for an entry/exit slit flow [2] and an extensional flow cross-slot configuration [3]; using both flow birefringence and direct optical visualisation.

The MPR pressure profile rheological data showed differences between the blends that were prepared by mechanical and solvent processing and the pressure change with volume fraction and flow-rate has been modelled in relation to the differences in hydrodynamic volume of the cross linked bends within the matrix for the solvent and mechanically blended materials. The birefringence and direct visualisation observations provided insight into the similarities and differences in rheolgical behaviour of the matrix alone and the blended materials. In addition an unexpected cavitation phenomenon was observed for certain processing conditions of the blend and it is speculated relative flow around the crosslinked beads causes local low pressure regimes where cavitation can occur.

[1] Mackley M.R., Marshall R.T.J., Smeulders J.B.A.F., "The multipass rheometer", Journal of Rheology, 39(6), 1293-1309 (1995); [2] Collis M.W., Mackley M.R., "The melt processing of monodisperse and polydisperse polystyrene melts within a slit entry and exit flow", J. Non-Newtonian Fluid Mech, 128, 29-41 (2005); [3] Coventry K.D., Mackley M.R., Cross-Slot Extensional Flow Birefringence Observations of Polymer Melts Using a Multi-Pass Rheometer Submitted Journal of Rheology 2007.

Thursday 2:50 Colton I-III MP53

A study of the rheology, processability and flow induced mesostructures of glass bead filled polystyrene

P. Hine, M Tassieri, and John Embery
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In this work, which is part of the UK government funded Microscale Polymer Processing Project (www.irc.leeds.ac.uk/mupp^2), we have investigated the effect of the addition of glass beads on the linear and non-linear rheology of a commercial polydispersed (shear thinning) polystyrene. As well as the effects on the bulk viscoelasticity, the addition of the glass beads was found to lead to interesting structural aspects such as chaining of the glass beads and cavitation depending on the concentration, deformation type and shear rate. The polystyrene was supplied by BASF (Mw = 274,000, polydispersity 2.7) and the coupled glass beads (Spheriglass 5000) by PQ Potters Europe. Blending was carried out using a solvent procedure (THF) and a thermal stabiliser (Irganox 7610) to limit degradation of polymer during the solvent drying process .First, a set of linear and non-linear rheology measurements were carried out on both the pure PS and a 20% v/v glass bead/PS blend. For the linear shear, the presence of the glass particles was found to raise the viscosity. The increase was found to be predicted well by the familiar empirical Kreiger-Dougherty relationship1 (a = 2 and $\phi_{max} = 0.68$), plus a novel horizontal shift factor for the frequency (ω) given by $\omega_{filled} = \omega^*(1- \phi)$: here ϕ is the volume fraction of the glass beads. This second factor adjusts for the enhanced strain in the matrix due to the presence of the rigid glass beads, and hence the earlier onset of shear thinning. Non-linear measurements, in both shear and extension flows, were also carried out: shear measurements used a cone and plate geometry and the extension measurements used a Sentmanat Extensional Rheology system (SER). The use of the same shifting factors gave good agreement at small strains in both cases, but divergence at higher strains. Currently this is thought to be due to two distinct effects. First, the presence of the glass beads affects the development of molecular orientation during flow, reducing the overshoot in non-linear shear and the amount of strain hardening in non-linear extension. Second, SEM analysis of the samples, particularly those from the non-linear extension test, showed the presence of cavities in the PS matrix linked to the glass beads, giving a strong indication that this is the major contributor to the strain hardening reduction and potentially to the shear viscosity reduction. These results have subsequently been incorporated into a flow predictor developed in-house in the muPP programme (flowSolve), to thereby model the effect of the particles on processing. Results will be presented showing a comparison between experimental results and theoretical predictions for extrusion, and in particular the effect of the glass particles on die swell.

1. Kreiger, I.M. and Dougherty TJ, Trans Soc Rheol 3 (1959) 137-152.

Thursday 3:10 Colton I-III 💿 MP54

The behavior of particle agglomerate in a Newtonian molten polymer in the dispersion and re-agglomeration processes

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The particle dispersion technology in a polymer is used for manufacturing polymer composites. The dispersed state as well as the volume fraction affects the performance and functionality. Though the dispersed state can be evaluated by dynamic rheological measurement, the transition of particle agglomeration has not been well researched. In this study, both of particle agglomeration and shear viscosity have been evaluated in dispersion and re-agglomeration, and their relationship was researched. For the observation of particle agglomerate behavior in a shear flow, a steady shear was applied to the molten polymer containing particle with different fraction by a cone-plate type rheometer. We used a Newtonian molten polymer as dispersing medium and 2.5um spherical silica as dispersed particles. To obtain a confined particle agglomeration in a polymer, a weak shear was applied to the mixture for a confined time (pre shearing). Just after that the shear rate was changed into the set value in a short time. After applying shear for a certain time, the number of agglomerated particles in a solidified mixture was calculated, and the distribution and average for shearing condition was evaluated. The viscosity was measured at the same time. For the mixture with the particle content of 0.15, agglomerate was dispersed following the change in shear rate and the agglomerated number approached the steady state according to the applied shear rate. The dependency of the applied shear rate on the particle dispersion could be observed as time progressed. And at a higher shear rate the agglomerate was dispersed more and the time to the steady state became longer. The dispersion behavior could be well explained by strain and it suggests the dispersion of agglomerate is strongly affected by the deformation of polymer. For this mixture composite, the viscosity changed according to the change in agglomeration. When the same shear rate applied to the polymers with different particle content, the fraction of large agglomerates became large as the increase in particle content. Just after the change in shear rate, the difference of agglomerate size distribution became small because large agglomerates were primarily broken up. Since small agglomerates were dispersed afterward, the fraction of completely dispersed particle increased significantly. The averaged agglomerated number for each mixture decreased similarly as shearing time independently of particle content. On the contrary, the viscosity of the mixture with lower particle content decreased more quickly than that of the higher particle content. We also have carried out re-agglomeration of dispersed particle by reducing shear rate at a confined agglomerated state. In the re-agglomeration process, the mixture with higher particle content showed more quickly increase in agglomerated number compared to that with lower content. Thus, the delay of the change of to that of agglomerated number is affected not only by the particle content but by the shear history.

Thursday 3:30 Colton I-III 💿 MP55

Studies for polyblend behaviour in screw extrusion and injection molding processes

Krzysztof Wilczynski, Zbigniew Szymaniak, and Andrzej Nastaj
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Polyblend behaviour in the single-screw extrusion and injection molding processes was studied. Melting mechanisms for LDPE/PS polyblend were investigated, as well as a morphology development was observed. The break-up mechanism and fibrillation, as well as coalescence were clearly visible. A computer model for screw extrusion was developed to study material behaviour. The model is based on the flow field description in the single-screw extrusion process given by SSEM model.

Thursday 3:50 Colton I-III MP56

Polymer rheology of PP, Cl-PP, sulfonated PP and their blends

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PP is one of the most general purpose polymers used in various industries. In order to expand its applicability further, it is interesting to consider the functional modification of PP such as chlorinated PP or sulfonated PP. Started from commercialized chlorinated PP, sulfonated PP is successfully prepared with sulfur contents from 10 -54 mmol-S/mol-C. PP/Cl-PP, PP/SPP and PP/Cl-PP/SPP blends are prepared in a Brabender mixer to study not only the rheological properties but also thermal properties for further processing. Chlorinated PP turned out to be well dispersed in PP because of its low viscosity. Instead SPP is not well dispersed in PP because of its high viscosity. Ternary blend shows similar trends with PP/SPP blend. ARES and DMA measurements are consistent with one another. In order to mix these polymer blends properly, it is necessary to control the viscosity levels of pure polymer PP, Cl-PP and SPP by adjusting their molecular weights and processing conditions such as temperature and shear rate.

Thursday 4:10 Colton I-III MP57

Dendritic-linear blends: Linear viscoelstic properties

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Rheological properties of blends of linear polystyrenes with dendritically branched polystyrenes are reported. Both the linear and the dendritic polymer have nearly identical weight average molecular weights near 300 kg/mol, however, their zero shear viscosities differ by three orders of magnitude. Remarkably, this implies that it is possible to prepare polymer blends of constant molecular weight that differ dramatically in the observed rheological properties. The entangled nature of the undiluted linear polymer is progressively lost as the dendritic material is added. At 60 wt% dendritic, Rouse dynamics are observed. The addition of a small amount (5 wt%) of dendritic to the linear material preserves the entangled nature but reduces the viscosity by two-thirds. As is observed in blends of high and low linear polymer blends, the steady-state compliance is non-monotonic passing through a maximum in the vicinity of 60 wt% dendritic. Finally, the scaling of the plateau modulus with dendritic concentration shows an unusually strong behavior.

Thursday 4:30 Colton I-III 💿 MP58

The rheology and processing of renewable resource polymers

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Bio-based polymers offer an alternative to conventional fossil fuel-based materials, in particular for commodity applications such as single-use products. In this work, we report on the rheology and processing of two bio-based polymers, namely poly-hydroxyalkanoate (PHA) and polylactic acid (PLA), and their blends. These materials are derived from renewable resources, and can degrade under the appropriate conditions. The rheology is investigated in shear, elongation, and transient modes. Of particular importance is the degradation of these materials at typical processing conditions, and the impact of polymer architecture on the extensional properties. Using results from these rheological investigations, appropriate thermal and flow conditions are employed in a DSM Xplore microcompounder, with the cast film attachment, to produce films of PHA copolymers blended with PLA. The resultant films are characterized, as a function of both material composition and processing history, using DSC, WAXD, tensile testing, and SEM, to investigate the effect of varying PHA content on the final properties.

Thursday 4:50 Colton I-III 💿 MP59

Deformation and rheology of co-continuous blends

Gibson L. Batch[1], Patrick C. Lee[2], Carlos R. Lopez-Barron[2], and Christopher W. Macosko[2]
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Model immiscible blends were tested for morphology and rheological properties. With planar compression comes a loss of co-continuity. Transient viscosity overshoot is larger with the blend than with either component. Storage modulus is affected by the blend morphology at low shear rates. Shear viscosity at high shear rates is 30 percent lower than either component. Normal stress and viscosity are both larger than the mean between the phases, and die swell with the blend is larger than with either component.

Thursday 5:10 Colton I-III MP60

Preparation and rheological properties of high impact polystyrene/organoclay nanocomposites

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High impact polystyrene (HIPS) nanocomposites with organophilic layered silicate (organoclay) via in situ polymerization were prepared and characterized with respect to their morphological and rheological properties. Three types of organoclays, BHDC, VBC and ODVC, were obtained by ion exchange reactions of pristine monotmorillonite (Na^+ MMT) with benzyldimethylhexadecyl N^+ Cl^-, trimethylvinylbenzyl N^+ Cl^- and dimethyloctadecylvinylbenzyl N^+ Br^-, respectively. The nanocomposites were synthesized by the free radical polymerization of styrene solution containing 5 wt% polybutadiene and organoclay ranging from 0 to 3 wt%. X-ray diffraction (XRD) peak of the nanocomposite prepared by ODVC disappeared, which indicates the exfoliation of silicate layers. It reveals that the alkyl chain having a vinylbenzyl group end-tethered to silicate layer participated in the chain reaction of polystyrene. Transmission electron microscopy confirmed well-dispersed silicate layers inside the matrix polymer. On the contrary, the peak of the nanocomposites prepared by BHDC shifted to lower angle, indicative of the intercalation of polymer chains into silicate layers. Rheological properties such as complex viscosity and storage modulus increased with increasing amount of organoclay. Even a small addition of organoclay as low as 1 wt% showed a substantial increase in the storage modulus in lower frequency region. Mechanical properties were evaluated and some properties were found to be superior to conventional HIPSs.

CG-3. Gels and Glasses

Organizers: Dimitris Vlassopoulos and Wilson C. Poon
Session Chairs: Ken Schweizer and Jan Vermant

Thursday 2:30 San Carlos I CG13

Long-time diffusion and glass transition in hard-sphere colloidal suspensions

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We present a Stokesian Dynamics simulation study of the dynamics of hard-sphere colloidal suspensions. Using the accelerated Stokesian Dynamics method, we investigate the long-time structural and transport properties of highly concentrated monodisperse hard-sphere colloids. The volume fraction-dependence of the velocity and stress autocorrelation functions are used to study the vanishing of the long-time self-diffusivity and the divergence of the zero shear viscosity as the glass transition is approached. Results are compared with available experimental data and theoretical predictions, and with simulation results in the absence of hydrodynamic interactions.

Thursday 2:50 San Carlos I CG14

Constitutive equation for dense colloidal dispersions

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We present a first principles approach to the rheology of dense colloidal suspensions subject to general homogeneous flow.

Starting from the fundamental Smoluchowski equation for interacting Brownian particles under flow we derive exact results for calculating general time dependent averages. This leads e.g. to a generalized Green-Kubo relation for the stress tensor. Using Mori-Zwanzig type projection operator steps we develop a formally exact equation of motion for the transient density correlator which captures structural relaxation Approximations to these quantities are then developed which lead to a general constitutive equation for dense dispersions under arbitrary (incompressible) homogeneous flow. As the approximations (e.g. in the handling of solvent mediated effects) used are tailored to treat high density systems, our final equations allow the time dependent rheology of glassy colloidal suspensions to be investigated.

We demonstate the effectiveness of our approach by presenting numerical results for shear [1] and general flows, including step-strain/compression, steady-shearing and creep. Comparisons with flow curves from experiment [2] and simulations [3] support the approach.

[1] J. Brader et al., Phys. Rev. Lett. 89, 058301 (2007); M. Fuchs and M.E. Cates, Phys. Rev. Lett. 89, 248304 (2002); [2] J. J. Crassous, M. Siebenbürger, M. Ballauff, M. Drechsler, O. Henrich, and M. Fuchs, J. Chem. Phys. 125, 204906 (2006); [3] F. Varnik and O. Henrich, Phys. Rev. B 73, 174209 (2006)

Thursday 3:10 San Carlos I CG15

Imaging slip and shear banding in the rheology of hard-sphere colloidal glasses

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Using cone-plate rheometry combined with simultaneous confocal microscopy we study the slip and flow of colloidal hard-sphere glasses, both for microscopically smooth shearing surfaces and for surfaces with roughness on the particle scale. For smooth surfaces, the global rheology exhibits a crossover from Bingham-like slip behavior at small applied shear rates to a Herschel-Bulkley response at large rate. Simultaneously measured velocity profiles show that the 'slip to shear' transition is strongly position dependent. We present a phenomenological model that quantifies both the local and global rheology, we show that the Bingham-type slip is directly connected with the onset of yield stress and that it is *generic* for hard-sphere colloidal glasses at smooth, non-sticky walls.

For microscopically rough boundaries, we find global Herschel-Bulkley flow curves, but the associated velocity profiles show pronounced non-linearity's, developing into strong localization (coexistence of solid and sheared regions) for stresses just above the yield stress. This localization has its onset at the glass transition volume fraction and becomes more pronounced at larger densities. We discuss the possible role of microscopic stress fluctuations or other inhomogeneities as origin for the localization, and emphasize that bulk rheological measurements in this case do not reflect the homogeneous constitutive relation for the material.

Thursday 3:30 San Carlos I CG16

Soft glassy materials: Relaxation and compression under shear

Hans Wyss[1], Alberto Fernandez-Nieves[2], Johan Mattsson[3], Giovanni Romeo[4], Melaku Muluneh[5], and David A. Weitz[6]
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The decrease of viscosity with increasing shear rate is commonly observed in suspensions of solid particles. We show that this effect can be greatly intensified if the particles are soft and deformable. Our experimental system of soft microgel beads allows us to study the mechanical behavior both macrosopically and locally, at the scale of the beads themselves. We combine the data obtained at different length scales to arrive at a simple picture of the observed accentuated shear thinning.

Thursday 3:50 San Carlos I CG17

Structure and rheology of dense micelles suspensions formed by hydrophobically end-capped PEO

Frederic Renou, Lazhar Benyahia, and Taco Nicolai
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Hydrophobically end-capped poly(ethylene oxide) (PEO) is a highly asymmetric diblock copolymer that forms spherical micelles in water. They resemble multi-arm star polymers with the difference that the number of arms can vary as a function of temperature or concentration. At higher concentration the micelles jam and a liquid-solid transition occurs, which is a function of concentration and temperature. Contrary to covalent star polymers, the transition is discontinuous and accompanied by crystalline ordering of the micelles. However, a disordered solid (glass) is formed first and the crystalline order appears more slowly (1). The flow behaviour of the solids under stress has been investigated in detail and shows a strong power law dependence of the flow rate on the applied shear stress, but no well-defined yield stress (2).

The effect of varying the length of the PEO chain or the alkyl end-group on the liquid-solid transition will be discussed. A particular situation occurs when the alkyl end-group is large so that it crystallizes in the core of the micelles at low temperatures. This system allows us to dramatically reduce the exchange rate of chains between micelles. We will show that this has profound implications for the rheological properties of the suspensions.

The solids can be melted by adding a small amount of un-functionalized PEO chains(3). This effect is stronger if the added chains are longer. The solid can also be melted by adding functionalized chains with a different chain length. As a result, mixing two solids formed by dense monodisperse micelle suspensions leads to the formation of a liquid. Static and dynamic scattering experiments showed that mixed micelles were formed in the mixtures. Possible mechanisms of the melting will be discussed.

Finally we will discuss the effect of mixing functionalized chains with the same PEO chain length but different lengths of the alkyl end-group.

(1) Nicolai, T.; Laflèche, F.; Gibaud, A. Macromolecules 2004, 37, 8066; (2) Nicolai T, Benyahia L. Macromolecules 2005, 38, 9794; (3) Renou F, Benyahia L, Nicolai T. Macromolecules 2007, 40, 4626.

Thursday 4:10 San Carlos I CG18

Shear gelation in block copolymer micellar solutions

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[1]ESPCI, Paris, France; [2]European Synchrotron Radiation Facility, Grenoble 38043, France

We investigate poly(lauryl methacrylate)-poly(styrene)-poly(lauryl methacrylate) block copolymers that self-assemble into spherical core-shell micelles in apolar solvents. Dilute solutions below the overlap concentration have a purely viscous behaviour. Yet, at higher concentrations, the solutions shear-thicken and/or become strong gels under the appropriate conditions. When the shear is stopped, the gel-like properties persist over extremely long periods of time exceeding weeks, at room temperature. On the contrary, upon heating they relax back to the liquid state very quickly. We study this intriguing phenomenon using rheology and a combination of experimental tools, such as DLS, SAXS and microscopy, which probe simultaneously the structure of the micellar solutions and interparticle interactions. The kinetics of gelation under oscillatory and steady shear flows and the properties of the resulting gels are characterized by scaling laws. We propose microscopic mechanisms that accounts for the observed behaviour.

Thursday 4:30 San Carlos I CG19

Intriguing two-time-scale elasticity in arrested phases of lysozyme solutions

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We investigated the competition between spinodal decomposition and dynamical arrest using aqueous solutions of the globular protein lysozyme as a model system for colloids with short range attractions [1]. Quenches below a temperature Ta lead to gel formation as a result of a local arrest of the protein-dense phase during spinodal decomposition. We studied the evolution of the microstructure using time-resolved small-angle light scattering and optical microscopy, and characterized the linear viscoelastic properties of gels formed in the course of the arrested liquid-liquid phase separation. Surprisingly, we found the material response function to be characterized by two distinct elastic moduli that are well separated in time. Phenomenologically our material response functions can be described by a serial arrangement of a spring and a Kelvin-Voigt element. Microscopically we tentatively account for this behavior assuming that the arrested spinodal phase separation leads to the formation of two kinds of strands, one corresponding to a stiff, the other one to weak over-damped spring.

[1] F. Cardinaux, T. Gibaud, A Stradner, and Schurtenberger, Phys. Rev. Lett. 99, 118301 (2007)

Thursday 4:50 San Carlos I CG20

Microscopic dynamics of shear recovery in nanopartcle depletion gels

Brian Chung[1], Ranjini Bandyopadhyay[2], Dennis Liang[3], Subramanian Ramakrishnan[4], Charles F. Zukoski[5], Robert L. Leheny[3], and James L. Harden[6]
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We describe x-ray photon correlation spectroscopy and diffusing wave spectroscopy studies of concentrated depletion gels formed from nanoscale silica colloids in solutions of nonabsorbing polymer. The experiments track the changing microscopic dynamics as these jammed, nonergodic systems recover following the cessation of large shear. The two techniques provide a quantitatively coherent picture of the dynamics as ballistic or convective motion of colloidal clusters whose internal motion is arrested. The evolution of the dynamics possesses features characteristic of nonergodic soft solids, including a characteristic relaxation time that grows linearly with the time since cessation of shear. However, comparison with the behavior of quenched supercooled liquids indicates the dynamics in these colloidal gels are not directly related to traditional aging and rejuvenation phenomena in molecular glasses.

Thursday 5:10 San Carlos I CG21

Network induced relaxation dynamics in colloidal gels

Emanuela Del Gado[1] and Walter Kob[2]
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In contrast to other systems that show a slow relaxation, such as, e.g., glass-forming liquids, the structure of gels is given by a open network that is thought to be responsible for the unusual dynamical properties of these systems. It would be therefore essential to deeper understand this connection and to be able to tune the mechanical response via the structural features.

We investigate the gel formation from the equilibrium sol phase in a simple model that has the characteristics of (colloidal) gel-forming systems at a finite temperature [1]. In the molecular dynamics simulations, at low volume fraction and low temperatures, particles are linked by long-living bonds and form an open percolating network. As a consequence, the dynamics show a non-trivial dependence on the wave-vector: At high wave vectors the relaxation is due to the fast cooperative motion of the branches of the gel network, whereas at low wave vectors the overall rearrangements of the heterogeneous structure produce the relaxation process. We analyse the contribution of different parts of the gel network (single bonds, nodes...) to the complex relaxation dynamics observed.

[1] E. Del Gado and W. Kob, Europhys. Lett. 71, 1032 (2005); Phys. Rev. Lett. 98, 028303 (2007); J. Non-Newt. Fluid Mech. 2007, in press.

SC-9. Dynamics and Scattering in Colloids

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Michael J. Solomon and Walter Richtering

Thursday 2:30 De Anza III SC55

Thermo diffusion of colloids

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The thermal diffusion coefficient of colloids can, in good approximation, be written as an additive contribution stemming from colloid-colloid interactions and a contribution due to single colloidal particle properties. A microscopic approach will be discussed that predicts the effect of colloid-colloid interactions on the thermal diffusion coefficient. The microscopic approach is based on an extension of the Smoluchowski equation that accounts for a temperature gradient. The predicted weak concentration dependence in case of hard-sphere interactions is confirmed by experiments. For charged colloids, an important contribution to the single-particle diffusion coefficient originates from the electrical double layer. The corresponding single-particle contribution is analyzed on the basis of an extension of the Debye-Hueckel theory that describes the temperature-gradient induced asymmetry of the double-layer structure. The asymmetry of the double layer gives rise to fluid flow. The effect of this flow on the thermal diffusion coefficient will be discussed as well. The predictions for the double-layer contribution to the single-particle thermal diffusion coefficient will be compared to experiments.

Thursday 2:50 De Anza III SC56

Hydrodynamic and electrokinetic effects on the dynamics of charge-stabilized colloidal particles

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In a joint theoretical-experimental study, we explore dynamic processes in suspensions of charge-stabilized colloidal particles. Various transport properties like diffusion coefficients and viscosities, and dynamic scattering functions have been calculated by means of a recently developed accelerated Stokesian Dynamics simulation tool, and using methods of many-body theory adapted to colloidal soft matter systems. Results obtained from theory and simulations are compared with static and dynamic scattering experiments on colloidal spheres, globular proteins and DNA fragments. Salient results of this study comprise the absence of screening of hydrodynamic flow in salt-free fluid suspensions, the influence of the electrolyte ion kinetics on the colloid diffusion in non-dilute systems, and a hydrodynamic explanation for the unexpected non-monotonic concentration dependence of long-time self-diffusion in suspensions of moderately charged particles. Furthermore, we analyze the validity of generalized Stokes-Einstein relations, and we point to the distinctly different behaviour of low-salt charge-stabilized systems in comparison to suspensions of neutral hard spheres.

Thursday 3:10 De Anza III SC57

Particle interaction measurements using laser tweezers optical trapping

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Laser tweezers optical trapping provides a unique noninvasive capability to trap and manipulate particles in solution at the focal point of a laser beam passed through a microscope objective. Additionally, combined with image analysis, interaction forces between colloidal particles can be quantitatively measured. By looking at the displacement of particles within the laser trap due to the presence of a neighboring particle or looking at the relative diffusion of two particles held near each other by optical traps, interparticle interaction forces ranging from pico- to femtoNewtons can be measured. Understanding interaction forces is critical for predicting the behavior of particle dispersions including dispersion stability and flow rheology. Using a new analysis method proposed by Sainis, Germain, and Dufresne, we can simultaneously calculate the interparticle velocity and particle diffusivity which allows direct calculation of the interparticle potential for the particles. By applying this versatile tool, we measure difference in interactions between various phosopholipid bilayers that have been coated onto silica spheres as a new type of solid supported liposome. We measure bilayer interactions of several cell membrane lipids under various environmental conditions such as pH and ionic strength and compare the results with those obtained for empty liposomes. These results provide insight into the role of bilayer fluctuations in liposome fusion, which is of fundamental interest to liposome based drug delivery schemes.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Thursday 3:30 De Anza III SC58

Tracer diffusion in a soft glassy material

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We use a Fluorescence Recovery After Photobleaching experiment to study the particle diffusion in a colloidal system as a function of the particle size. The studied colloidal system is a laponite suspension in which the distance between the laponite particles is roughly 30 nm. The probe size ranges from 1 nm to 100 nm. In this complex fluid, the mere Stokes-Einstein relation loses its validity, the probe migrating in a nonhomogeneous medium. The main result is that the probe diffusion is entirely given by the ratio between the probe size and the laponite inter-disk distance. This suggests that the laponite-probe physico-chemical interaction is negligible: the change of probe diffusion coefficient stems from the hindrance of its motion due the hydrodynamical interaction with the disk walls. Our results also stress on the importance of the inter-disk distance for characterizing the laponite structure.

Thursday 3:50 De Anza III SC59

Restricted defect dynamics in sheared colloidal peanut crystals

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We report that monolayers of hard peanut-shaped colloidal particles consisting of two connected spherical lobes order into a crystalline phase at high area fractions. In this "lobe-close-packed" (LCP) crystal, the peanut particle lobes occupy triangular lattice sites, much like close-packed spheres, while the connections between lobe pairs are randomly oriented, uniformly populating the three crystalline directions of the underlying lattice. Using optical microscopy, we directly observe defect nucleation and dynamics in sheared LCP crystals. We find that many particle configurations form obstacles blocking dislocation glide. Consequently, in stark contrast to colloidal monolayers of close-packed spheres, dislocation pair nucleation is not the only significant energetic barrier to relieving an imposed shear strain. Dislocation propagation beyond such obstructions can proceed only through additional mechanisms such as dislocation reactions. We discuss the implications of such restricted defect mobility for the plasticity of LCP crystals.

Thursday 4:10 De Anza III SC60

Nanoparticle stability in concentrated polymer solutions and melts

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Engineered nanocomposites are often formulated by grafting polymer brushes to the surfaces of colloids to optimally disperse them in semidilute and concentrated polymer solutions as well as in polymer melts. In spite of the ubiquity of these filled materials, the essential mechanisms in producing an optimal dispersion have not been well quantified. To this end, rheology and light scattering were performed to connect the static wetting and dynamic flow properties of polydimethylsiloxane (PDMS)-grafted silica nanospheres in PDMS solutions and melts. By controlling the brush graft density and the matrix chain length of these model systems, results indicate that the wetting and the flow behaviors can be quantifiably linked. Overall, these studies represent new ways of quantifying the factors that control the dispersion of polymer-grafted nanoparticles in polymer solutions and melts.

Thursday 4:30 De Anza III SC61

Molecular weight effects on the flow mechanics of a strongly adsorbing polymer nanocomposite

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In this paper we explore the rheological behavior of polymer nanocomposites of increasing molecular weight and relate the flow mechanics to the particle microstructure probed with ultra small angle x-ray scattering. These studies were conducted to understand polymer mediated particle-particle interactions, filler effects on polymer chain dynamics, and potential particle-polymer phase separation. The phase behavior of polymer nanocomposites will be governed by enthalpic and entropic contributions. A variety of phases are expected as particle volume fraction, polymer molecular weight, and segment-surface interactions are varied: homogeneous fluid, phase separation, or nonequilibrium gel. We have investigated nanosilica dispersions in low molecular weight polyethylene oxide (PEO). In previous work, nanosilica was shown to be stable in PEO melts witnessed by the particle second virial coefficient being slightly greater than unity and to interact as hard spheres of slightly larger excluded volume through measurement of the zero shear rate viscosity. These results imply immobilized polymer on the particle surface which provides steric stabilization due to a favorable attraction between the particle surface and polymer segments. In recent studies, we find that as the particle separation approaches the length scale of the polymer, namely Rg, we see an arresting of flow witnessed by a plateau in the elastic modulus. As we increase the polymer molecular weight, the polymer experiences particle induced confinement at a lower particle volume fraction. Below entanglement, the flow behavior near polymer confinement mimics that of a colloidal glass. Above entanglement, the flow behavior is qualitatively different. We see two strain yielding events and a strain hardening regime when the polymer is confined.

Thursday 4:50 De Anza III SC62

Ultra-soft colloids: Non-equilibrium phenomena in sheared bottlebrush polymer solutions

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Due to the low compliances and long relaxation times in soft matter systems the coupling between an applied shear field and the structure can be very strong with the consequence that shear can result in shear induced phase transitions. Dynamic phase transitions do not only take place between steady states but also can result in non-equilibrium phenomena leading to chaoticlike or oscillating rheological response. In almost all observed cases rheo-oscillating and rheo-chaotic response was accompanied by shear band formation.

We performed insitu-rheological x-ray scattering experiments on a concentrated bottlebrush polymer solution [1]. The time-resolved experiments allow a direct correlation between the rheological response and the structural changes occurring in the sample. We followed the complex structural changes occurring in a, perpendicular to the flow direction pre-aligned sample during its reorientation into the flow direction. In the stress-controlled rheometer mode the reorientation is accompanied by a shear thinning process with a reduction in viscosity of two orders of magnitude. In the strain-controlled mode we observed an oscillating rheological response of the sample with periodic changes in the viscosity of almost two orders of magnitude. The rheo-oscillations are a consequence of a shear induced reentrant phase transition between a low viscosity shear molten state and a line hexatic phase with high viscosity. The phase transition involves the whole sample, thus, the rheo-oscillations are not due to shear band formation. To our knowledge there is only one more study on a lamellar (onion) phase surfactant system where the chaoticlike rheological response is due to a structural transition of the whole sample from a disordered onion phase to an ordered onion phase [2]. With the studies of Strey et al. [3] on polydisperse, chiral DNA molecules and Ramos and Molino [4] on oil swollen surfactant tubes under shear it is also to our knowledge the only experimental evidence for the appearance of a three dimensional line hexatic phase.

[1] Rathgeber S., Lee H.-I., Matyjaszewski K., Di Cola E., Macromolecules 40, 7680 (2007); [2] Wunneberger A.S., Colin A., Leng J., Arnéodo A., Roux D., Phys. Rev. Lett. 86, 1374 (2001); [3] Strey H.H., Wang J., Podgornik R., Rupprecht A., Yu L., Parsegian V.A., Sirota E.B., Phys. Rev. Lett. 84, 3105 (2000); [4] L. Ramos and F. Molino, Phys. Rev. Lett. 92, 018301 (2004).

SC-10. Multiphase Flows

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Guillaume Ovarlez and Alan Graham

Thursday 2:30 Portola SC64

A continuum model for structure formation and particle migration in time-dependent flows of concentrated suspensions

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Concentrated suspensions of spherical, non-Brownian particles exhibit a number of structure-related phenomena that are poorly understood, particularly in time-dependent flows. We have used the principles of continuum mechanics to develop a frame-indifferent model for the structure and rheology of such concentrated suspensions. The suspension structure is represented by a symmetric, second-order tensor that is determined from the cage-like shell of nearest neighbors that surrounds each suspended particle. A total of 11 unknown parameters have been evaluated by comparing predictions of the model with Stokesian dynamics simulations of concentrated suspensions in steady shear flows. Here we compare predictions of the model with simulation results and experimental data for time-dependent shear flows. In addition, we use the model to develop equations governing rates of particle migration in steady and oscillating pressure-driven channel flow. The unsteady equation governing particle migration is solved by using a two-step MacCormack method, with simultaneous calculation of the structure tensor via a fourth-order Runge-Kutta method. We interpret the solutions for the transient development of the particle concentration profiles in terms of the suspension microstructure, and also compare them with experimental and numerical results from the literature.

Thursday 2:50 Portola SC65

Flow of concentrated suspensions in asymmetric bifurcations

Chunguang Xi and Nina C. Shapley
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Concentrated suspensions flowing in complex geometries are often encountered in materials processing applications such as injection molding and extrusion. One example of a practical complex geometry is a branching, or bifurcation flow. Previous work on the behavior of dispersed particles in branching flows has generally emphasized dilute suspensions where the particle diameter is similar to the channel width. Meanwhile, a high loading of small particles, where the suspension can be compared to a continuum material, and the resulting impact on the concentration and flow fields have not received as much attention.

In our study, suspensions of neutrally buoyant, noncolloidal spheres in Newtonian liquids undergo steady, pressure-driven flow in a rectangular channel (4:1 aspect ratio) that divides into two branches at an asymmetric T-junction. We examine two cases, where the downstream branches either have equal width or unequal widths in a ratio of 1.5. Particle concentration and velocity profiles are obtained by nuclear magnetic resonance imaging (NMRI). We aim to determine the effect of the branching ratio and geometry on the observed concentration and flow fields, for particle volume fractions of 0.4-0.5 and low flow and particle Reynolds numbers. We find that the particles follow flow streamlines fairly closely for the unequal branch flow cell, while in the case of equal branches, the particles are more evenly distributed between the downstream branches than expected. Recent results from bifurcation flow experiments will be presented, comparing the two bifurcation geometries in terms of dividing streamlines, concentration inhomogeneities, particle fluxes in the branches and cross-stream particle motion.

Thursday 3:10 Portola 💿 SC66

Flow of dense granular suspensions on an inclined plane

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Particle laden flows such as avalanches, mud flows are ubiquitous in nature as they may display solid or fluid-like behaviour. In spite of their catastrophic human and economical tolls, the perspective of risk modelling is hindered by the lack of conceptual clarity since the rheological law remains poorly understood at the most fundamental level. Recently, significant advances in the understanding of dry granular flows were made, in part due to the systematic use of avalanche plane as a rheometer suited to access a central constitutive parameter: the effective friction coefficient (dependent of the shearing rate). Here we seek to extend such studies in the context of dense granular suspensions flowing down an inclined plane in order to investigate if similar constitutive relations may exist. The suspensions are prepared at high packing fractions and consist of non-Brownian spherical particle with density matched in salty water. For various tank flow rates and tilt angles, we performed systematic studies of the flow height and the surface velocity by using a P.I.V. technique. Therefore, we are in a position to assess the pertinence of previously found constitutive relations available for dry granular materials but in the context of dense granular suspensions.

Thursday 3:30 Portola 💿 SC67

Shear stress measurements of non-spherical particles in high shear rate flows

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The behavior of liquid-solid flows varies greatly depending on fluid viscosity, particle and liquid inertia, and collisions and near-collisions between particles. An initial investigation by Bagnold found two different flow regimes: a macro-viscous regime where the shear and pressure forces are proportional to the shear rate, and a grain-inertia regime defined by a dependence on the square of the shear rate [1]. In an examination of that work, Hunt *et al.* found that Bagnold's experiments were marred by secondary flows in the fluid [2].

The current experiment addresses this rheology further. Shear stress measurements used a coaxial rheometer with a height to gap ratio (b/r_o) of 11.7 and gap to outer radius ratio (h/b) of 0.166 that was specially designed to minimize the effects of secondary flows. Experiments were performed for a range of Reynolds numbers, solid fractions and ratio of particle to fluid densities. With neutrally buoyant particles, the dimensional shear stress exhibits a linear dependence on Reynolds Number: the slope is monotonic but a non-linear function of the solid fraction. Though non-neutrally buoyant particles exhibit a similar linear dependence at higher Reynolds numbers, at lower values the shear stress exhibits a non-linear behavior in which the stress increases with decreasing Reynolds number due to particle settling.

[1] R.A. Bagnold, *Proc. R. Soc. Lond. Ser. A*, **225**, p.49 (1954); [2] M.L. Hunt etc., *J. Fluid Mech.*, **452**, p.1 (2002).

Thursday 3:50 Portola SC68

An experimental investigation of bubble rise characteristics in a crystal suspended non-Newtonian fluid

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Bubbles play an important role in many applications such as; in the fermentation process, in the cooking processes, in determining the rates of heat and mass transfer and coalescence, in the pipeline transport applications, in polymer and sludge processes and others. Bubble rise characteristics in Newtonian fluid have been well studied. However, research on bubble rise characteristics in non-Newtonian fluids is limited and there is a need for further research as most of the industrial fluids are non-Newtonian in nature. An experimental investigation of the bubble rise characteristics in a non-Newtonian fluid with crystal suspension will be presented in this paper. The rheological properties of the non-Newtonian fluids with crystal suspension will be measured using an Advanced Rheometric Expansion System (ARES) with bob and cup and vane geometry. The suspension will be made from different concentration of xanthan gum solutions with 0.25 mm polystyrene crystal particle. In particular, different percentage of crystal content (by weight) will be used for rheological characterization. The experiments will be conducted in 125 mm and 400 mm cylindrical column at fluid heights of 1 m, 1.2 m, 1.4 m and 1.6 m by introducing different bubble volumes corresponding to each height. The bubble rise velocity and bubble trajectory will be measured using a combination of non-intrusive (high speed photographic) method and digital image processing. The effect of crystal particles and bubble volumes on the bubble rise velocity and bubble trajectory will be analysed. The influence of different bubble sizes on the bubble shape will be reported. A correlation of the drag coefficient at high Reynolds number will be developed and compared with the results of other analytical and experimental studies available in the literature.

Thursday 4:10 Portola SC69

The settling velocity for non-colloidal and colloidal suspensions

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The determination of the settling velocity of a homogeneous suspension of rigid particles through an ambient fluid at moderate Reynolds number is a century-old problem. The upward fluid flow compensating the downward motion of particles is known to retard the settling velocity and this phenomenon is generally referred as `hindered settling'. Beginning with Smoluchowski, numerous theoretical and empirical approaches have been developed in the attempt to describe the retardation resulting from finite particle concentrations, but none of the arguments are completely satisfactory. The slow spatial decay of the Stokes flow that inhibits absolute mathematical convergence presents a formidable challenge to any theoretical analysis. Even the dilute limit of mono-dispersed suspensions (equal-sized particles), is somewhat unresolved as analysis based on ordered structures (particles spatially constrained on lattices) lead to settling velocity scaled by the cube root of the volume fraction of particles while for a spatially random suspension, the settling velocity is a linear function of the volume fraction of particles. Hitherto no quantitative explanation has been presented for this fundamental difference in the concentration dependence of the settling velocity. We present a novel approach, based on boundary integral techniques, for the determination of the ensemble-averaged settling velocity of homogeneous mono or poly-dispersed (unequal-sized particles) suspensions. The computational cost of our approach is proportional to the number of particles in contrast to the cost of standard integral formulations. Our approach is based on the particles being placed on a number of regular lattices, but by increasing the number and changing the relative positions of the various lattices, we can gradually and controllably reduce the order of the suspension and observe the transition in the settling velocity from an order structure to a random structure. As our results remain fully consistent with previous theoretical results in the dilute limit we can in this fashion provide novel insight to the underlying physics. We present calculations for the entire practical relevant concentration spectrum for mono as well as for poly-dispersed suspensions. Finally, we extend our approach to colloidal systems to study the effects of the non-hydrodynamic inter-particle potentials on the settling velocities.

Thursday 4:30 Portola SC70

Hindered rising in aggregating polydisperse particle suspensions

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We describe a direct simulation method that effectively determines the appropriate hindered rising behavior of polydisperse particle suspensions. Our method allows adequate representation of the hydrodynamic interactions as well as system specific colloidal interactions. Simulation results are in good agreement with experimental data obtained by MRI imaging. Our results demonstrate the importance of particle aggregation in the hindered rising suspensions.

Thursday 4:50 Portola SC71

Applied rheology in large scale flow system of dilute suspensions with a novel approach

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It is well-known that some aqueous suspensions (pulp fibre suspensions and sewage sludge) are non-Newtonian and show a shear-thinning behaviour, meaning that the apparent viscosity decreases with increasing rate of shear deformation. This characteristic is observed even for rather moderate concentrations even for dilute suspensions. Shear flows are present in many industrial processes specifically papermaking and wastewater treatment where pumping and mixing of large volumetric flows are of extreme importance. In both processes the total capacity is presently the key design parameter, but of growing importance is the energy efficiency. When pumping suspensions, the change in pump performance due to the suspensions characteristics compared to water is a critical design parameter, which usually can be made generic with appropriate scaling and normalisation. The system design parameter is the pipe pressure loss. The challenge, given the energy efficiency perspective, is an increased predictability as well as an improved understanding of the role of suspension rheology and to some extent involves multiphase flow aspects. A breakthrough would lead to improved process control, system availability and reduced energy consumption. The purpose of this study is to quantify how the overall pumping performance is affected by the non-Newtonian shear-thinning suspension rheology present in a large scale flow system. We have tested different suspensions in a flow loop using water as the reference fluid. Experiments have been performed with a polymer solution, sewage sludge and pulp fibre suspensions. The experiments were carried out using a 5kW (N-3102) centrifugal pump, where key design parameters were recorded (pump pressure head, electrical input power, flow rate) and the pipe pressure loss was measured as the system design parameter. In addition, standard rheometer tests were performed and the effects of polymer addition and shear pretreatment were also evaluated. Studies of flocculation, i.e. suspension macroscopic structure, were also conducted using image analysis. The results showed a moderate de-rating in the pump performance compared to the Hydraulic Institute Standard, but somewhat similar to what have been reported for slurry applications. The obtained de-rating in pump performance is of the order magnitude of the suspension solids volume fraction. The system design parameter confirmed the reduction in certain flow velocity condition exceeding the losses for water. The modified Reynolds number in pipe flow was confirmed and used for predicting the change in behaviour in the transition regime of laminar to turbulent pipe flow. However, interesting feature was observed and quantified for the modified suspensions. The structural changes are yet to be analysed. It is believed that the findings provide direction for energy saving strategies and novel pump design approaches.

Thursday 5:10 Portola SC72

On the stability of shear flows of suspensions

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Structural models of thixotropy have become increasingly popular in recent years to describe the behaviour of suspensions, see e.g. Mujumdar, Beris & Metzner, JNNFM 102, (2002). A lot of research effort has been invested into the study of phenomena such as shear-banding in these models, which occur when these models are structurally unstable. In other parameter regimes these models are structurally stable, i.e. steady shear flows have a unique solution. A question that is less well explored is how the inclusion of a structure equation to describe thixotropic effects can influence flow stability? We address this question and present results on the stability of the Quemada model in Couette and Poiseuille configurations.

CF-9. Hydrodynamics in Confining Media

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: Wim J. Briels

Thursday 2:30 Steinbeck CF58

Numerical modeling of micro fluidics of polymer melts

José Manuel Roman Marín and Henrik K. Rasmussen

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Recent years have shown an ever-increasing interest in the patterning of micro and nano structured polymer surfaces. Polymers may be processed using techniques such as injection moulding (IM) and hot embossing (HE). The latter includes Nanoimprint lithography (NIL). In NIL a sub micrometer pattern is transferred to a thin (sub micrometer) polymer film on a hard substrate. Modeling of IM and NIL requires three dimensional (3D) time dependent numerical methods for viscoelastic free surface flow. Currently, large efforts are put upon two dimensional (2D) time dependent numerical methods to solve viscoelastic free surface flow. 3D methods are still in its initial stage. Most of these 2D and 3D methods are based on differential constitutive equation. To our knowledge, only one numerical method has been presented to solve 3D time dependent viscoelastic flow based on integral constitutive equations (Henrik K. Rasmussen. J. Non-Newt. Fluid Mech., 92 (2000) 227-243). This approach is based on a Lagrangian kinematic scheme and uses a K-BKZ type of constitutive equation. The convergence is second order both in time and space. Only one fully 3D problem has been resolved using this method. Here we present a new implementation, which can achieve a third order convergence in time and space. Combined with a more efficient implementation on parallel computers, compared to the original method, it allows time efficient 3D time dependent free surface flow computations of K-BKZ fluids. The physics of sub micrometer fluidics of polymer melts is the interaction between interfacial forces, surface tension and the (continuum) flow of the polymer melt. Examples of the numerical modeling of the dynamics of the three dimensional (3D) sub micrometer scale surface patterning in the NIL process are shown.

Thursday 2:50 Steinbeck CF59

Quantitative characterisation of complex fluids in microfluidics

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The intriguing flow phenomena of complex fluids in microfluidic systems has attracted enormous attention. The small scale of microfluidics makes flow of large deformation rate easily accessible. Hence even a low-viscosity polymer solution with a short relaxation time can reach the high Weissenberg (Wi) number flow regime, in which elastic forces dominate over viscous forces, and so exhibit strong viscoelastic effects and turbulence-like instabilities . However quantitative data in such a highly non-linear flow regime are still very much limited. Model fluids - poly(ethylene oxide) of two molecular weights (Mw = 1.25×10^{6} and Mw = 1.0×10^{5}) with a narrow distribution (Mw/Mn = 1.16 and Mw/Mn = 1.04) in aqueous solutions are prepared. We will report comprehensive data from molecular and rheometric characterisation to full flow characterisation of the model fluids in the well-defined benchmark flow problem, with X:1 planar abrupt contraction following by 1:X expansion geometry (X = 8 and 16 respectively), in a range of the elasticity (El) number, Wi number and Re number. We will compare the experimental data with numerical predictions of some well-established constitutive models. This will provide physical insight for further improvements of the constitutive models.

Thursday 3:10 Steinbeck CF60

Polymer dynamics in shear and Poiseuille flow

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Experimental studies of individual DNA molecules in steady shear flow by fluorescence microscopy have provided a wealth of information on single polymer dynamics [1,2]. In particular, these experiments reveal remarkably large conformational changes due to tumbling motion, i.e., a polymer stretches and recoils in the coarse of time. Hybrid mesoscale simulations of polymers in nano- or micro-channels, where confinement plays an important role, yield a similar type of motion [3]. In this contribution, analytical results for the dynamics of semiflexible polymers in shear flow will be presented. An explicit expressions will be provided for the orientational distribution function and for the dependence of the tumbling time on the shear rate, in quantitative agreement with experiments [4]. In addition, multiparticle-collision dynamics simulation results for polymers confined in a channel will be presented. Here, confinement leads to migration of the polymer towards the channel center and modifies the tumbling behavior, which reflects the importance of hydrodynamic interactions even in narrow channels. Moreover, the simulations show that the flow velocities of polymers with a radius of gyration larger than the channel radius are independent of the molecular weight. Hence, in such a geometry no separation of polymers according to molecular weight is possible by flow.

[1] C. M. Schroeder, R. E. Teixeira, E. S. G. Shaqfeh, and S. Chu, Phys. Rev. Lett. 95, 018301 (2005); [2] S. Gerashchenko and V. Steinberg, Phys. Rev. Lett. 96, 038304 (2006); [3] L. Cannavacciuolo, R. G. Winkler, G. Gompper, cond-mat/arXiv:0709.3822; [4] R. G. Winkler, Phys. Rev. Lett. 97, 128301 (2006).

Thursday 3:30 Steinbeck CF61

Dynamics and conformation of single polymer chain in a slot coating flow

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To guarantee good mechanical and optical properties of coating products, it is important to control molecular orientation of polymer chains in liquids to be coated on the substrate. In this study, Brownian dynamics (BD) and the conventional computational flow dynamics (CFD) simulations have been incorporated to elucidate dynamics and conformation of a polymer molecule in coating flow regime. Flexible polymer chain alters their conformation, relying on their flow strength (Weissenberg number, Wi) and flow type parameter (α). Interestingly, in slot coating flow, the chain can be more extended by the extension-like flow field near the downstream free surface curvature. Due to the complex flow field within the slot coating bead region, the extensibility of polymer chain moving along the streamline has been systematically investigated by correlating with the effective $\mathrm{Wi}_{,\mathrm{eff}}$ (e.g, $\mathrm{Wi}_{,\mathrm{eff}}=\mathrm{Wi}*\alpha^{0.5}$) and process conditions such as coating gap, web speed, Deborah number, and so on.

Thursday 3:50 Steinbeck CF62

The effects of molecular weight on polymeric fluid filament thinning & drop breakup

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The effects of polymer molecular weight (MW) and elasticity on filament thinning & breakup are investigated in microchannel cross flow. When a viscous solution is stretched by an external immiscible fluid, dilute poly-acrylamide (PAA) solutions strongly affect the breakup process, compared to the Newtonian case of the same shear viscosity. At late times when viscoelastic stresses become important, polymer filaments show much slower evolution, morphology featuring multiple connected drops, and different scaling with the ratio of flow rates. These effects diminish monotonically but nonlinearly as the polymer MW is decreased. For all fluids, we find two regimes that govern filament thinning: a flow-driven and a capillary-driven regime. In the flow-driven regime, the filament thinning process can be described in terms of extensional viscosities of the immiscible fluids, which for the polymeric solutions includes strain hardening.

Thursday 4:10 Steinbeck CF63

Evolution of patterns in thin polymer films driven by an electric field: Long-time dynamics and coarsening

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An electric field applied normally can destabilize a polymer-air interface, due to the mismatch of the dielectric constants. Pillar-like microstructures can form spontaneously with a characteristic spacing predicted via a linear stability analysis. We find, however, that the microstructures consistent with linear and weakly nonlinear theory are themselves unstable. As time progresses, neighboring pillars coalesce, increasing the average size of the pillars until the thin residual layer on the substrate renders further merging impractically slow. This phenomenon, in morphology, resembles coarsening in spinodal decomposition of a binary mixture and thin film dewetting due to van der Waals forces. However, the mechanism differs qualitatively due to the significant effect of Maxwell stresses and geometric confinement on the disjoining pressure. Microscopic observations with polydimethylsiloxane films show three distinct stages of the nonlinear dynamics. In the first stage, the average size of pillars increases slowly due to occasional merging between neighboring pillars, while the overall pattern remains almost unchanged. Most coarsening takes place during the second stage, characterized by a power-law relationship between the average pillar size and time. In the final stage, coalescence becomes extremely slow because of the thin residual layer mentioned above. The effect of fill ratio on the coarsening dynamics is significant. Theoretically, by studying perturbations of truly steady state structures, we reduce the original partial differential equations into ordinary ones that govern the widths and positions of interacting pillars. The scaling laws that should emerge for the coarsening will be compared qualitatively and quantitatively with the data.

Thursday 4:30 Steinbeck CF64

Rheo-optic flow-induced crystallization of polyethylene and polypropylene within confined flow geometries

Lino Scelsi[1], Dietmar Auhl[2], Harley Klein[3], and Malcolm R. Mackley[1]

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Experimental observations on the way Polypropylene (PP) and Polyethylene (PE) can crystallise during flow are reported. Preliminary linear viscoelastic rheological tests enabled the temperature window for quiescent crystallisation to be established. Flow-induced crystallisation (FIC) studies were performed using a Multi-pass Rheometer (MPR) [Mackley MR et al., J of Rheo, 39 (1995): 1293-1309] in a temperature regime above the normal quiescent crystallisation conditions. Both a deep and a shallow slit geometry were chosen for the rheo-optical study. In the case of PE, FIC occurred during flow at the sidewalls of the slit and in localised regions downstream and the processing pressure increased during the piston movement. In the case of PP, flow-induced crystallisation was generally observed after flow cessation and the processing pressure did not change during flow. For PP, FIC also occurred preferentially at the walls in the form of elongated crystallites but in this case the fibres gradually emerged after flow cessation. The difference in the FIC behaviour was attributed to differences in the crystal growth kinetics of the two materials at the particular super-cooling used. The shear and extensional rheology just above the crystallisation temperature were determined and fitted with a multi-mode Pom-Pom constitutive model. Subsequently, 2D numerical simulations of the polymers flowing in a MPR deep slit geometry were performed using Flowsolve, a Lagrangian solver developed at Leeds university [Harlen OG et al., J. Non-Newt Fluid Mech. 60 (1995): 81-104]. The local stress, orientation and stretch of the molecules in the flow at the onset of crystallisation for a range of piston speeds were determined.

Thursday 4:50 Steinbeck CF65

Boundary layer flow of a FENE dumbbell fluid

Liviu Iulian Palade

Pole de Mathematiques, Inst. Camille Jordan, CNRS UMR 5208, INSA de Lyon, Villeurbanne cedex 69621, France

Boundary layer flows of viscoelastic liquids are common (and of relevance) to many industrial applications, including polymer processing, thin film coating of surfaces, etc. As the general flow behavior is strongly influenced by the liquid microstructure, it is therefore naturally expected that the velocity profile inside the boundary layer of the polymer fluid, as well as its thickness, to depend on macromolecules chain geometry and elasticity, polymer concentration, polymer - solvent interactions, etc. In this paper we deal with the issue of finding steady state, isothermal, slow flow solutions to the boundary layer flow problem of a dilute viscoelastic liquid containing polymer chains modeled as FENE dumbbells, immersed in a Newtonian solvent. The flow is assumed to occur over a flat surface. The work consists of three parts. After reviewing recent results on thin film non-Newtonian flows, we calculate the probability density and evaluate the stress tensor components for the flow domain. Next we formulate the corresponding boundary value problem. The type, and the existence and unicity of the solutions are also addressed. Next we detail the numerical method used to compute the velocity field components. Finally, the velocity profile inside the boundary layer is plotted for various polymer molecular parameters.

GA-2. Modeling and Expt. in Quasi-Static Limit

Organizers: V Kumaran and Melany Hunt
Session Chairs: Melany Hunt and Antoinette Tordesillas

Thursday 2:30 Bonsai III GA7

Dry granular flow at the quasi-static limit

Matthew R. Kuhn

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Dry granular flows are important in many industrial, geophysical, and geotechnical processes. The presentation begins with an overview of dense steady flow and how it differs from the elastic behavior of granular materials at small strains, primarily in the manner of micro-fabric evolution and the distribution of internal micro-scale force among particles. Granular flows also exhibit interesting phenomena when viewed as continua at the macro-scale. These phenomena include the possible non-coaxiality of the deformation rate and stress increment; a dependence of stress upon the deformation gradient near hard boundaries or within shear bands; and the effect of the intermediate principal deformation rate on the flow stress. The presentation briefly describes these phenomena and the micro-scale patterning that is commonly expressed during flow, patterning in the form of internal force chains, particle rotation bands, shear bands, and micro-bands. Such spatial patterning is likely the result of continual material instability at the micro-scale. The presentation then focuses on the analysis of such micro-scale instability during dry quasi-static flow. Two approaches are available for analyzing instability. The first approach is purely statical (or kinematic), in which the grains are treated as rigid objects. This approach has, thus far, only been effectively applied to frictionless granular systems. The second approach explicitly includes the stiffnesses of the grains at their points of contact, and the approach relies upon quantifying the stiffness matrix of the discrete system of grains. This approach leads to characterizing the particle arrangements as either incrementally stable or unstable and permits calculation of possible micro-scale bifurcations of movement or deformation. The presentation pursues the second approach by analyzing the results of discrete element method (DEM) simulations of small assemblies of disks that are undergoing dense quasi-static flow. This simulation technique uses dynamic relaxation without explicitly employing the statical or stiffness matrices. The method does, however, allow the taking of snapshots of the particle arrangements, the particle velocities, and all of the contact force information at any time during the simulated flow. The stiffness matrices of several representative particle arrangements are analyzed, and the presentation shows how local instabilities are manifested among the particle samples. These instabilities, which would continually arise during steady flow, lead to rapid rearrangements of the particles. The sampled stiffness matrices also reveal potential bifurcations of the fields of particle motion, which might be responsible for the onset of localized patterning of the motions and internal force. The presentation ends with a discussion of how the stiffness matrix results are consistent with micro-fabric evolution and the development of internal force chains within granular flows.

Thursday 2:50 Bonsai III GA8

Fluid injection into granular media under confinement

Haiying Huang[1] and Ruiting Wu[2]

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The process of fluid injection into granular media is relevant to many practical applications such as fluidization of packed beds, hydraulic fracturing and water flooding in unconsolidated and highly permeable sedimentary rocks. While the general fluidization behavior has been extensively studied for many decades, hydraulic fracturing and water flooding in granular materials emerged only recently and remains a challenge. In particular, conditions of fracture initiation and propagation in granular materials are not well understood. A distinct feature of the hydraulic fracturing and water flooding processes is the existence of far field confining stresses. Confining stresses instead of the pressure gradient due to gravity as in the case of fluidization therefore affects the critical conditions that govern the transition between different flow patterns. In this work, fluid injection from an inlet into a two-dimensional rectangular domain under a biaxial stress state was investigated numerically using a discrete element code PFC2D. Fluid flow in the domain is modeled using a fixed coarse grid scheme while the mechanical deformation of the particle assembly was simulated using the discrete element method with the soft contact approach. Results indicated that three types of flow patterns can be identified: i) fixed bed flow; ii) formation of a stable cavity; iii) propagation of an unstable cavity. In the limit of inertia-governed (still laminar) flow, the induced cavity is finger-like with a nearly constant width, whereas in the limit of viscosity-governed flow, the cavity tends to grow more in the width direction rather than the length direction. A criterion of the critical injection velocity as a function of material properties and the far field confinement for transition between flow patterns was established. The scaling relationship between the material properties and the confining stress was verified numerically.

Thursday 3:10 Bonsai III GA9

Using Newton's cradle to explore wetted, 3-particle collisions

Carly E. Donahue[1], Christine M. Hrenya[2], Gustavo G. Joseph[2], Robert H. Davis[2], Kenshiro J. Nakagawa[2], and Alexandra P. Zelinskaya[2]

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An apparatus inspired by the desktop toy, the Newton's cradle, is used to explore the agglomeration and de-agglomeration behavior of collisions involving three solid particles coated with a thin layer of viscous fluid. Experiments are run with variations in fluid viscosity, thickness of fluid layer, particle material, and velocity of impacting sphere. An experimental regime map is obtained in which three of the four possible outcomes (fully agglomerated, fully separated, Newton's cradle, and "reverse" Newton's cradle) are observed across a range of Stokes numbers. A toy model, which treats this 3-body interaction as a series of 2-body interactions, predicts the same three outcomes, though quantitative differences do exist. Insight into these quantitative differences is obtained by consideration of a similar treatment for the traditional (dry) Newton's cradle.

Thursday 3:30 Bonsai III GA10

Rheophysical investigation in concentrated particle suspensions

Sébastien Wiederseiner, Christophe Ancey, Martin Rentschler, and Nicolas Andreini

Laboratoire d'Hydraulique Environnementale, Ecole polytechnique fédérale de Lausanne, Lausanne 1015, Switzerland

An optical visualization apparatus has been designed to measure the particle-velocity and solid-concentration profiles of highly concentrated coarse-particle suspensions in a wide-gap Couette rheometer. The main objective is to investigate the frictional-viscous transition, a phenomenon that has been already be reported in recent papers [1, 3, 4, 6], but still remains partially understood. A related issue is the Couette problem, which underpins the rheometrical treatment for viscometric flows in coaxial-cylinder rheometers; we compare shear-rate computations obtained by solving the Couette problem (bulk estimate) and by differentiating the velocity profile (local measurement).

Ancey [1] showed that for concentrated particle suspensions there is a transition from a frictional to a viscous behavior that occurs at a given critical shear rate, which depends a great deal on the particle diameter. He suggested that particle lubrication is the key mechanism responsible for this transition: at sufficiently high shear rates, fluid inertia increases; part of the fluid can then break and lubricate contacts between particles, which leads to a "fluidization of the material". Another interpretation has been suggested by geophysicists [5]: a concentrated suspension of coarse non-buoyant particles behaves like a soil and according to Coulomb theory, shear strength drops to zero when pore fluid pressure is sufficiently high to balance particle buoyancy forces, which results in a "liquefaction" of the material. To gain insight into this delicate problem, we are conducting experiments, where particle buoyancy can be controlled. By adjusting the fluid refraction index, we can make also our suspensions transparent and use non-invasive techniques (Fluorescent Particle Image Velocimetry) to probe both velocity and density profiles within the suspension. We will present our preliminary results obtained with a PMMA-particle suspension.

Another interesting aspect of this experimental setup concerns flow curve derivation. For wide-gap viscometers and complex fluids, the flow curve must be computed by solving the Couette inverse problem [2, 7]. An alternative way of obtaining the flow curve is to measure the velocity profile across the gap, then differentiate it to derive the local shear rate. The locally derived measurements (shear rate, concentration) can finally be used as benchmark data to test the various techniques developed for solving the Couette inverse problem (e.g., Tikhonov regularization, spline interpolation, wavelet-vaguelette decomposition). We will present the results of this benchmark.

[1] Ancey C., J. Rheol. 45, 1421-1439 (2001); [2] Ancey C., J. Rheol. 49, 441-460 (2005); [3] Ancey C., Coussot P., Comptes Rendus Acad. Sci. Paris 327, 515-522 (1999); [4] Huang N. et al., Phys. Rev. Lett. 94, 028301 (2005); [5] Iverson R., Rev. Geophys. 35, 245-296 (1997); [6] Prasad D., Kytömaa H., Int. J. Multiphase Flow 21, 775-785 (1995); [7] Yeow Y. et al., J. Rheol. 44, 1335-1351 (2000)

Thursday 3:50 Bonsai III GA11

Densification of a 3D granular bed by horizontal vibrations

Ahmed Raihane[1], Olivier Bonnefoy[1], Gérard Thomas[1], Jean m. Chaix[2], and Jean L. Gelet[3]
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When a granular medium is submitted to horizontal vibrations, various phenomena can be observed. Some works have been focussed on the transition to flow , in which the granular medium, partly or entirely, changes from a solid-like state to a fluid-like state when the energy brought by the vibrations is high enough. Other ones have studied the granular movements and highlighted counter-rotating rolls of convection . The present paper reports an experimental study which analyses the compaction phenomena in a 3D granular medium submitted to horizontal sinusoidal vibrations.

An electromagnetic shaker transmitting sinusoidal vibrations, with frequency f, amplitude A and relative acceleration Γ ($\Gamma=(2\Pi f)^2A /g$), to a container filled with granular material. The container is fixed to a mobile plate connected mechanically to the shaker and guided in its motion by rails in order to make sure that the movement is purely horizontal. The granular material is a silica sand with regular rounded grains and a rather small size dispersion around the mean value d = 0.6 mm (span = 0.7). To characterize the state of the granular medium, we measure his overall compacity with an optical roughometer. Compacity is measured during the vibrations (dynamic compacity) and after the vibrations are stopped (relaxed compacity). A parametric study was performed to determine and understand the influence of the parameters of vibrations (frequency f between 20 and 100 Hz, acceleration Γ between 0 and 8) on the densification stage of the granular medium.

Starting from an initial compacity around 62% and by increasing acceleration, we observe a first compaction at a critical acceleration of about 0.5, accompanied by a simmering movement of grains on the surface. For higher values of Γ? a convective movement is initiated in an upper layer of the granular medium, accompanied by a second compaction. The compaction increases until a critical acceleration is reached, at which the medium begins to dilate. We also observed the influence of initial compacity on the relaxed one. This influence is important for the low values of accelerations and is attenuated by increasing the acceleration of the vibrations.

Using a technique of aspiration to remove, layer by layer, the upper parts of the relaxed samples, z-profiles of local relaxed compacity were measured for various accelerations. The profiles evidence a front of compaction which is propagated downward from the top in the granular medium when acceleration is increased; and, for higher values, a front of dilatation which propagates in the same way.

Thursday 4:10 Bonsai III GA12

Initiation of submarine granular avalanches: Role of the initial volume fraction

Mickael Pailha, Olivier Pouliquen, and Maxime Nicolas
CNRS, Université de Provence, Marseille, France

Many geophysical flows involve a mixture of grains and fluids in a dense regime where contacts between grains are important. In order to better understand the dynamics of such complex systems, we perform laboratory experiments on the initiation of submarine granular avalanches. The experiment consists in preparing a uniform static layer of glass beads in a long box full of liquid. The initial volume fraction of the layer can be precisely controlled by tapping on the set up. The box is then suddenly inclined from horizontal. The deformation of the layer, the evolution of the pore pressure and the evolution of the volume fraction are then recorded. The avalanche dynamics is shown to strongly depend on the initial volume fraction of the granular material, its initiation being dramatically delayed when the granular layer is initially slightly compacted. In parallel to this experimental work, a theoretical model based on two phase-flow equations is developed. The model relies on recent advances in the rheology of dense granular media and takes into account the change of volume fraction and the associated pore pressure variation. The theroretical approach gives quantitative predictions when compared with the experimental measurements.

Thursday 4:30 Bonsai III GA13

Dynamics, packing porosity, and conformation variations of granular chains

Xialing Zhang and Amy Shen
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We report results concerning the dynamical behavior of collections of beaded chains rotated in a two dimensional cylinder. During our experiments, we observe a variety of complex spatio-temporal patterns. These patterns depend on the chain length, the size of the system, and the rotation rate of the cylinder. We report the porosity of the granular chains under flow, the conformation of chains, and the end-to-end distance of chains in comparison to the polymer melt system.

Thursday 4:50 Bonsai III GA14

Triggering stick-slip motion in granular shearing

Andrea Baldassarri[1], Fergal Dalton[2], Alberto Petri[2], and Stefano Zapperi[1]
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Fluctuations play an extremely important role in the physics of granular media. The dynamics of slowly sheared glass beads is characterized by a highly intermittent and irregular stick-slip motion, wich can be described by probability distributions reminescent of other very different physical systems, as earthquakes or Barkhausen effect in ferromagnets. Here we present results for a long lasting series of experiments, considering different thicknesses of the sheared systems, ranging from the solid-on-solid case, where only two layers are in contact, to the opposite case of a thick system, where even a single slip event can result from a rearrangement of many layers deep inside the system. Particular attention have been paid to the triggering of the instability by external perturbations. A stochastic model gives a theoretical framework to the experimental observations, allowing an interpretation of the results in terms of statistical correlations of grain motion and internal forces.

Thursday 5:10 Bonsai III GA15

Dense granular flows: Rheology and segregation

Devang Khakhar

Department of Chemical Engineering, IIT Bombay, Mumbai, India

Granular materials (e.g., sand, gravel, cement, food grains, coal, fertilizer, catalyst pellets, pharmaceutical powders, etc.) may flow like a fluid under some conditions. The flow behaviour is complex and an understanding of the flow would be useful for a better description of several industrial processes (e.g., pharmaceutical tablet making) and natural phenomena (e.g., landslides). Flowing mixtures tend to segregate altering the flow characteristics and introducing an additional level of complexity. We have been using high speed video imaging to study the motion of individual particles in dense granular flows. Experimental results will be presented for free surface flows of monodisperse particles and binary mixtures of monodisperse particles. Simple models for flow and segregation will be discussed and compared to experimental results. The flowing material exhibits some characteristics similar to glassy materials and these will be highlighted.

EM-6. Extreme Rheology

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: Mike Johns

Thursday 2:30 De Anza I EM34

The high normal force partitioned plate rheometer MTR 25

Thomas Schweizer, Jürg Hostettler, and Fredy Mettler

Materials, ETH Zürich, Zürich CH-8093, Switzerland

During shear of polymeric fluids in cone-plate geometry, flow inhomogeneities, such as deviations from the linear velocity profile across the gap or slip at the interface fluid/boundary are inevitable. So far, the study of these phenomena was hampered by rheometer compliance, poor temperature control, or limited normal force capacity. We built an axially stiff rheometer MTR 25, allowing 25 kg of normal force and keeping temperature constant within ±0.005°C. Thanks to this device, the limits of the rheological playfield are now set by the physics of the fluid. The partitioned plate of the rheometer allows determining shear stresses with an up to now unmatched precision and both normal stresses from a single experiment. The homogeneity of the flow can be observed in situ by surface particle tracking. It led to the following observation: The rate of formation and the magnitude of flow inhomogeneities is not set by Weissenberg number, chemical nature of the polymer, and polydispersity alone, but essentially depends on the initial shape of the sample's rim. Thus, its control via a time-temperature pre-treatment is crucial. If slip at the interface fluid/boundary occurs, the following observations are made for a melt of monodisperse polystyrene: "Steady state" values of shear stress and both normal stresses obey the time temperature superposition principle and for a given shape of the sample's rim, rheometric curves are perfectly reproducible. This poses the question, whether the observed slip is a constitutive phenomenon? This issue is dealt with in this talk.

Thursday 2:50 De Anza I EM35

Determination of normal stress in micrometer thin films

Seung Jae Baik, Paula Moldenaers, and Christian Clasen

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The term microrheology is very often related to active or passively driven particle tracing or AFM techniques, that probe a sample very locally and only within the linear viscoelastic regime. On the other hand, microrheological investigations of bulk samples of complex liquids in plane Couette shearing flows of micrometer thin films, as demonstrated with the flexure-based microgap rheometer (FMR) [1, 2], lacked so far the possibility to detect the nonlinear response of the elastic components, in particular the normal stresses. This is unsatisfying because the effect of confinement on the normal stress development of a complex fluid with internal dimensions on the order of the confinement is so far not known. The normal stress presents furthermore the missing link from microrheology to the wide area of tribology and elasto-hydrodynamic lubrication under controlled normal force conditions, which has traditionally been considered to be a subject apart from classical bulk- and microrheology. We demonstrate in this paper how a novel, flexure carried force feedback sensing system integrated in the sliding plate setup of the FMR allows the detection of a normal force with a sensitivity of < 1 mg while maintaining absolute, parallel shearing gap dimensions with an accuracy < 100 nm. The applicability of the instrument to determine the effects of confinement on the normal stress in thin films with thicknesses from 1-100 um is demonstrated with 2 phase model systems with varying dimension and elasticity of the dispersed phase. ([1] C. Clasen, B.P. Gearing, and G.H. McKinley, "The flexure-based microgap rheometer (FMR)", Journal of Rheology 50, 883-905 (2006); [2] C. Clasen, and G.H. McKinley, "Gap-Dependent Microrheometry of Complex Liquids", Journal of Non-Newtonian Fluid Mechanics 124, 1-10 (2004).)

Thursday 3:10 De Anza I EM36

A flexible platform for tribological measurements on a rheometer

Patrick Heyer and Joerg Laeuger

Anton Paar Germany GmbH, Ostfildern, Germany

Tribology is the science and technology of interacting surfaces in relative motion, and embraces the study of friction, lubrication and wear. Contrary to rheology in tribology no fixed gap is maintained, but two fixtures are pressed together by a normal load. At certain sliding speeds between the two fixtures a hydrodynamic pressure builds up separating the two fixtures, i.e. the gap is changing as a function of the lubricant and the measuring conditions. Different geometries might be used for different tribological applications. However, a tribometer requires speed and normal force control as well as a torque measurement to acquire tribological data. An air bearing supported rotational rheometer allows the measurement of the same variables but in a broader range and with better accuracy and higher precision as in typical tribometers as they are used nowadays. This fact and the intension to perform both speed and torque controlled experiments to measure Stribeck curves as well as the static friction with one single instrument let to the idea to design an accessory turning a commercial available rheometer into a high resolution tribometer based on the ball on a pyramid or ball on three plates principle. The aim of this paper is the twofold, first, to describe the new designed tribological cell and the corresponding accessories, and second, to demonstrate its use for different applications. Tribological measurements using the designed accessory on dry, oil and grease lubricated systems have been conducted and illustrate the performance of the Rheo-

Tribometer. Oil lubricated measurements of Stribeck curves and the static friction are used to compare the obtained results with measurements from more traditional tribometers. Dry system, in which no additional lubricant is used, are important when for example the friction between two polymer surfaces or between a polymer and a metal surface are investigated, respectively. Exemplary results from such measurements under dry conditions are discussed. The flow behavior of greases is more complex and extensive rheological and tribologcal testing was performed on three different model greases at the temperatures of 25 and -40°C. The influence of temperature could be monitored and a correlation between rheology and tribology was found. By changing the plates from solid to being elastic measurements in the so-called soft elasto- hydrodynamic-lubrication (soft-EHL) regime are possible thus extending the range of applications to for example food and consumer products. Tests on dairy products reveal a good correlation between the friction properties and the fat content of the samples. In order to cover different applications beside the ball on pyramid setup different fixtures for the tribological attachment have been designed and will be described as well.

Thursday 3:30 De Anza I EM37

From rheology to tribology: Multiscale dynamics of biofluids, food emulsions and soft matter

Jason R. Stokes, Jeroen H. Bongaerts, Georgina A. Davies, Damiano Rossetti, and Gleb Yakubov
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Many soft matter systems undergo shear and confinement at length scales approaching that of their underlying microstructure, particularly during lubrication and coating type processes as well as flow processes involving narrow length scales, such as in microfluidics, porous media, nozzles, membranes, and within biological systems. This is particularly apparent for food and personal care products, many of which are highly structured multiphase complex fluids, whereby they are broken down to very thin films and subjected to high shear rates during use. The sensorial response and functional attributes of such products then depend on their dynamic response when confined between interacting biosubstrates (e.g. toungue-palate, finger-skin/hair, etc.).

We focus here on our recent developments in micro-gap rheometry and soft-tribology / biolubrication for probing the dynamics of multiphase complex fluids from the macro- to the nano-scale. Narrow gap parallel plate rheometry, provided gap errors are accounted for, enables gap-dependent rheometry to be performed down to gaps of the order of 10 μm and provides access to shear rates exceeding 10^5 s^{-1}. Soft-Tribology involves rolling/sliding a ball and plate against one another under an applied load in the presence of test fluids; this allows lengths scales to be probed down to the nano-scale as asperities come into contact. The tribological substrates are comprised of PDMS to form compliant surfaces with a similar modulus and hydrophobicity to that of biosurfaces. Adsorbing saliva to the surfaces provides a potential mimic of oral substrates; human whole saliva is both extremely elastic ($N1/\sigma \sim 100$) and highly lubricating ($\mu \sim 0.01$) although these attributes are not related. We demonstrate that during confinement, the dynamic response of multiphase complex fluids (including food emulsions and particle suspensions) no longer necessarily depends on their bulk rheological properties, but can also depend directly on the physical properties and micro/nano-structure of the individual phases, as well as the adsorption of surface active constituents onto the biosubstrates. We explore the material properties and surface parameters governing biolubrication processes, including how components interact with the adsorbed salivary film.

Thursday 3:50 De Anza I EM38

Novel miniature-scale mixing device for deformable materials

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Material compounds are typically developed via a mechanical mixing process during which time the ingredients are subjected to both shear and extensional deformations. The overall integrity of said compounds strongly depends upon the shear and extensional rheological properties of the polymeric matrix. In addition, the rheological properties also control the final quality and commercial attractiveness of the final products. A new miniature-scale mixer has been developed to monitor and optimize the preparation protocol of various compounded systems. The effect of mixing time and other basic processing parameters on the shear and extensional rheological properties of said compounds is examined in order to understand the effect of undermixed and/or overmixed conditions on the rheological properties and thus the quality of the final products. Results from said new miniature-scale mixer will be compared with the results from other conventional mixing techniques in order to assess the scalability of the new mixing protocol.

Thursday 4:10 De Anza I EM39

Development and testing of measurement equipment to determine the viscoelastic behaviour of polymer melts at high pressure

Mathias Krebs and Olaf Wuensch
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In many branches of process industries, highly viscous liquids like polymer melts have to be conveyed and processed in technical apparatus. These liquids often have non-Newtonian fluid behaviour. Shear-thinning viscosity, normal stress differences and elastic properties affect the fluid flow. Additionally the material is strained through a high pressure at operation conditions. Inside of an extruder or an injection moulding machine the pressure reaches values about 150 bar and more. In the process of designing and optimizing such apparatus it is necessary to know the material properties not only in dependence of temperature also in dependence of pressure. Actually the viscous and viscoelastic material properties of melts are measured with different instruments under atmosphere conditions.

In this paper we present a measurement equipment to determine the material properties of polymer melts at high pressure. A commercial control stress rheometer is modified by a pressure cell, which can be pressurized to 140 bar (2000 PSI) over a temperature range up to 300 °C. The cell consists of a sealed cylindrical vessel. In contrast to commercial accessories we do not use a concentric cylinder system inside the vessel but a parallel plate tool in order to enable measurements of highly viscous liquids. The moment at the plate tool is measured contactless using a high-powered magnetic coupling and low-friction bearing design. The equipment uses a controlled radiant heating concept to adjust the temperature. In order to prevent thermal damage of the melt material we take gaseous nitrogen for pres-surization. One focus in the construction process of the pressure cell was to ensure the exact gap between the parallel plates during the measurement.

First of all we show experimental results for highly viscous liquids with Newtonian behaviour in order to test and determine the limits of the measurement equipment. Than we represent first results for polycarbonate melts at different pressure: The shear viscosity as a function of the shear rate in a stationary mode and the storage and loss modulus in dependence of the frequency in the dynamic oscillation mode.

Thursday 4:30 De Anza I EM40

Capillary rheometry of low viscosity fluids

Eva G. Barroso[1], Fernando M. Duarte[1], Miguel Couto[2], and Joao M. Maia[1]
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Capillary rheometry is the simplest and most popular system to measure the viscosity of fluids at high shear rates and because of that is normally used to simulate industrial processes, namely in the polymer processing industry. Thus, traditionally the rheometers are equipped with high-pressure transducer, which means that they present some limitations in the characterization for low viscosity (lower than 10 Pa·s) fluids. The aim of this project is to modify a laboratory capillary rheometer in order to allow for low viscosity fluids to be tested. This is a simple adaptation that works as an add-on to the rheometer and contains a new pressure transducer with a pressure range of 0 to 120 psi. In the presentation, the concept is introduced and validated with Newtonian liquids and results are presented for different non-Newtonian fluids, such as emulsion-based and micro suspension-based PVC pastes for textile coating.

Thursday 4:50 De Anza I EM41

The effects of stressing rate on measurements of the cavitation threshold of monograde lubricants by pulses of tension

Rhodri L. Williams, Rhodri P. Williams, and Hoi Houng Chan
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This paper reports the results of experiments in which samples of degassed monograde lubricants, namely 10W and 40Diesel motor oils, are subjected to dynamic stressing by pulses of tension. The pulse reflection technique employed allows the rate of development of tension in the liquid to be varied in a systematic manner, in order to investigate its influence on the resulting measurement of the liquid's cavitation threshold (or ‘effective’ tensile strength), F_c. Results are reported for experiments involving a range of stressing rates,from 0·6 bar/μs to 1.4 bar/μs for monograde 10W and 40Diesel motor oils over the temperature range 25°C $< T <$ 110°C. These experiments, which are the first of their kind to be reported, indicate that, at any given temperature, F_c increases with increasing stressing rate (156 bar $< F_c <$ 228 bar at 25°C and, 130 bar $< F_c <$ 156 bar at 110°C for the 10W oil and 155 bar $< F_c <$ 223 bar at 25°C and, 124 bar $< F_c <$ 177 bar at 110°C for the 40Diesel oil). These results provide evidence to substantiate the claim made by previous workers that the rate of dynamic stressing is an important consideration in understanding the cavitation properties of liquids. The experiments also indicate that stressing rate and temperature are important considerations when evaluating a lubricants performance.

SE-6. Liquid-Liquid Systems and Blends

Organizers: Denis Weaire and Lynn M. Walker
Session Chair: Sachin Velankar

Thursday 2:30 De Anza II SE37

Deformation and relaxation of PMMA/PS and PMMA/PSOX blends

Jorge Silva[1], Ana Vera Machado[1], Paula Moldenaers[2], and Maia João[1]
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In this work we study the role of the interface in the rheological behavior of blends of polymethylmethacrylate (PMMA) with polystyrene (PS) and polystyrene functionalized with oxazoline (PSOX), especially the relaxation behavior in both shear and extensional flows. The cessation of flow after steady shear experiments reveal the appearance of second very slow relaxation mechanism in the PMMA/PSOX blend as do those of that upon cessation of a step uniaxial extension. Small Angle Light Scattering (SALS) was used during step shear to infer about the relaxation of the droplets and/or interface and the patterns show that this behavior is not due to a higher deformation of the PSOX droplets, but should be attributed to a relaxation of the interfaces. The reason for the very high elasticity of the interface is not *a priori* obvious, but is probably related with the existence of extra physical entanglements at the interface in the PMMA/PSOX blends since the chemical analysis indicates that both types of blends are immiscible.

Thursday 2:50 De Anza II SE38

Numerical simulation of the deformation and break-up of droplets subjected to complex, time dependent strain rates

James R. Waldmeyer[1], Malcolm R. Mackley[1], Michael Renardy[2], and Yuriko Renardy[2]
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This paper reports an investigation into deformation and break-up of droplets experiencing complex, time dependent strain rates such as those found in engineering flows. A volume-of-fluid (VOF) method has previously been developed to simulate numerically the deformation and break-up of a single droplet (see, for example, Li *et al.*, 2000) undergoing steady or oscillatory shear. Further developments, presented here, have been made to study the effect of arbitrary, time dependent shear rates on a droplet.

Simulations were carried using a two-part approach. The global single phase flow patterns within an industrially relevant flow constriction were firstly modelled using commercial CFD software (*Fluent 6.2*); this was followed by a separate localised two phase (VOF) simulation of a single unconfined droplet surrounded a volume of the continuous phase. Whereas the global simulation was fixed in the laboratory frame, the localised simulation was centred on a single droplet as it was tracked through the constriction passing through different flow conditions, which were generated by the global simulation. A number of velocity gradient histories were extracted from the global simulation, corresponding to fluid elements travelling along different streamlines and thus experiencing different flow conditions. Droplets were assumed not to affect the flow, but to travel along streamlines at the same velocity as the surrounding fluid, thus experiencing the same velocity gradients. The droplet interface was reconstructed from the VOF concentration function and was tracked with time to show the deformation, and break-up, of the droplet.

This technique for modelling droplets undergoing complex strain rates has been successfully applied to a number of different flow constrictions studied experimentally. Droplets approaching the constriction were extended along the flow direction and break-up was predicted at the entrance to the constriction, particularly if an abrupt change of flow direction was encountered. Depending on the trajectory, shear strain rates within the constriction can promote break-up of the extended droplet. Typically, the droplets broke into a large number of small fragments, which could be tracked following break-up though neither satellite droplet formation nor a detailed size distribution of the fragments were predicted using these simulations. It is envisaged that a simulation of this type could be used to predict the break-up mechanism and droplet size distribution occurring in flow constrictions. The overall simulation results show that droplet break-up is very sensitive to the time dependent variations in strain rate type and magnitude and these effects are not necessarily apparent if only steady shear conditions are considered.

Li, J, Renardy, Y. and Renardy, M., 2000, Numerical Simulation of breakup of a viscous drop in simple shear flow through a volume-of-fluid method. *Physics of Fluids*. **12**, 269-282

Thursday 3:10 De Anza II SE39

Universal retraction process of a droplet shape after a large strain jump

Lazhar Benyahia and Souad Assighaou
PCI, University of Le Mans, Le Mans, France

We evidenced a universal relaxation behaviour of a droplet embedded in a immiscible fluid of same density. After a large strain jump, the relaxation can be characterized by two related relaxation times t1 = 4.4 t2 independently of the viscosity ratio and of the applied strain. The change in the kinetic process is driven by the drop geometry and happens invariably when the shape of the drop is an oblate ellipsoid of revolution where the relation between the major (L) and the minor (B) axis is given by ln(L/B) ~ 0.5. This universal behaviour can be explained by considering the normal stress difference across the droplet interface i.e. the curvature of the drop.

Thursday 3:30 De Anza II ⊛ SE40

Evidence of droplet coalescence in extensional flow using microfluidic devices

Deniz Z. Gunes, Xavier Clain, and Adam S. Burbidge
Food Science and Technology, Nestlé Research Center, Lausanne, Switzerland

Coalescence under flow is one of the major causes for emulsion or foam destabilization in food processes and consequently, understanding the hydrodynamic part of the coalescence mechanism(s) is key in order to prevent it. Chesters (1991) provided a theoretical framework with equations governing the drainage kinetics of the lubricated film for a collision of droplets of equal size. Recently, very specialized experiments where the flow is computer-adjusted at any instant (to a large extent in the group of Leal), demonstrate that in the case of non-head-on collisions, coalescence can occur when drops are being pulled apart by the global flow after the phase of drainage. In our experimental investigations, we use micro- or milli-fluidic methods to vary the parameters governing size and Capillary number of head-on or nearly head-on collisions – further work is needed to vary independently size, capillary number and collision rate. We have however already noted some qualitative features of the head-on collision observed, when size, collision velocity and surfactant load were varied. Droplets were exposed to and initially predominantly compressional and subsequently extensional flow field by means of a flow-through device with an expansion followed by a contraction. Our results show that even when the transient compressional flow is insufficient to allow the film to drain to critical thickness, the drops will often coalesce in the following 'extensional' phase. Moreover, a small amount of surfactant (polyglycerol polyricinoleate : liposoluble and non-ionic) that is sufficient to provide relative stabilization in the compressional part, apparently favors coalescence in the extensional part by easing locally the drop's stretching. In fact this suggests intuitively being a kind of 'Marangoni'-jetting instability, although it is enhanced by, and not totally driven by surfactant, so there are other phenomena at work also. Furthermore, this observed mechanism of coalescence in extensional flow is suspected to have a significant role in the propagation of avalanches. For larger surfactant loads, the extension results in break-up of the stretched part of the drops, showing a surfactant-stabilization mechanism fundamentally different from the case of approaching droplets.

Thursday 3:50 De Anza II SE41

The effect of interfacial slip on drop coalescence

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In certain immiscible polymer blends, partial slip at the interface of the drop and external fluids can profoundly affect drop coalescence. The extent of slip depends largely on the tangential shear stress at the interface, the inherent incompatibility of the polymers forming the blend, the drop size and ratio of the viscosity of the drop and external fluids. We define a "slip" parameter that quantifies the role of interfacial slip during coalescence and show that when the "slip" parameter is O(1) or larger, interfacial slip cannot be ignored in any scaling or numerical analysis. Incorporating the effect of interfacial slip, we compare the results from numerical and scaling analysis for two equal-sized drops undergoing head-on collision in biaxial extensional flow to previously reported experiments performed in a four-roll mill [Park, Baldessari and Leal, Journal of Rheology (2003)].

Thursday 4:10 De Anza II ⊛ SE42

Morphology and rheology of model immiscible blends with interfacial crosslinking

Candice DeLeo and Sachin Velankar
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Reactive compatibilization - generating a compatibilizer by an interfacial chemical reaction between polymers in different phases - is a well-established method in the polymer blend industry. Typically, an end-functional polymer such as polyamide in one phase reacts with a multifunctional polymer such as a maleated polyolefin in the other phase to form a graft copolymer. In this paper we explore immiscible polymer blends in which both reactive species are multifunctional, and thus form a crosslinked network at the interface.

We compare two model blends, a "reference" blend compatibilized by a diblock copolymer, and a reactive blend compatibilized by an interfacial crosslinked network. Optical microscopy shows that the diblock-containing blend forms a typical droplet matrix morphology. In contrast, the reactive blend shows a droplet-matrix morphology with non-spherical drops, sometimes with wrinkled interfaces. Interestingly, the drops of the reactive blend are joined together in a space-spanning network. All these features are attributable to the interfacial crosslinking in the reactive blend.

The rheological properties (creep, recovery, and dynamic oscillatory) of the diblock-containing blend are similar to those of compatibilized droplet-matrix blends studied previously. In contrast, the reactive blend exhibits gel-like behavior due to the space-spanning network formed by the drops. Upon shearing, the reactive blend shows a large viscosity and a large creep recovery at short shearing times suggesting a breakdown of the network structure upon shearing.

A significant risk when dealing with multifunctional reactive systems is the possibility of crosslinking the entire bulk and rendering the material an unprocessible solid. Notably in the present case, the steady shear viscosity of the reactive blend remains comparable to that of the diblock blend. This suggests that in spite of the crosslinked nature of the compatibilizer, because the crosslinking is restricted to the interface of the drops, the reactive blend remains processible.

Thursday 4:30 De Anza II SE43

Effects of partial miscibility on drop-wall and drop-drop interactions

Carmela Tufano[1], Gerrit W. Peters[2], Han Meijer[3], and Patrick D. Anderson[3]

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The effects of mutual diffusion on interfacial tension, drop-drop and drop-wall interactions in quiescent conditions is investigated experimentally and numerically for a highly-diffusive system (PB/PDMS) and a slightly-diffusive system (PBD/PDMS) at room temperature. Just after contact between the phases, the transient interfacial tension of the highly-diffusive system reduces as a consequence of the low-molecular weight (LMW) species migration from the drop into the interphase, yielding to the formation of a thick diffuse layer around the drop surface. While time proceeds, after reaching a minimum, the interfacial tension increases due to LMW species migration from the interphase into the matrix, leading to depletion of the diffusive layer. Once the diffusion process is exhausted, a plateau in interfacial tension is reached and sustained. The slightly- diffusive system, in contrast, shows only an increase in the interfacial tension, corresponding to migration of the fewer migrating molecules (polydispersity is close to one) into the matrix, followed by leveling off to a higher plateau value compared to the PB/PDMS system, which is attributed to the higher molecular weight of the drop phase.

Drop-drop interaction experiments, carried out with isolated pairs of drops and in quiescent conditions, show that partial miscibility affects the ?nal morphology of the system. Drops of the highly diffusive PB/PDMS system attract and coalesce when placed at initial distances smaller than their equivalent radius. The rate of attraction, in the last 100s of the experiments, is the same for a wide range of drop sizes (radii ranging between 90 µm and 350 µm) and different initial distances between them. The attraction is explained in terms of overlap of the diffusive layers around the drops, yielding gradients in interfacial tension and, thus, Marangoni flows acting in the film drainage direction, i.e. enhancing coalescence. When the slightly-diffusive system (PBD/PDMS) is considered, with a thin diffuse-interface, no attraction occurs and, when the drops are placed close together, repulsion between them is observed.

A three-phase diffuse-interface model is implemented, describing the LMW, drop and matrix phase using a Flory-Huggins type of free energy, and the observed trends in transient interfacial tension are qualitatively predicted. Numerical simulations also support the drop-drop and drop-wall interactions, as observed in the experiments.

Friday Morning – 8 August 2008

KL-13. Keynote Lecture 13

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Hiroshi Watanabe

Friday 8:30 Serra I KL13

A new look at stress relaxation in melts of unlinked rings

Scott T. Milner
Chemical Engineering, Penn State University, University Park, PA 16802, USA

As is well known, unlinked rings in a melt of same have conformations akin to "lattice animals", made of segments of length Me along which the chain contour is doubled. Stress relaxation in such systems is an interesting theoretical challenge because a "simple" change in chain topology completely changes the dynamics from reptation to something quite different. An ingenious treatment of the problem was given over 20 years ago by Rubinstein, who argued for a power-law stress relaxation function G(t). Recently, good experimental results for dynamic rheology of ring melts have been obtained by Vlassopolous and coworkers, which are in qualitative agreement with predictions. I have developed a theory for stress relaxation in unlinked ring melts that makes a strong analogy to star polymers. Every doubled segment in a ring configuration divides it into two subtrees; the segment is relaxed when one of the subtrees "evaporates", by the diffusive motion of kinks back and forth across the segment. The equilibrium distribution of subtree masses implies an entropic potential for the extent variable, similar to the retraction potential for stars. From this, the distribution of segment lifetimes and the stress relaxation function can be found. Though qualitatively similar to Rubinstein's result, the exponents differ. Further, by applying methods used to test the double reptation and dynamic dilution approximations, one can assess the importance of constraint release in melts of rings.

KL-14. Keynote Lecture 14

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Melany Hunt

Friday 8:30 Steinbeck KL14

A geophysical perspective of grain-fluid flows

Richard M. Iverson
Cascades Volcano Observatory, U.S. Geological Survey, Vancouver, WA 98683, USA

Flows of concentrated grain-fluid mixtures occur in many geological contexts, ranging from deforming fault zones and landslides to debris flows and pyroclastic flows. The solid grains in these flows typically have volume fractions exceeding 0.5 as well as a great diversity of sizes and shapes, distinguishing them from most manmade grain-fluid flows. Despite their inherent complexity and variability, nearly all geological grain-fluid flows exhibit large-scale behavior that reflects the importance of three small-scale phenomena: #1) the influence of pore fluid on intergranular normal stress, #2) the effect of normal stress and shear rate on intergranular shear stress, and #3) the sensitivity of #1 and #2 to slight changes in solid volume fraction. A simple theoretical model of one-dimensional landslide motion resisted by Coulomb friction in a deforming, water-saturated basal shear zone serves to illustrate the sometimes profound ramifications of these effects, and the model yields predictions that agree qualitatively with experimental results and field observations. The simple 1-D model also serves as a kernel for more sophisticated continuum models that can account for many of the influences of realistic three-dimensional deformation and terrain on flow dynamics -- provided that appropriate formulae for frictional forces are known. In real landslides and debris flows, however, frictional resistance commonly varies with time and position because grain-size segregation facilitates dissipation of pore-fluid pressure at flow margins, where large grains tend to accumulate. Size segregation associated with grain-scale dynamics thereby produces feedback that influences macroscopic flow. Prediction of this emergent behavior poses a theoretical challenge with great practical importance because the extent of areas inundated by landslides and debris flows depends sensitively on flow dynamics in the waning stages of motion, when frictional effects are paramount.

HS-7. Telechelic/Associative Polymers

Organizers: Hiroshi Watanabe and Pier-Luca Maffettone
Session Chair: Justin J. Cooper-White

Friday 9:45 San Carlos IV HS46

Rheology of telechelic polymers assembled with rare earth and metal elements

Megan Romanowich[1], Michael E. Mackay[1], Justin Kumpfer[2], Justin Fox[2], and Stuart J. Rowan[2]
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We use telechelic polymers with specific end groups that assemble with rare earth and metal elements to make materials that behave as very strong gels. Rheologically they appear to behave as very big polymer molecules with extremely large relaxation times. The rheological properties are investigated as a function of Zinc and Europium content that act as linking agents with degree of functionality of two and three, respectively. Interestingly, the Europium tends to degrade the network in some cases to produce a material with lower viscosity. In order to ascertain the mechanism for this unusual behavior we performed large amplitude oscillatory shear and elongation tests to extract the relative association and dissociation rates in the network which is found to be a sensitive test to demonstrate the Europium produces a significant change in the relative rates.

Friday 10:05 San Carlos IV HS47

Rheology of ionomers

Robert A. Weiss
Polymer Program and Dept. of Chemical Eng., University of Connecticut, Storrs, CT 06269-3136, USA

The rheology of low molecular weight PS sulfonated polystyrenes was studied by steady shear and dynamic shear measurements. The molecular weight of the starting PS (Mw ~ 4000/mol) was far below the entanglement molecular weight, and the oligomer behaved extensively as a Newtonian fluid. The introduction of bonded alkali metal sulfonate groups significantly increased the viscosity of the melt and produced not only non-linear viscosity behavior, but also generated finite elastic effects (i.e., a first normal stress coefficient). The magnitude of the viscosity and elasticity increased as the ratio of the concentration of the ionic species increased and the size of the cation decreased. The latter variable is inversely related to the strength of the ion-pair. The ionomer melt rheology can be explained by an ion-hopping mechanism, whereby nanophase separated ionic aggregates behave as labile crosslinks or entanglements. A rubbery plateau typical of a crosslinked polymer was observed in the dynamic measurements, and the magnitude of the plateau modulus was a function only of the ion concentration. The rheological material functions, however, depended on the choice of the cation, which controlled the kinetics of the ion-hopping mechanism. As few as two metal sulfonate groups per chain (on average) increased the zero-shear viscosity, the zero-shear first normal stress coefficient and the terminal relaxation time of PS by as much as 7, 9 and 9 orders of magnitude respectively. In some instances, shear thickening behavior was observed, which is commonly seen in structured solutions or melts.

Friday 10:25 San Carlos IV HS48

Viscoelastic behavior of supramolecular polymers formed by a bisurea type compound in apolar solvents

Toshiyuki Shikata[1], Takuya Nishida[1], and Laurent Buteiller[2]
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Structure and dynamics of a supramolecular polymer formed by a bisurea type compound, 2,4-bis(2-ethylhexcyluredio)toluene (EHU2T), in an apolar solvent, n-decane (C12), were examined in detailed. The EHU2T/C12 organo-gel system forms a long, stable chain-like supramoledular polymer, which makes condensed entangling networks to show remarkable viscoelastic behavior with two major relaxation modes. A slow relaxation mode with an approximately single relaxation time, tS, was observed in a flow region and the other, fast, relaxation mode with a time, tF1 (< tS), was observed in a high frequency range. Because no dielectric relaxation behavior was observed over a frequency region including the mechanical tS and tF1 relaxation modes, the nano-structure of the formed supramolecular polymer does not possess any total dipole moments due to anti-parallel intermolecular hydrogen bond sequence for two ureic groups of each EHU2T unit. A structural model for the supramolecular polymer of EHU2T in C12 responsible for the mechanical and dielectric behavior was proposed and the validity of the model was confirmed by semi-empirical quantum chemical calculations.

Friday 10:45 San Carlos IV HS49

Self-assembly and gelation of benzylidene-D-sorbitol derivative under geometric confinement

Wanyu Chen, Chang Lee, and Amy Shen
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The self-assembly and gelation of benzylidene sorbitol derivatives, 1,3:2,4-di-O-benzylidene-D- sorbitol (DBS) and 1,3:2,4-di-O-p-methylbenzylidene-D-sorbitol (MDBS) as gelators were investigated based on their molecular structure, solvophilic effect, and enthalpies of phase transition under geometric confinement. The self-assembly process for the gelators is dependent on the amount of methyl groups and the size of the confined dimensions. Dynamical rheological measurements, DSC, and TEM studies were conducted to elucidate the formation of nanofibrillar structure of MDBS under confinement.

Friday 11:05 San Carlos IV HS50

Using colloidal suspensions to investigate epitaxial growth phenomena

Itai Cohen, Rajesh Ganapathy, and Mark R. Buckley
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We describe the epitaxial growth of thin films comprised of hard-sphere colloidal particles sedimenting in the presence of a depletant polymer. The depletant polymer induces an effective attraction between microspheres, causing them to nucleate islands that grow and coalesce with one another. In addition, we use photolithography to control the morphology of the substrate. This allows us to investigate the effects of the underlying substrate structure on the epitaxial growth process. Using confocal microscopy, we image and track colloidal particles as they diffuse, aggregate and rearrange their configurations during deposition. Island density and degree of layer-by-layer growth are determined as functions of the deposition rate and depletant concentration. The ease with which we are able to image deposition in real time and the similarity of our results to those obtained in atomic deposition experiments suggest that our system will allow us to model various processes that occur in atomic thin film epitaxial growth.

Friday 11:25 San Carlos IV HS51

Influence of molecular structure on the gelation behaviour of Fmoc-dipeptides

David J. Adams, Leanne Mullen, and William J. Frith
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The formation of hydrogels through the self assembly of oligopeptides and other small molecules containing peptide residues is receiving considerable attention in the literature because of their potential usefulness as novel structurants. Whilst the synthesis and characterisation of many of these materials and hydrogels has been investigated in some detail (1), there are relatively few studies of the structure-property relationships in terms of the chemical character of the gelator used. Systematic studies of the gelation "phase diagram" in terms of gelator concentration and pH are also rare.

Recently, the gelation behaviour of dipeptides coupled to a fluorenylmethoxycarbonyl (Fmoc) moiety has been studied and reported (2-5). These materials can be gelled using a pH trigger, such that the sodium salt of the Fmoc-dipeptide (which is soluble) is converted to the acid form (which gels) by a drop in pH. As such, these materials represent an exciting opportunity to examine the effect of altering a single amino acid residue on the properties of the final gel.

Here, we report the results of a detailed rheological investigation of the formation and properties of Fmoc-dipeptide gels. We show that the hydrogels produced by a range of Fmoc-dipeptides have properties that are determined by the constituent amino acids, and specifically by the hydrophobicity of the dipeptide. At low hydrophobicity stable gels are not formed, instead, extensive syneresis is seen; as the hydrophobicity of the dipeptide residue increases, more stable and stiffer of the gels are formed until a point is reached at which gels can no longer be formed due to the Fmoc-dipeptide being too insoluble in water. We also discuss how the gel properties of some selected Fmoc-dipeptides depend on the pH and concentration at which they are formed.

[1] L.A. Estroff and A.D. Hamilton,. *Chem. Rev.*, 2004, **104**, 1201-1217; [2] Z. Yang, H. Gu, D. Fu, P. Gao, J.K. Lam and B. Xu, *Adv. Mat.*, 2004, **16**, 1440-1444; [3] Y. Zhang, H. Gu, Z. Yang and B. Xu, *J. Am. Chem. Soc.*, 2003, **125**, 13680-13681; [4] V. Jayawarna, M. Ali, T.A. Jowitt, A.F. Miller, A. Saiani, J.E. Gough and R.V. Ulijn, *Adv. Mat.*, 2006, **18**, 611-614; [5] A. Mahler, M. Rechter, S. Cohen, M. Reches and E. Gazit, *Adv. Mat.*, 2006, **18**, 365-1370.

SG-8. Polymer Viscoelasticity

Organizers: C. Michael Roland and Didier R. Long
Session Chair: Jai A. Pathak

Friday 9:45 San Carlos II SG52

A Simplified Potential Energy Clock (SPEC) model for predicting the thermomechanical behavior of glassy polymers: Part I

Douglas B. Adolf[1] and Robert S. Chambers[2]
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A constitutive equation for glassy polymers must predict a broad range of nonlinear viscoelastic material behavior including relaxations in stress, volume and enthalpy as well as various manifestations of physical aging and “yielding”. One way to develop such a model is to adopt the Rational Mechanics approach using the Helmholtz free energy as a potential function from which the stress-strain relationships are derived. This assures thermodynamic consistency, even at large strains, and provides access to other thermodynamic state variables (e.g., internal energy, entropy) for the construction of a material clock. The Potential Energy Clock (PEC) model was derived in this fashion [Caruthers et al., Polymer 45 (2004) 4577-4597]. Although it works well, having been extensively validated for several materials [Adolf et al., Polymer 45 (2004) 4599-4621], it is remarkably unforgiving in its demand for consistent and accurate material properties. This stems from the fact that the strain and temperature dependencies residing in the underlying potential function (i.e., Helmholtz free energy) propagate directly into all the other derived quantities (heirs of the potential) including the material clock. The formalism has no free-fitting parameters that allow for a redistribution or blending of errors. To simplify the material characterization and parameterization, a more phenomenological engineering model has been proposed by decoupling certain clock parameters from the related inputs in the stress-strain equations. This introduces new degrees of freedom into the equations making it easier to fit the model with limited data.

In this presentation, a new phenomenological Simplified Potential Energy Clock (SPEC) model will be introduced along with a description of the required characterization data and model parameterization process. SPEC predictions will be compared to the results from the more physically based and consistent PEC model.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Friday 10:05 San Carlos II SG53

Validation of a Simplified Potential Energy Clock (SPEC) model for predicting the thermomechanical behavior of glassy polymers: Part II

Robert S. Chambers[1] and Douglas B. Adolf[2]
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A validated constitutive equation is expected to be able to predict quantitatively the behavior of glassy polymers under the broad spectrum of temperature and loading environments encountered in engineering practice and to do so using a single set of material model parameters. Clearly, this requires a more physically based formalism than what can be derived by selectively curve fitting a reduced set of data. The previous presentation referenced the development and validation of the Potential Energy Clock (PEC) model and proposed a simplified version (SPEC) based on a different strain measure and the use of phenomenological parameters in the material clock. This presentation will systematically explore the impact of the engineering simplifications by comparing the SPEC predictions to those of the PEC model and to data. The comparisons will include thermal straining under cyclic cooling/heating, compression yield under various temperatures, the change in compressive yield stress during physical aging at different temperatures, volumetric implosion on samples subjected to tensile strains, the dependence of shift factor on aging time and applied stress, and creep and creep recovery. From these data and analysis predictions, the model fidelity and limitations will be defined.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Friday 10:25 San Carlos II SG54

The strain accumulation process in periodically loaded polymer based products due to viscoelastic behavior of polymers

Igor Emri, Barbara Zupancic, Urska Florjancic, and Anatolij Nikonov
Center for Experimental Mechanics, University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana 1000, Slovenia

We investigate the time-dependent behavior of polymeric structural elements, which are exposed to dynamic tooth-like periodic (cyclic) loading. The shape of periodic loading depends on the frequency of periodically applied load and defines the ratio of the loading and unloading phase within one cycle. The strain accumulation process, assuming viscoelastic behavior of material, regarding the effects of the operating frequency and the ratio of the loading and unloading phase is analyzed. We choose different time-dependent material models, which properties are expressed with distribution of spectrum lines that extends over several decades. For defined types of time-dependent materials we study the effect of spectrum line location on strain accumulation process and on the area of critical operating conditions. Performed analysis shows that by knowing the operating conditions we can suggest for what type of material (spectrum location, shape of the spectrum) the strain accumulation will be the least intensive. Secondly, by taking into account that the change of response times of the material actually simulates the effect of temperature change in the material, it turns out that relatively small increase or decrease in temperature at the same operating conditions may significantly change the magnitude of accumulated strain.

Friday 10:45 San Carlos II SG55

Effects of strain on the long term rheology of filled viscoelastic solids

Chris C. White, Don Hunston, and Kar T. Tan
Building and Fire Research Laboratory, National Institue of Standards and Technology, Gaithersburg, MD 20899, USA

Filled viscoelastic solids, have been used for the last 40 years as building sealants to separate indoor from outdoor environments. The most important property of the sealant is the ability to respond to imposed strain while maintaining the critical moisture-barrier properties for decades. During this decades long service life, chemical and molecular changes within the sealant are accelerated by the weather and give rise to changes in the rheological and adhesive properties. At some point, the sealant is no longer able to withstand the imposed strain and will fail. The three factors have generally been considered critical to influencing the changes that occur within the sealant are: ultra-violet light, temperature, and humidity. Recent studies have shown that imposed strain on the sealant during the exposure has a significant affect on the measured rheological properties. This is the case throughout the life cycle of the building joint sealant. During fabrication, the sealant transforms from an viscous liquid to a viscoelastic solid. Strain imposed during or shortly after fabrication (within the first 8 h of cure) has been shown to lower the performance of the material. Once fully cured, further studies show that cyclic strain in the presence of other weathering factors such as heat or high humidity result in significant modulus changes. The direction and type of these changes areas formulation dependent and several examples from all the major chemistries will be presented and discussed. In outdoor experiments it is shown that dynamic strain, such as that encountered in an installed building environment is much more challenging for the sealant than the equivalent static strain. Also presented are results that show that imposed strain affect the solubility of water in the sealant. Sealant under strain will either increase or decrease in solubility depending on the base chemistry. Consequently, strain and strain history are critical factors for understanding the long-term rheological properties of the sealant.

Friday 11:05 San Carlos II SG56

Molecular mobility of soft segment of polyurethane elastomers under elongation

Ken Kojio[1] and Mutsuhisa Furukawa[2]
[1]MatSE, Nagasaki University, Nagasaki 851-8521, Japan; [2]Nagasaki University, Nagasaki, Japan

We synthesized various polyurethane elastomers with various hard segments and soft segments and investigated relationship between molecular mobility of polyurethane and elongation state with pulsed NMR and dynamic viscoelastic property measurements.

HP-11. Entangled Polymers I

Organizers: Lynden A. Archer and Alexei E. Likhtman
Session Chairs: Jay D. Schieber and Christian M. Bailly

Friday 9:45 San Carlos III HP73

Blob-spring model for the dynamics of ring polymer in obstacle environment

Ashish Lele[1], Balaji Iyer[1], and Vinay Juvekar[2]
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The dynamical behavior of cyclic macromolecules in a fixed obstacle (FO) environment is very different than the behavior of linear chains in the same topological environment; while the latter relax by a snake-like reptational motion from their chain ends[1] the former can relax only by contour length fluctuations since they are endless.[2] Duke, Obukhov and Rubinstein proposed a scaling model (the DOR model) to interpret the dynamical scaling exponents shown by Monte Carlo simulations of rings in a FO environment.[2] We have developed a rigorous modified-Rouse formulation (the MR model) based on the concepts of the DOR model to derive the molecular weight dependence of the various dynamical parameters and the constitutive equation for linear viscoelasticity of a ring in a FO environment. Further, we use this model to predict the diffusional behavior of rings in semi-dilute solution and compare it qualitatively with experiments.

[1] P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971); [2] S. P. Obukhov, M. Rubinstein, and T. Duke, *Phys. Rev. Lett.* **73**, 1263 (1994).

Friday 10:05 San Carlos III HP74

Viscoelastic response of cyclic polyoctenamer

Gregory B. McKenna[1], Miao Hu[1], Xia Yan[2], Robert H. Grubbs[3], and Julia A. Kornfield[2]
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There is continuing interest in the dynamics of macrocylic polymers or polymer rings. Here we are working with novel polyoctenamer rings synthesized by a ring opening metathasis polymerization (ROMP)route that precludes linear contamination when pure catalyst is used. While the rings are polydisperse in their molecular weights, the method permits synthesis of extremely high molecular weight entitities. Here we report results on the dynamic moduli and the zero shear rate viscosities of both the cyclic polyoctenamer of Mw up to nearly 400,000 g/mol (which is nearly 50 entanglements) and the linear analogue. Comparisons will be made with prior literature results on rings made by ring closure methods in dilute solution where contamination with linear chains was problematic and where the entanglement density was less than 20.

Friday 10:25 San Carlos III HP75

Viscoelastic properties of ring-shaped polystyrenes

Atsushi Takano[1], Yutaka Ohta[1], Sinpei Tokuno[2], Daisuke Kawaguchi[1], Yoshiaki Takahashi[2], and Yushu Matsushita[1]
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A series of ring polystyrenes with high purity were successfully prepared by anionic polymerization, SEC-fractionation, and furthermore fractionation by liquid chromatography at the critical condition (LCCC). The dynamic storage modulus (G') and dynamic loss modulus (G") of a ring polystyrene of the molecular weight of 41.7K (Mw/Mn = 1.02, purity >99.7%) were measured in at temperatures between 115 and 175°C and compared with those of the linear counterpart. Glass transition temperature and time-temperature shift factor of the ring and linear samples were practically the same. The data in high frequency region of the both samples were the same, while those at low frequency region were slightly different. The data for the ring polymer did not show the apparent plateau region and had shorter relaxation time than the linear one. Further purification of the other ring samples with different molecular weights are now under the progress and their viscoelastic data will be also presented at the meeting.

Friday 10:45 San Carlos III HP76

Dynamics of ring-linear blends

Sachin Shanbhag
School of Computational Science, Florida State University, Tallahassee, FL, USA

An algorithm to identify primitive paths of a melt of ring polymers is presented. The bond-fluctuation model was used to simulate ring-linear blends with N=150 and 300 monomers at different compositions. The radius of gyration, the primitive path length, and the average number of entanglements of the linear component were found to be independent of the blend composition. In contrast, the primitive path length and the average number of entanglements on a ring molecule increased approximately linearly with the fraction of linear chains, and for large N, they approached values comparable with linear chains. Threading of ring molecules by linear chains, and ring-ring interactions were observed only in the presence of linear chains. It is conjectured that these latter interactions facilitate the formation of a percolating entangled network. Self-diffusivity measurements suggest an approximate theory for the motion of the ring polymers, which appears to be in good agreement with recent data on entangled DNA solutions.

Friday 11:05 San Carlos III HP77

Dynamics of partially hydrogen-bonded polymer chains

Osamu Urakawa, Hiroyoshi Ikuta, Miho Fujita, Toshiyuki Shikata, and Tadashi Inoue
Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

We investigated viscoelastic and dielectric relaxation behavior of partially saponified poly (vinyl acetate), i.e. poly (vinyl acetate-ran-vinyl alcohol). The formation of the hydrogen bonds due to the presence of the OH group was confirmed by FTIR measurements. Specifically, two types of H-bonds, i.e., OH–O=C and OH–OH, were detected and analyzed as a function of the degree of saponification (OH content). On the other hand, both the rheological (terminal) relaxation and dielectric (segmental) relaxation times increased with increasing the OH content. The relationship between the segmental and global chain dynamic and the H-bonding structure will be discussed.

Friday 11:25 San Carlos III 💿 HP78

Start-up and transient flow effects from molecular weight distribution

Tommi Borg[1] and Esko J. Pääkkönen[2]
[1]Tomcoat Oy, Evijarvi 62500, Finland; [2]Laboratory of Plastics and Elastomer Technology, Tampere University of Technology, Tampere 33101, Finland

Start-up and transient shear stress flows are modeled using the recently generated constitutive model for linear viscoelasticity of polymers. The relation has been developed between the relaxation modulus, dynamic viscosity and molecular weight distribution (MWD). Modeling starts with control theory and continues with a generated melt calibration; i.e. the relations between time, frequency or shear rate and the molecular weight scales. This procedure has similarities with the widely used universal calibration. The study extends the linear principle on start-up, decay and transient effects for stress, viscosity and relaxation modulus. The paper is using classical shear viscosity measurements done by IUPAC to get relaxation modulus for polyethylene (LDPE) with known MWD. At first are modeled time-dependent stress and viscosity transitions at imposed new shear rates. Gained results can be used for modeling start-up situation and moreover for shear stress growth and decay coefficients. Also simulations for relaxation modulus measurements at different shear history are performed. As practical results of models simulations of capillary runs and injection molding process are presented. Cellular phone covers are modeled to obtain pressure loss and orientation level for every finite element, which forecasts the shrinking and warping of the end products.

BR-6. Cell Mechanics

Organizers: James L. Harden and Christoph F. Schmidt
Session Chair: Paul Janmey

Friday 9:45 Redwood BR37

Correlation between extracellular matrix (ECM) stiffness, intracellular viscoelastic properties, and invasive ability of cancer cells

Erin L. Baker[1], Muhammad H. Zaman[1], and Roger T. Bonnecaze[2]
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Tumors exhibit elevated stiffness compared to normal tissue, and some aspects of tumor cell invasive ability are in part governed by extracellular matrix (ECM) stiffness. Yet neither the relationship between ECM stiffness and intracellular mechanical properties, nor that between intracellular mechanical properties and invasive ability, is well understood. In order to establish these relationships quantitatively, we employ particle-tracking microrheology to investigate the intracellular viscoelastic properties of single cancer cells that are attached to two-dimensional (2D) substrates, as well as those that are embedded within three-dimensional (3D) matrices. While particle-tracking rheological protocols have been established, these techniques have yet to be applied in linking the cytoplasmic mechanical environment of cancer cells to their invasive ability. Specifically, the intracellular mechanical properties of elasticity, viscosity, and compliance of human prostate cancer (PC-3) cells and transformed human breast cancer (MCF-10A) cells of varying invasive ability are extracted from Brownian motions of individual 1.0μm polystyrene spheres that are ballistically delivered to their cytoplasm. Results indicate that the cytoplasmic mechanical environment of PC-3 cells attached to a 2D substrate is non-homogenous, independent of matrix stiffness. Furthermore, the heterogeneously varying intracellular viscoelastic properties show a strong correlation with matrix chemistry and mechanical architecture. These viscoelastic properties are also shown to correlate with the invasiveness of the cancer cells.

Friday 10:05 Redwood BR38

The analysis of microrheological data in non-equilibrium, motor-activated F-actin networks

Alex J. Levine[1] and Fred MacKintosh[2]
[1]Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, CA, USA; [2]Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands

The mechanics of the in vivo cytoskeleton is strongly modified by the action of molecular motors. We develop a two-fluid model of a semiflexible network that is driven into a non-equilibrium steady-state by endogenous motors exerting transient contractile stresses. Using this model we show that motor activity dramatically increases the network's elastic moduli. We also show that, due to the motor-enhancement of low-frequency noise in the strain field, tracers in this elastic network will appear to diffuse even when the radius of the tracer is significantly larger than the mesh size of the network. Using these calculations, we discuss new ways to interpret microrheology in non-equilibrium, active networks.

Friday 10:25 Redwood BR39

Response and fluctuations in active bacterial bath

Andy Lau
Physics Department, Florida Atlantic University, Boca Raton, FL 33431, USA

Active systems contain microscopic components that continuously consume and dissipate energy to their surroundings, creating a state that is far from equilibrium. They arise primarily from biology, e.g., the cytoskeleton of living cells, active gels (polymer-network with molecular motors), active membranes (cell membranes with ion pumps), and self-propelled microorganisms. Not only do these active systems exhibit physical phenomena that are quite distinct from those of conventional equilibrium soft materials, more importantly, they also represent systems in which one can quantitatively study biological phenomena. In this talk, we will focus on a model active system, namely, a bacterial bath, which consists of a population of rod-like motile or self-propelled bacteria suspended in a fluid environment. By generalizing the theoretical framework for deriving the fluctuating hydrodynamic equations of an equilibrium system, we construct a phenomenological theory for the dynamics of a bacterial bath, and show, in particular, that the non-equilibrium contributions to the stress arising from the swimming of the bacteria and the non-equilibrium couplings between the alignment tensor and bacterial density, lead to a scaling in the power spectrum of the active stress fluctuations, as observed in a recent microrheological experiment.

Friday 10:45 Redwood BR40

A particle-based model for cell mechanics: From microstructures to rheology

Seyed Majid Hosseini and James J. Feng
Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia V6T 1Z3, Canada

In cancer and malaria, external factors such as bioactive lipids and parasites change the internal structure and mechanical behavior of living cells through biochemical reactions. The modified cell response, manifested by elevated or suppressed elastic modulus, facilitates disease progression in the body. We present a particle-based model of living cells based on the Smoothed Particle Hydrodynamics concept. The discrete nature of the model allows us to go beyond the continuum framework to probe micro- and nanostructural responses to external stimulation. We apply this model to investigate cytoplasmic reorganization in metastasizing cancer cells and malaria-infected red blood cells. In each case, we show that the molecular and structural changes in the cytoplasm and the membrane explain the anomalous rheology and motility of the cells.

Friday 11:05 Redwood 💿 BR41

Dissipative particle dynamics simulation of polymer- and cell-wall depletion in micro-channels

Dmitry A. Fedosov[1], Bruce Caswell[2], and George E. Karniadakis[1]

[1]Division of Applied Mathematics, Brown University, Providence, RI 02912, USA; [2]Division of Engineering, Brown University, Providence, RI 02912, USA

A rising interest in physics of biological systems stimulates a great number of experiments and numerical simulations involving a variety of biological entities. These include real organism vesicles and capsules, artificial vesicles used in drug delivery and cells. Eventhough they greatly differ in their functions and material properties, they appear to have similar construction such as a membrane which encloses some type of a fluid or suspension. Recently developed models differ in constitutive equations and constraints which generally include membrane in-plane visco-elastic energy, bending energy, area and volume constraints. We employ dissipative particle dynamics (DPD) method to model a coarse-grained cell membrane. We investigate cell-wall depletion interactions for cells having vesicle-like shape and red blood cells. The cell deformation and cross-stream migration is studied for basic shear flows (e.g. Couette and Poiseuille). We compare our results with available experiments and numerical simulations. We correlate our results with membrane coarse-graining and material properties such as membrane shear and area compression modulus.

MP-9. Stability and Crystallization

Organizers: Kyung Hyun Ahn and Paulo R. de Souza Mendes
Session Chair: Verônica Calado

Friday 9:45 Colton I-III 💿 MP61

In-situ structural characterization by SAXS and flow properties of colloidal suspensions during crossflow ultrafiltration

Frédéric Pignon[1], Christopher David[1], Albert Magnin[1], and Michael Sztucki[2]

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Understanding the mechanisms that control the filtration of complex colloidal suspensions is a major challenge in the development of membrane-based processes in industry. One of the main limiting factors for the development of these processes lies in the formation of a polarization layer and/or deposit near the separating membrane. Elucidating the structure of the first layer of deposited colloids during the first steps of filtration, constitutes a considerable technological jump in the understanding of the physical mechanisms implied in the formation of these deposits. It is also important to identify the effects of the physicochemical properties, the rheological behavior and the hydrodynamic fields on the organisation of the colloids during filtration. The focus of this work is the in-situ characterization of the induced structures and flow properties of the polarization layers of colloidal suspensions when simultaneously subjected to a transmembrane pressure and tangential flow over the membrane. To fulfill this challenge a new tangential ultrafiltration SAXS cell has been developed at the "Laboratoire de Rhéologie" Grenoble, France. This cell allowed combining small angle x-ray scattering (SAXS) at the European Synchrotron Radiation Facility (ID02 beamline) with membrane separation processes. Systems studied are anisotropic colloidal aqueous dispersions composed of sepiolite fibers 1 micrometer long and 0.01 micrometers in diameter, a natural non-swelling fibrous clay. The initial concentration of the filtered suspensions was in the semi-dilute domain for which the suspensions exhibit a shear thinning rheological behavior. During filtration, a transmembrane pressure was applied and successive tangential flows were imposed. The permeation flux was continuously measured and simultaneously the x-ray beam (40 x 250 micrometer) crossed the lateral dimension of the cell to probe the structure of the deposit with time at different heights above the membrane. As already described in previous studies concerning frontal filtration mode [1-2], a calibration curve relating the absolute scattering intensity to the particles concentration has allowed to deduce the concentration profiles in the deposits at distances to the membrane above 300 micrometers. During these experiments the high level of concentration reached in the deposit up to 50 times the initial concentration, and the highly anisotropic structure formed has been identified as one of the main mechanisms controlling the filtration flux decrease. The results prove the possibility to obtain pertinent structural information in the vicinity of membrane surfaces during ultrafiltration. It offers essential experimental data necessary for improvement in theoretical and numerical modeling of the filtration process.

[1] F. Pignon, A. Alemdar, A. Magnin, and T. Narayanan, Langmuir, 19, 8638 (2003); [2] F. Pignon, G. Belina, T. Narayanan, X. Paubel, A. Magnin and G. Gésan-Guiziou, The Journal of Chemical Physics, 121(16), 8138 (2004).

Friday 10:05 Colton I-III 💿 MP62

Stability of the annular Poiseuille flow of a Newtonian liquid with slip along the walls

Maria Chatzimina[1], Georgios C. Georgiou[1], Kostas Housiadas[2], and Savvas G. Hatzikiriakos[3]

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The annular Poiseuille flow of a compressible Newtonian fluid is studied assuming that slip occurs along the wall. Different slip models relating the wall shear stress to the slip velocity are employed. In the case of linear slip, it is easily shown that the slip velocity along the inner cylinder is always greater than the slip velocity along the outer cylinder. In the case of a non-monotonic slip equation, there exist linearly unstable steady-state solutions corresponding to the negative-slope regime of the slip equation. As a result, the resulting flow curve is also non-monotonic with an intermediate unstable negative-slope branch which corresponds to the stick-slip extrusion instability regime. It is shown for small radii ratios $\kappa = R_1/R_2$, two stable steady-state solutions are possible in a certain range of the volumetric flow rate. As a consequence, the stick-slip instability regime is reduced in size and eventually disappears as κ is decreased. This provides an explanation for the fact that the stick-slip instability is not observed in annular extrusion experiments.

Friday 10:25 Colton I-III MP63

Stability of shear-extensional flow in film extrusion of liquid crystalline polymer-anisotropic viscoelastic fluid

Shifang Han
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The extrusion process near the die exit of liquid crystalline (LC) polymer melt sheet can be considered as a flow dominating extension with shear motion element.The shear-extensional flow is of practical significance for the sheet processing of LC polymer. Using the constitutive equation developed by Shifang Han (Acta Mechanica Sinica, 2007) for LC polymer-anisotropic viscoelastic fluid , the stability of shear-extensional flow is studied for the extrusion process near the die exit of the sheet of the fluid. Disturbed constitutive equation is derived for the problem. Stability criterion of the fluid sheet is given. Typical shear-extensional flows such as uniaxial, biaxial, planar and ellipsoidal are discussed. The following conclusions are drawn: 1. shear motion has important influence on instability of the fluid sheet; 2. ellipsoidal and biaxial extensional flows are more stable than uniaxial one; 3. director tumbling leads to oscillation of stability criterion of the fluid sheet.

Friday 10:45 Colton I-III MP64

Precursors, crystallization and melting in sheared bimodal HDPE melts

Luigi Balzano[1], Gerrit W. Peters[2], Nileshkumar Kukalyekar[1], and Sanjay Rastogi[3]
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In a crystallizable polymer melt, flow can induce metastable precursors of crystallization with very low or no crystallinity. These flow induced precursors (FIPs) can the following developments of the crystalline morphology. FIPs are active in the early stages of crystallization, enhancing the kinetics and promoting the formation of oriented shish kebabs. To enhance the formation of FIPs in shear flow, we make use of a specially synthesized blend of low and high molecular weight (LMW and HMW) linear HDPE. Remarkably, we found that, at 142?, just above the equilibrium melting temperature, shearing the melt can induce needle-like precursors that are clearly detectable with X-ray scattering. At this high temperature, only FIPs with an extended chain structure are stable and those that are large enough crystallize forming a suspension of shishes without kebabs. The other FIPs (with folded chain structure or with extended chain structure but too small to grow) have a limited lifetime and relax back to the melt state. The relaxation timescale of subcritical precursors matches the disengagement time of HMW suggesting that the early FIPs are HMW rich. Analysis of the flow conditions indicate that FIPs arise with the stretching of the network formed by the mutually entangled HMW molecules, but only if a critical strain is exceeded. FIPs and shishes generated with shear at 142? can be used as seeds for the nucleation of the rest of the molecules. On cooling, the onset of bulk crystallization can shift up to 132? depending on the flow conditions. Bulk crystallization starts with nucleation of kebabs at high temperature and, if there is molten material available, proceeds, at lower temperature, with homogeneous nucleation of randomly oriented lamellae that decrease the degree of orientation of the crystalline morphology. We observe that with certain flow conditions shishes are sufficient to template a fully oriented morphology where the homogeneous nucleation of randomly oriented lamellae is suppressed. Shish-kebabs exhibit an enhanced thermal stability. The crystallization of kebabs is reversible and melting of kebabs restores a suspension of shishes that, eventually, melt at a higher temperature.

CG-4. Yielding

Organizers: Dimitris Vlassopoulos and Wilson C. Poon
Session Chairs: Matthias Fuchs and Michel Cloitre

Friday 9:45 San Carlos I CG22

Aging and yielding for colloidal suspension by MRI velocimetry

Alexandre Ragouilliaux[1], Benjamin Herzhaft[2], Guillaume Ovarlez[1], and Philippe Coussot[1]
[1]LMSGC, Institut Navier, Champs sur Marne, France; [2]IFP, Rueil, France

We studied a suspension of water droplets in oil which, due to organoclay particles links, exhibits a yielding and thixotropic behavior. The local rheological behavior in time was determined with the help of MRI velocimetry in a Couette flow. Under constant rotation velocity, in a first stage we observe a progressive displacement of the fluid/solid interface towards the inner cylinder, which is associated with the increase of a critical shear rate below which there is apparently no flow. It is remarkable that during this stage our local and macroscopic measurements show that the constitutive equation of the liquid region does not vary in time: only the thickness of the sheared region and the critical shear rate vary. Then we focus on the solid and liquid regimes as a function of the droplet concentration ϕ (from 20 to 70%). The solid regime is studied by measuring the elastic modulus (G) in time for the different formulations. The initial level of G increases with ϕ but G also increases with time, witch is the hallmark of the thixotropy (aging) at rest. In a rather astonishing way, the effect of time on the restructuring is much larger than the effect of concentration increase. In order to study the liquid regime, we build the local flow curves from MRI velocity profiles as a function of time under the same rotation velocity of the inner cylinder for each formulation. The yield stress and critical shear rate do not significantly vary with the droplet concentration, and the flow curves are rather similar. Thus the effect of a significant increase in droplet concentration on the material behavior in the liquid regime is minor, in contrast with the effect on the behavior in the solid regime. This is explained by the fact that the behavior in the solid regime is mainly controlled by the droplet aggregation, a process which plays a much smaller role as soon as the liquid regime is reached.

Friday 10:05 San Carlos I CG23

Yielding and flow of carbon black gels

Thomas Gibaud, Nicolas Taberlet, and Sebastien Manneville
Laboratoire de Physique, Ecole Normale Superieure de Lyon, Lyon 69364, France

Carbon black particles suspended in oil at volume fractions of a few percents form weak fractal gels that result from attractive interactions between the particles. Rheological measurements point to a Herschel-Bulkley behaviour with a yield stress of a few Pascals. We use ultrasonic velocimetry combined to standard rheometry in Couette geometry to investigate the deformation and flow of carbon black gels at the yielding transition. We focus on the influence of the gap width and of wall surface roughness as well as responses under imposed shear stress vs shear rate. Our measurements reveal complex flow profiles involving a transition from a stick-slip regime to homogeneous shearing. These experiments are completed with preliminary measurements in microchannels and with direct visualization of carbon black films flowing down an inclined plane.

Friday 10:25 San Carlos I CG24

Yielding and aging in sheared lyotropic phases of interconnected bilayers

Yann Auffret[1], Denis C. D. Roux[1], David E. Dunstan[2], Nadia El Kissi[1], and François Caton[1]
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The amphiphilic properties of surfactant molecules as AOT (docusate sodium salt) confer the ability to form microstructures when mixed with apolar/polar solvent mixtures such as Isooctane (2-2-4 trimethylpentane) and water. In the concentrated regime, complex lyotropic liquid crystal phases with various degrees of order may be formed. The potential use of such systems as templates for the design of nanoporous materials and in other applications necessitates the characterization of their complex rheological properties. As a consequence, this study is focused on the characterization of the yielding phenomena occurring in a given lyotropic phase.

Using polarized light microscopy, and X-ray scattering, the structures formed within an AOT/Isooctane/Water molecular system were identified as bilayers. The distance between two monolayers is controlled by the ratio of polar to apolar solvent. Cryo-electron microscopy and cryo-TEM indicate that these bilayers may be interconnected. Since no counter-ions are added in the system, Coulomb interactions exist between neighbouring bilayers which may be at the origin of the complex flow properties we have uncovered using conventional and optic rheometry.

The results of preliminary stress and strain controlled measurements have shown that a steady and reproducible state is reached after a complex transient regime as long as the applied stress remains in the range, 5 Pa to 30 Pa. This allows us to define a reliable creep procedure to characterize the flow properties of the material. (i) at first, the sample is brought to a reference state by applying a constant stress so that a steady state is reached (ii) a second stress is then applied and the resulting strain is monitored as a function of time.

The ensuing results show the existence of a yield stress defining two regimes of stresses where the material behaves either as a solid or as a liquid. In both regimes, inertial coupling between the rotating part of the rheometer and the sample induces early oscillations of the strain. Fitting these oscillations with theoretical models, the parameters controlling the deformation either in the liquid or solid regime are identified. In the fluid regime, a steady state is reached after a complex transient regime. Based on flow birefringence measurements this transient regime is interpreted in terms of large scale structure reorganizations. In the solid regime, the strain 'plateau' is followed by a puzzling decrease which is interpreted as a consequence of delayed viscoelastic effects.

Friday 10:45 San Carlos I CG25

Motion and shape of bubbles rising through a yield-stress gel

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We study the velocity and shape of air bubbles rising through dispersions of Carbopol, a transparent yield-stress fluid. The bubbles are small enough compared to the experimental vessel that wall effects are not large. We find that the terminal rise velocity of the bubbles increases with a power law dependence on volume over the range of volumes accessible in our experiments. The bubbles have a rounded head and cusp-shaped tail. We are able to fit the shapes of all of our bubbles to a simple empirical function. The dependence of the bubble shape on volume and yield stress will be discussed.

Friday 11:05 San Carlos I CG26

Gravitary free surface flows used as a rheometrical tool: The case of viscoplastic fluids

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We present experimental results concerning the behavior of two viscoplastic fluids in a free surface flow configuration. Those fluids are tested to be used as model materials for the muddy matrix of natural debris flows. Our aim is to get better insight, through laboratory experiments, in the rheological and mechanical processes involved in these natural flows. Our experiments are conducted on a 3 meter long and 0.4 meter wide inclined channel whose bottom consists of a conveyor belt moving upstream with controlled velocity. At channel upper boundary, fluid recirculation is forced by a rigid wall perpendicular to the bottom. These specificities allow us to generate gravitary surges that are stationary in the laboratory frame and thus, that can be studied in details. If the volume of fluid is sufficient, the obtained surges systematically present a zone where flow height is uniform. We studied the evolution of this uniform height as a function of imposed belt velocity and slope angle for two different fluids: a carbopol gel and a kaolin dispersion. The rheological properties of these two fluids were determined independently using a rotational rheometer. Both behave as Herschel-Bulkley fluids with a yield stress around 15 Pa for the concentrations used in this study. Hence, height measurements performed in the channel experiments are compared to the classical two-dimensional height-discharge relationship for a Herschel-Bulkley fluid in steady uniform flow down a slope. In the model, we suppose that the average velocity is equal to the belt velocity imposed in our experiments, thus assuming that the conveyor belt does not change the overall shape of velocity profile. Despite the similar flow curves of the two used materials, the results obtained on the channel appear significantly different. With kaolin slurry, measured heights appear in good agreement with model predictions, whereas with carbopol, the model systematically underestimates experimental data. This difference could be related to the visco-elastic properties of carbopol, whose typical shear modulus is much smaller than that of kaolin. We propose a refined model accounting for these visco-elastic effects in our experiments. Finally, conclusions regarding the respective advantages and limits of both fluids for debris flow modeling will be drawn.

Friday 11:25 San Carlos I CG27

Influence of the shear stress applied during the flow stoppage and the rest on the mechanical properties of thixotropic suspensions

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We study the mechanical properties at rest of several thixotropic suspensions. The materials we study are first destructured by applying a strong preshear. Then, once the preshear is stopped, we measure the evolution of their elastic modulus and their yield stress with the resting time, under various stress conditions (below the yield stress) applied during their flow stoppage and during their aging at rest. We show that the mechanical state of thixotropic suspensions depends on the shear stress applied at flow stoppage (i.e. during their liquid/solid transition) but does not depend on the stress applied during their aging (i. e. after their liquid/solid transition). Their elastic modulus and yield stress increase strongly with the stress applied during flow stoppage. Moreover, these materials age: their elastic modulus and their yield stress increase with the resting time. However, the increase rate of these mechanical properties is independent of the stresses applied during both the aging and the liquid/solid transition.

We show that this phenomenon may reflect differences in the microstructures that are frozen at the liquid/solid transition. In a simple picture of a colloidal suspension with repulsive and attractive pair interactions, we show that a liquid/solid transition under a non-zero stress imply a particle pair orientations that yields an increase of the elastic modulus roughly proportional to this stress. The independence of the increase rate of the mechanical properties on the stress applied during aging requires an aging mechanism that is insensitive to the stress transmitted in the solid network: this is consistent with a structure build-up through new contacts creation.

We also show that the new phenomenon we evidence may have important macroscopic consequences. We show how careful rheometrical tests must be designed to measure correctly the static yield stress, and compare the use of velocity-controlled and torque-controlled rheometers. In the example of the simple inclined plane test, we show that the angle at which the flow starts depends strongly on the way the flow stopped. Moreover, we observe that the yield surface also depends on how the flow stopped: in some cases, the flow restart may be heterogeneous. Finally, in any practical case, this implies that any measurement procedure must be designed for its specific application.

SC-11. Field Effects: ER and MR Fluids

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Howard See and Daniel J. Klingenberg

Friday 9:45 De Anza III SC73

Direct numerical simulation of three-dimensional flows with suspended paramagnetic particles

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A three-dimensional direct simulation method, based on the Maxwell stress tensor and a fictitious domain method, has been developed to solve flows with paramagnetic particles suspended in a non-magnetic Newtonian fluid. The numerical scheme enables us to take into account both hydrodynamic and magnetic interactions between particles in a fully coupled manner, regardless of the shape of particles. We assume that fluid flow is governed by the Stokes equation neglecting inertia. Particles are assumed to be non-Brownian with negligible inertia. Rigid body motions of particles are described by a rigid-shell description implemented by Lagrange multipliers in the combined finite element formulation. The magnetic force, acting on the particles due to magnetic fields applied externally, is represented by the divergence of the Maxwell stress tensor, which acts as a body force added to the momentum balance equation. Using a continuous pressure interpolation and a collocation method for the rigid body constraint, we observed numerical problems such as spiky velocity field near particle boundary and failure to satisfy the rigid body constraint of the particles. These numerical issues are resolved by using a discontinuous pressure interpolation and the use of a weak formulation for the rigid body constraint. First, we choose a single-particle problem for validation of the numerical method. As for the magnetic forces working on particles, we compared the results obtained from our scheme with those from the dipole-dipole interaction model. The convergence with mesh refinement is verified by comparing results from regular mesh problems with those from a boundary-fitted mesh problem as references. We apply the developed numerical scheme to two problems: actuation of magnetic particles in a non-uniform magnetic field and dynamics of interacting two particles in a rotating field, demonstrating the capability of the method to tackle general problems.

Friday 10:05 De Anza III SC74

Viscosity of a suspension with internal rotations

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When an insulating particle immersed into a low conducting liquid is submitted to a sufficiently high DC field, **E**, it can rotate spontaneously around itself. This instability, known as Quincke rotation, can be understood looking at the action of free electrical charges which are contained in the liquid. Indeed, when the E field is applied, the charges contained in the liquid migrate under coulombic force and, since the particle is insulating, accumulate at the particle/liquid interface. It can be shown that this charge distribution around the particle is equivalent to a dipole moment, **P**, which is in the direction opposite to the field direction. If the particle is slightly rotated, the deviation of the dipole produces a torque given by the cross product of **P** and **E**, which tends to increase the angular tilt further. So, if the E field intensity is high enough for the electric torque to balance the viscous resistant torque exerted by the surrounding liquid on the particle, the particle will rotate continuously around itself with an axis pointing in any direction perpendicular to DC field.

We have already shown that Quincke rotation could have important consequences on the rheology of a suspension of such particles. Indeed when the suspension is motionless and a DC field is applied, particles start rotating around themselves in any direction perpendicular to the field and so the average spin rate of the suspension is zero. But, when a velocity gradient is applied along the field direction, the particles rotation axes is favoured in the vorticity direction. Therefore, the degeneracy of the rotation direction is lifted giving rise to a nonzero spin rate of the ensemble of particles. This macroscopic spin rate drives the suspending liquid and thus leads to a decrease of the apparent viscosity of the suspension.

The purpose of this paper is to provide a relation between the apparent viscosity of the suspension, the spin rate of the particles and the E field intensity. First, the steady state solutions are searched for the angular velocity of a particle subjected to both DC E field and simple shear flow. Since the solutions are multivalued, their stability is studied using a linear stability analysis. Then, the stable solution for the particle angular velocity is used to deduce the value of the apparent viscosity of the suspension. The predictions of the model are compared to experimental data which have been obtained with a suspension of PMMA particles dispersed in a low polar dielectric liquid. The agreement between experiments and theory is rather good even if the model overestimates the viscosity decrease induced by the field.

Friday 10:25 De Anza III SC75

The electrorheological effect in suspensions of different conductivity under A.C. electric field

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We study the electrorheological effect of suspensions of polarizable particles under a variable electric field in three different liquids of different conductivity by steady state and transient rheological experiments and microscopy. Two types of structure are induced by the electric flied which depend on the particle concentration, the intensity and the frequency of the electric field. The electrorheological properties of the suspensions are analyzed with a kinetic rheological model that describes the flow-induced modification of the structures formed by the particles under a.c. electric field. The effects of non-linear conductivity and non linear permittivity are introduced in the model to account for the maxima observed in the viscosity at high electric fields and particle concentration. The model further describes the variation of viscosity with shear rate under a given electric field, and time-dependent phenomena arising from the dynamics of the breakage-reformation process of the structures.

Friday 10:45 De Anza III SC76

Electrokinetics over liquid/liquid interfaces

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Just over a century ago, Smoluchowski derived his celebrated formula for the electrokinetic slip velocity, which handles both the electrophoresis of colloids and electro-osmotic flows over solid surfaces under a range of conditions. Here we discuss interesting and surprising effects that arise with electrokinetics over liquid-liquid interfaces. A central observation is that the (strong) shear rates that arise in electro-osmosis can drive liquid/liquid interfaces to flow, unlike their solid/liquid counterparts, and thus enhance electrokinetic velocities, potentially by orders of magnitude. We pay particular attention to the electrophoretic mobility of liquid drops, which has been the subject of over a half-century's debate. Levich and Frumkin argued via electrocapillarity that the electrophoretic mobility of a charged mercury drop should significantly exceed that of a similarly-charged solid particle. By contrast, the more conventional electrokinetic calculation by Booth revealed no such enhancement. In the decades since, various efforts have been made to resolve this discrepancy, reconcile the two pictures and delineate the conditions under which this dramatic enhancement should occur. We present a clear physical picture for the mechanism behind this dramatic increase in mobility, provide an intuitive sense for when and why such increases can be expected, and discuss implications and adaptations for microfliudic systems.

Friday 11:05 De Anza III SC77

The response of elongated particles under shear and electric fields

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A new simulation framework is proposed for the computational modelling of elongated or rod-like particles dispersed in electrorheological suspensions. Current computer simulations of electro and magneto rheological suspensions are restricted to suspensions that contain only spherical particles. As a result, the possibility of different field-induced response of electrorheological suspensions containing elongated particles or a mixture of different shaped particles has been overlooked. The proposed framework is based on particle-level dynamics, in which particles are made from linked spheres, to model the hydrodynamics of single particles and inter-particle interactions. Electrostatic interactions between the particles are modeled by the point dipole approach. This modeling framework will then be used to examine the link between the field-induced microstructure and rheological response.

Friday 11:25 De Anza III SC78

Electrorheological suspension of core/shell structured polymeric microspheres with polyaniline and its shear stress analysis

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In order to prepare model electrorheological (ER) fluids, core/shell structured particles with poly(methyl methacrylate) (PMMA) core and conducting polyaniline (PANI) shell were synthesized both with and without surface modification. Initially, monodisperse PMMA microspheres ranging from 6 to 10 micron in diameter as a core material were synthesized by dispersion polymerization, and then PANI was coated on the PMMA core via a chemical oxidation [1]. In the case of surface modification, the pristine PMMA was treated with glycidyl methacrylate and ethylene glycol dimethacrylate for swelling agent and crosslinker, respectively. PANI shell was synthesized via grafting polymerization. Various characteristics were examined via SEM, TGA, 13C-NMR and optical microscope, demonstrating its successful formation of core/shell structured PMMA microspheres. The flow curves of these ER fluids under several applied electric field strengths and particle concentrations were constructed and their flow characteristics were examined via three different rheological constitutive equations of Bingham model, De Kee-Turcotte model and our proposed model. Yield stress of the ER fluid under an applied electric field was observed to be increased with a particle size, and this result was analyzed via a dielectric spectrum. Furthermore, a universal scaling equation of the yield stress was applied [2].

[1] M. S. Cho, Y. H. Cho, H. J. Choi, and M. S. Jhon, Langmuir 2003, 19, 5875; [2] I. S. Sim, J. W. Kim, H. J. Choi, C. A. Kim, and M. S. Jhon, Chem. Mater. 2001, 13, 1243.

SC-12. Colloids, Nanotubes and Nanocomposites

Organizers: Norman J. Wagner and Jeff F. Morris
Session Chairs: Nina C. Shapley and Chongyoup Kim

Friday 9:45 Portola SC79

Extensional rheology of single walled carbon nanotubes in liquids

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The major roadblock to achieving progress in using Single Walled Carbon Nanotubes (SWNTs) to produce high performance materials has been the difficulty of arraying SWNTs into ordered macroscopic samples. Recent major advances indicate that macroscopic objects of SWNTs can be produced by processing SWNTs in the liquid state. By using a variety of means such as stabilization by surfactants, or by dissolution in superacids, pristine SWNTs have been dispersed at sufficient concentrations to enable the extrusion of continuous, well-aligned, macroscopic fibres. Similarly, films of SWNTs have been produced by coating and spraying processes. A key determinant of the properties of liquid-spun fibres and films is the extent of alignment of SWNTs in the dispersion induced by the processing. This aspect is related to the rheological properties of SWNT dispersions, particularly the coupling between rheological properties and the flow-induced evolution of the microstructure. Because extrusion and coating flows are extension-dominated, understanding the extensional rheology of SWNT dispersions is fundamental to controlling the liquid state processing of SWNTs.

The present study is aimed at characterizing the extensional behaviour of SWNT dispersions using the filament stretching rheometer. Currently, published measurements of the extensional behaviour of rodlike polymer solutions are scanty, except for a recent publication by Sridhar's group on the uniaxial extensional flow of non-Brownian fibre suspensions. Efforts so far on characterizing the shear rheology of SWNT dispersions have focused on the relationship between the intrinsic shear viscosity and mean carbon nanotube length. Pure SWNTs prepared by the High-Pressure Carbon Monoxide (HiPCO) process have been shown to have a length in the range of 500 to 700 nm, which has been corroborated independently by Atomic Force microscopy experiments. In the present work, various concentrations of SWNTs have been dispersed in a range of surfactant solutions consisting of pluronic F68 in water, or mixtures of pluronic F68 and polyethylene glycol (PEG). The viscosity of the solvent was tailored to achieve an extensional flow of the uniformly dispersed SWNT dispersion. At the dispersion concentrations that could be achieved, however, reliable experiments could only be performed at extension rates at which the high strain rate asymptotic extensional viscosity, which is independent of the imposed strain rate and where Brownian forces are likely to be negligible, was measured. We show that identical extensional viscosities are measured, independent of the particular solvent used, provided the dispersion concentration and the viscosity ratio of solution to solvent is the same. An estimate of the mean length of the SWNTs obtained by fitting the steady state extensional viscosity to Batchelor's theory for the extensional viscosity of rods is shown to lead to values that are in excellent agreement with previous measurements through shear rheology and atomic force microscopy.

Friday 10:05 Portola SC80

A model system for rheological simulation: Silica-polydimethylsiloxane colloids in low molecular weight silicon oil

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Colloidal systems are a common model for study of fundamental materials science questions related to defect structure and dynamics, crystallization and interfacial structure between crystals, and rheological response of colloidal systems. The rheological response of colloidal systems is often used to determine such characteristics. This work presents the experimental development of a model colloidal system for comparison to the computational rheological modeling program ongoing at Sandia National Laboratories. The colloidal system is based on monodisperse silica spheres modified with low molecular weight polydimethylsiloxane chains, and dispersed in a low molecular weight polydimethylsiloxane fluid. Characterization of the adsorbed amount of PDMS, colloidal dispersion, and rheological properties will be presented.

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Friday 10:25 Portola SC81

The rheology of carbon nanotube (CNT) suspensions: Experiments and modelling

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This presentation reports the latest experimental results and rheological modelling for Carbon Nanotube (CNT) suspensions. CNTs belong to a relatively new class of nano-scale fibres having fascinating physical properties. In terms of experimental rheology, there are some similarities between CNT suspensions and classical carbon, glass, or polymeric fibre suspensions. For instance, suspensions of CNTs with a Newtonian matrix were found to be shear-thinning in simple shear. The extent of shear-thinning, however, varies significantly depending on the type of CNTs used. As-produced untreated CNTs tended to give a much higher low-shear viscosity coupled with optically resolvable CNT aggregates [1], whereas CNTs that have been chemically treated showed little optical microstructure with less pronounced shear-thinning. When subject to uniaxial elongation, the addition of treated CNTs prolonged the filament thinning process and increased the extensional viscosity, whilst untreated CNTs created instability to the filament formed, consequently resulting in non-uniform curvature along the filament axis and early filament breakup [2]. Both treated and untreated CNT suspensions have characteristic viscoelastic properties.

In terms of modelling, although CNTs have a smaller length scale than classical fibres, referencing to well-established fibre suspension theories provides a good starting point for understanding the rheology of the suspensions. Stress-nano/microstructure modelling has been developed to describe the experimentally observed rheology and microstructure for both treated and untreated CNT suspensions. Treated CNTs have been successfully modelled as short and rigid fibres that can align in the flow, but there are also randomising events due to Brownian rotary diffusion and tube-tube interactions. In the case of untreated CNTs, CNT orientation consideration alone are inadequate in explaining the experimentally observed shear thinning and a new model taking into account both elements of CNT orientation and aggregation kinetics has been formulated to describe the experimental data.

In terms of microstructure, direct visualisation of individual treated CNTs in a uniformly dispersed suspension is difficult and normally requires thermal/photo-curing or cryogenic treatments before techniques such as AFM, SEM and TEM can be applied. However, in the case of aggregating CNT suspensions, a number of unexpected microstructure patterning was observed by applying steady shear to the CNT suspensions [3]. Aggregate alignment in both vorticity and flow directions have been observed and the alignment strongly depends on the flow conditions and the types of CNTs used. Finally, a photo-curing protocol has been developed to preserve the shear-induced structures, thereby allowing for further nanostructure analysis and conductivity measurements.

[1] Rahatekar et al., J. Rheol. **50**, 599-610 (2006); [2] Ma et al., Rheol. Acta, in press; [3] Ma et al., Rheol. Acta **46** 979-987 (2007).

Friday 10:45 Portola SC82

Rheology and phase behavior of single-walled carbon nanotubes in acid

Micah J. Green[1], Nicholas G. Parra-Vasquez[1], Natnael Behabtu[1], Virginia A. Davis[2], and Matteo Pasquali[1]

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Individual single-walled carbon nanotubes (SWNTs) display remarkable electrical, thermal, and mechanical properties. However, the production of neat, high-performance SWNT-based materials has been hindered by the difficulty of dispersing SWNTs in the liquid phase; attractive van der Waals forces cause SWNTs to bundle together rather than dispersing. We show that SWNTs can be dispersed and processed at high concentrations in strong acids because the acids protonate their sidewalls, induce repulsion, and balance the attractive forces. The ability to control and predict SWNT-acid rheology and phase behavior is critical to the processing of these SWNT-acid solutions into structured articles such as fibers and films. To this end, experimental rheological techniques are developed to quantify solution properties (such as the quality of dispersion) as a function of acid strength, SWNT concentration, and SWNT length distribution. Also, extensions of the Onsager theory for polydisperse rigid rods are developed to account for variations in acid strength and attractive rod-rod forces; these models are applied to the isotropic/liquid-crystalline phase behavior of SWNT-acid solutions.

Friday 11:05 Portola SC83

Rheological behavior of polyamide-6 based nanocomposites: Experimental study and modeling

Maryam Sepehr, Kalonji K. Kabanemi, and Jean-François Hétu

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Rheological behavior of polyamide-6 based nanocomposites (PNC) with 2-wt% organoclay was studied in a simple shear transient flow, using a rate-controlled rheometer. During the stress growth experiments (in forward or reversed flow direction), the viscosity and normal stress differences have shown stress overshoot. Changing the PNC compounding parameters resulted in different degrees of clay dispersion in samples having the same composition, what in turn resulted in different transient behavior. A commercial PA-PNC prepared by in-situ polymerization, with high degree of exfoliation and strong polymer-clay interactions, was also used as reference. The experimental data were compared with the modified Giesekus model used to study the effect of polymer-particle interactions on rheological properties. The model includes two parameters characterizing the effect of the existence and orientation of nanoparticles on the hydrodynamic drag acting on the polymer molecules. This behavior is modeled by using an affinity-dependent friction coefficient in classical models of polymer dynamics. The Advani-Tucker equation of change for the second-order orientation tensor of the disc-shaped particle was used to describe the dynamics of particle orientation. The role of interaction parameters on the viscoelastic behavior was critically studied to obtain a deeper understanding of their contributions. The effect of the matrix nature (Newtonian and viscoelastic) was also numerically investigated. Comparison of the experimental data with the model predictions showed good agreement of transient behavior of PNC with different degrees of clay dispersion and polymer-clay interactions.

CF-10. Computational and Multiscale Modeling 4

Organizers: Antony N. Beris and Jan K. Dhont
Session Chair: James J. Feng

Friday 9:45 Steinbeck CF67

Operator-splitting schemes for the flows of compressible viscoplastic fluids

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After reviewing the existing operator-splitting schemes for incompressible Bingham fluids, a new scheme is proposed for compressible Bingham fluids. As a benchmark problem, the isothermal cavity flow of the compressible fluid is solved by finite element methods and the velocity profiles are compared with those in the incompressible material. Both linear and exponential variations of the density with respect to the pressure are considered.

Friday 10:05 Steinbeck CF68

A 1.5D numerical model for weakly compressible viscoplastic and thixotropic flows: Application to the start-up of waxy crude oils in pipeline

Guillaume Vinay and Anthony Wachs

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In this paper, we examine the numerical simulation of a weakly compressible viscoplastic and thixotropic fluid in an axisymmetric pipe geometry using a new 1.5D lubrication-like numerical model which is a compromise between a fully 1D and a fully 2D scheme. Indeed, pressure is assumed to be constant in a section and only the axial velocity component is non-zero and can vary both in axial and radial directions. The industrial situation refers to the start-up of gelled waxy crude oil flows in pipeline, modelled by a thixotropic and viscoplasctic Houska model.

Actually, the main difficulty concerning the restart of waxy crude oils relies on the estimation of the minimum pressure required at the pipe inlet. In a previous paper (Vinay et al. JNNFM (136), 2006), we have pointed out that compressibility leads to strong pressure drop at the upstream part of the pipe and provides high strain rates at the first stages of the restart. So since the breakdown gel mechanism of the Houska model is governed by shear rate, we believe that a thixotropic and viscoplastic fluid, which usually can not restart in incompressible situations, should restart thanks to the combined effects of compressibility and gel breakdown mechanism. We show that this intermediate model yields accurate results which are consistent with the predictions of the fully 2D model. At the practical level, we evidence that the flow is able to restart for a pressure drop D_p below the value predicted by the conservative relation $D_p = 4\ \tau_y\ L / D$ where τ_y is the yield stress, L the pipe length and D the pipe diameter.

Friday 10:25 Steinbeck CF69

A constitutive model for flow-induced anisotropic behavior of viscoelastic complex fluids

Huaning Zhu and Daniel De Kee
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Flow-induced structural anisotropy could result when a complex fluid system is removed from equilibrium by means of hydrodynamic forces. Such flow-induced structural changes may often dominate the rheological behavior of complex systems. A flow-induced rheological response cannot be explained by a homogeneous structural orientation alone. We will report on a kinetic theory to model flow induced anisotropic behavior of complex viscoelastic systems. The model we developed is a continuum model, which incorporates the microstructure information of the complex fluid system. The rheological properties are characterized by viscosity and relaxation time tensors. We consider a second order tensor as a measure of the microstructure. We also consider the effect of the flow on the structural changes: i.e. the evolution of the microstructure tensor is governed by a relaxation-type differential equation. In addition, the viscosity and the relaxation time tensors depend on the second order microstructure tensor, i.e. as the microstructure tensor changes with the applied rate of deformation, the viscosity and relaxation time tensors evolve accordingly. We consider the elongational flows of two complex fluids as examples to validate the proposed model.

Friday 10:45 Steinbeck CF70

Diffusion of colloidal spheres in rod-networks: Hydrodynamic screening and electrostatic interactions

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Diffusion of tracer spheres in a hindering environment consisting of a (isotropic and nematic) network of very long and thin colloidal rods is discussed. When the tracer sphere is large compared to the mesh size of the network, the network structure will be distorted during diffusion of the sphere. When the tracer sphere is smaller than the mesh size, however, the rod network structure is essentially not distorted. In this case the diffusive properties of the sphere are determined by hydrodynamic interactions with the rod network as well the distortion of the sphere-rod pair-correlation function (which we shall refer to as the ‘shadowing effect’). Hydrodynamic interactions are screened as a result of strong entanglement of the rods. We propose a theory, where the long-time self diffusion coefficient is expressed in terms of the hydrodynamic screening length of the network. There is as yet no independent theory for the screening length of rod networks. Dynamic Light Scattering and Fluorescence Correlation Spectroscopy data will be presented for the long-time self diffusion coefficient of apoferritin (a spherical protein) in isotropic and nematic networks of fd-virus (very long and thin, stiff rods), as a function of the rod concentration. The relative contribution of hydrodynamic interaction as compared to the shadowing effect is varied by changing the ionic strength. The above mentioned theory allow to extract the hydrodynamic screening length from the experimental diffusion data. In this way the rod-concentration dependence of the hydrodynamic screening length is determined. The screening length decreases with increasing rod concentration in the isotropic state, but increases in the nematic rod networks. This is attributed to the increase of nematic order with increasing rod concentration.

Friday 11:05 Steinbeck CF71

Colloidal asphaltene deposition and aggregation in capillary flow: Experiments and mesoscopic simulation

Edo S. Boek[1], Hemant K. Ladva[1], Johannes T. Padding[2], and John P. Crawshaw[1]
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The deposition of colloidal asphaltene in reservoir rock is a significant problem in the oil industry. Therefore we have studied the deposition of asphaltene in capillary flow by experiment and simulation. We have used the Stochastic Rotation Dynamics (SRD) simulation method [1], which provides both hydrodynamics and Brownian motion. The asphaltene colloids interact through a screened Coulomb potential with varying well depth E. We tune the flow rate to obtain Pe_flow >> 1 (hydrodynamic interactions dominate) and Re << 1 (Stokes flow). Imposing a constant pressure drop over the capillary length, we observe that the transient solvent flow rate decreases with increasing well depth E. For E = 2 kT, a monolayer deposits on the capillary wall. With increasing well depth, the capillary becomes totally blocked. The clogging is transient for E = 5 kT, but appears to be permanent for E = 10 - 20 kT. We compare our simulation results with flow experiments in glass capillaries. The deposition was monitored in a slot capillary [2] using optical microscopy. Maintaining a constant flow rate, we found that the pressure drop across the capillary first increased slowly, followed by a sharp increase corresponding to a complete local blockage. We calculate the change in the dimensionless conductivity as a function of time for both experiment and simulation. By matching the experimental and simulation results, we obtain information about the interaction potential well and flow conditions associated with the asphaltene deposition process.

[1] J.T. Padding and A.A. Louis, Phys. Rev. Lett. 93, 220601 (2004); [2] D. Broseta, M. Robin, T. Savidis, C. Fejean, M. Durandeau and H. Zhou, SPE 59294 (2000).

GA-3. Advances in Simulation Techniques

Organizers: V Kumaran and Melany Hunt
Session Chair: Christine Hrenya

Friday 9:45 Bonsai III GA16

A dissipative Coulomb model for dense granular flows

Riccardo Artoni, Andrea C. Santomaso, and Paolo Canu
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We address the slow, dense flow of granular materials as a continuum with the incompressible Navier-Stokes equations plus the fluctuating energy balance including granular temperature. The pseudo-fluid is given an apparent viscosity which depends on an order parameter which we choose to be granular temperature. We derive the fluctuating energy balance following Babic (M. Babic, Average balance equations for granular materials. Int. J. Eng. Sci. 35 (1997), pp. 523-548); this balance includes a 'mobility enhancing' term due to ‘viscous heating’ effects and a dissipative term which we assume, as a constitutive hypothesis, dependent on the isotropic part of the stress tensor and on shear rate, based on local friction considerations. From a chemical point of view, the absolute rate of the process is governed by shear rate as a kinetic constant, while the 'activity' of the process is given by the distance from Mohr-Coulomb yield stress. For its particular structure the model is called Dissipative Coulomb Model. Solving the equation system we get an appreciable agreement with experiments in standard geometries (simple shear, vertical chute), and more complex ones (silos, hoppers). The model predicts also the typical behaviour of stresses in these configurations, thus predicting phenomena like the hourglass effect. The model is being validated on all these types of flow.

Friday 10:05 Bonsai III GA17

Direct numerical simulation of polygonal particles sedimentation with collisions

Anthony Wachs[1], Rajendra Chhabra[2], and Calin Dan[1]
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A detailed understanding of solid/solid and fluid/solid interactions in moderately to highly concentrated particulate flows is of great interest from both fundamental and practical points of view. As inertia of particles and/or fluid cannot always be neglected in such flows, a common situation in many industrial and scientific applications, the probability of collisions between particles increases dramatically. To accurately model this type of flows, we present here a new Fictitious Domain method where the multi-body collisions are handled by an efficient Discrete Element Method (DEM) solver. An obvious advantage of our DEM solver, beyond other methods available in the current literature to treat collisions, is its ability to consider particles of polygonal shape (and even any other convex shape). New results, which, to the best of our knowledge have never been reported elsewhere, in terms of 2D sedimentation of particles of isometric polygonal shape in Newtonian and non-Newtonian power law fluids are presented. We compare qualitatively the mean settling velocity as a function of the solid concentration to a Richardson-Zaki type correlation. Our Direct Numerical Simulation (DNS) tool exhibits very promising capabilities for the survey of a wide range of particulate and suspension flow problems and, for the first time in DNS of complex flows with solid particles, enables one to investigate the effect of particle shape.

Friday 10:25 Bonsai III GA18

Shear flow of sphere packings in the geometric limit

Pierre-Emmanuel Peyneau and Jean-Noël Roux
Laboratoire des Matériaux et Structures du Génie Civil, Université Paris-Est, Champs-sur-Marne 77420, France

Homogeneously sheared packings of stiff frictionless equal-sized beads are studied in the quasi-static limit, i.e. the limit of vanishing inertial number I, by numerical simulation. Steady state rate-controlled shear simulations, where the number I can be tuned at will, have been used to simulate steady flows, whereas static approaches, in which packings are equilibrated under growing deviator stresses, have been employed to assess the vanishing I limit. No enduring shear localization is observed. Thanks to an accurate time series analysis tool (the so-called blocking method), we thoroughly investigate the dilatancy properties and the macroscopic friction of the model material. Both the friction coefficient and the volume fraction exhibit a power law increase as a function of I in the $I \ll 1$ range. In the quasi-static limit, we find that the material is devoid of dilatancy and that the macroscopic friction angle is 5.65 ± 0.22 degrees. Results obtained for steady state shear flows in the limit of vanishing strain rates are in good quantitative agreement with those collected through static simulations in the thermodynamic limit. Dissipation at the macroscopic level results from repeated network rearrangements entailing stress fluctuations. We show that the amplitude of fluctuations measured in steady shear flow simulations decreases with an increase in the number of particles. A strong connection between these temporal fluctuations and the variability in the results produced by static simulations is evidenced. Within both the limit of rigid particles and the quasi-static limit, a detailed parametric study shows that the macroscopic constitutive law is determined by the sole geometry of the packing which adapts its microstructure to the shear flow. The material state is characterized by the random close packing density, and isostatic, anisotropic contact networks which continuously break and reform. The nonvanishing macroscopic friction angle originates in stress-induced fabric anisotropy. Other microstructural quantities are also investigated.

Additionally, we compare this set of results with outcomes of numerical experiments on perfectly lubricated dense suspensions. Given a configuration, the velocity vector is derived from the balance between conservative (elasticity), dissipative (hydrodynamic resistance and friction) and externally applied forces. The method we have used to calculate the hydrodynamic interactions only keeps the lubrication forces between neighboring particles. To avoid unphysical divergences of lubrication forces, one limits the lubrication force intensity by introducing a cut-off. Results obtained through this method are compared with the aforementioned ones.

Friday 10:45 Bonsai III GA19

Flow and blockage of concentrated granular suspensions

Abdelhak Kaci[1], Guillaume Racineux[2], and Mohend Chaouche[3]
[1]LMT, ENS-Cachan, Cachan, France; [2]Institut de Recherche en Génie-Civil et Mécanique, Ecole Centrale de Nantes, Nantes, France; [3]LMT, CNRS, Cachan, France

Modeling the flow behavior of highly concentrated granular suspensions represents a great challenge since they are characterized by a rather complex rheological behavior. Moreover macroscopic heterogeneities may be induced by the flow during rheological measurements due to the eventual relative motion between the liquid and the granular phases that may take place under certain conditions. Hence, in order to model the flow of such materials in the framework of continuum mechanics, one has to explicitly consider that it comprises at least two phases. In the present approach we consider that these phases are continuous and behave as power-law fluids. The coupling between the two media is accounted for using a generalized Darcy's filtration law. The model is solved using the Finite Element Method in the case of squeeze flow geometry. Our numerical simulations are in qualitative agreement with the experimental results obtained with granular suspensions in xanthan solutions. In particular a transition from a homogeneous flow of the suspension to a situation in which we have significant relative liquid-solid motion and ultimately blockage is obtained. The influence of the rheological properties of the liquid phase on this transition is investigated both numerically and experimentally.

EM-7. Squeeze Flow Rheometry

Organizers: Gareth H. McKinley and Malcolm R. Mackley
Session Chair: David C. Venerus

Friday 9:45 De Anza I EM43

Linear viscoelasticity on short timescales: Real-frequency mechanical spectroscopy up to kHz range

Torsten Remmler[1], Richard Tweedie[2], and Wolfgang Pechhold[3]
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The rheological behaviour of viscoelastic fluids, polymer melts and other soft materials is characterized using mainly motor-drive controlled rheometers, either at constant stress or strain rate, or in the oscillatory mode. The latter has proved advantageous in analyzing the viscoelastic functions G^*, η^*, J^* as fingerprints of the material under investigation, its composition, molecular modelling and applicability. A conclusive analysis of such viscoelastic spectra can only be achieved if the amplitudes chosen guarantee linearity and if the frequency range covers more than 6 decades in order to reach the low kHz-domain. Investigations of many materials with motor-drive controlled rheometers are limited at higher frequencies and only reach the above mentioned goal by applying the time-temperature superposition principle, i.e. the mastercurve technique. Since this method is restricted to rheologically simple materials (e.g. some polymer melts), but exclude those of small activation energies and others with temperature-sensitive chemical/physical structures including phase transitions, oscillatory rheometry should be extended into higher real-frequency ranges, to establish useful linear viscoelastic spectroscopy. This goal has been achieved by adapting a new high-frequency option into a commercially available rheometer. The available continuous frequency range with integrated high frequency option covers now approximately 8 – 9 decades. In this presentation, the advantages and limits of classical oscillatory rheometry will be covered, the handling and principle of operation of the high frequency option are introduced and typical examples for real frequency spectra on soft matter, such as weak gels, polymer solutions and suspensions will be shown.

Friday 10:05 De Anza I EM44

A continuous lubricated squeezing flow technique to study the rheological behavior of polymer melts in equibiaxial elongational flow

David C. Venerus, Teresita Guadarrama-Medina, and Tai-Yi Shiu
Chemical and Biological Engineering Dept, Illinois Institute of Technology, Chicago, IL 60616, USA

Despite its technological significance, the rheological behavior of polymer melts in equibiaxial elongational flow is largely unexplored and, consequently, is inadequately understood. The simple reason for this is that methods for generating equibiaxial elongational deformations are either very complicated or not reliable. The most widely accepted method for generating rheologically controlled, equibiaxial elongational flow is the rotating clamp method, or MultiAxiale Dehnung (MAD), developed by Meissner. However, the extremely complicated nature of the MAD rheometer has resulted in a relatively limited set of experimental data. A promising method that has been used with some success is known as Lubricated Squeezing Flow (LSF), where a polymer melt is squeezed between lubricated surfaces. Unfortunately, uncontrolled lubricant thinning limits the LSF technique to rather modest strain levels. Here we report the first direct comparisons of data obtained with the LSF and MAD techniques. We find that the data obtained using LSF deviate from the MAD data at Hencky strains of less than one, and display behavior that could easily be mistaken for strain hardening. For the past few years, we have been developing a modified LSF technique that involves the continuous injection of lubricant through porous metal plates. We report the first measurements of transient equibiaxial elongational viscosity obtained using the modified LSF technique and make comparisons with data from the MAD rheometer.

Friday 10:25 De Anza I EM45

Novel instrument for parallel superposition measurements

Sandro Dinser, Klaus Hausler, and Jurg Dual
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Many fluids consisting of multiple phases change their structure when subjected to shear. One of their phases might disaggregate, orient itself, be sheared or stretched, which influences the viscosity or elasticity of the material. This change of structure can be observed with an oscillating resonator described below since the oscillation has a tiny shearing amplitude (about 1 micron at the surface) thereby not affecting the structure. The presented superposition rheometry setup is a combination of a rotational rheometer with a resonator such that a parallel superposition of shear results. In a cone and plate or plate-plate geometry, the resting plate is exchanged here with a mechanical resonator performing rotational oscillations. This resonator is the core of a highly sensitive method which measures the viscosity and elasticity of a fluid at one or several of the resonator's eigenfrequencies. By bringing the resonator into contact with a fluid, such that the former induces a sinusoidal shear in the fluid, an increase of damping and mass loading occurs. Observing the damping and the resonant frequency with a phase locked loop allows the determination of the mechanical behaviour of the fluid. The resonant frequencies are given by the design of the resonator and can be set to any frequency between 50 and 1000 Hz. The presented resonator operates at 339 Hz. A mechanical model of the resonator consisting of impedances has been derived. Therewith, fluids with low viscosities such that the shear wave decays within the gap can be measured as well as highly viscous fluids, where a shearing takes plate throughout the gap. The sensitivity of the presented resonator allows the measurement of fluids with viscosities between 0.1 mPa·s and 1 Pa·s. Complex viscosity measurements of PIB in decalin at different shear rates are presented. This solution shows a highly shear rate dependent behaviour. Its effect on the parallel superposition modulus G is shown with the help of this new instrument.

Friday 10:45 De Anza I EM46

Investigation and removal of gap dependence in squeeze film rheometry: A broadband spectral approach

Harry Esmonde
Mechanical Engineering, Dublin City University, Dublin, Ireland

Broadband random squeezing of fluid samples may be used to determine their constitutive properties. Results from this type of analysis in the past have been gap dependent and hence rather unreliable. The cause of the variability arises due to system compliance and lack of parallelism between the plates. Using non-linear spectral techniques and modified geometry a more robust methodology is developed which provides reliable estimates of material properties. Beginning with the appropriate analytical equations a non-linear input/output relationship between plate motion and plate force is determined for the modified squeeze film rheometer. Experimental data is then analysed in the frequency domain taking account of the non-linear relationship so that accurate predictions of viscosity are obtained that are independent of film thickness.

Friday 11:05 De Anza I 💿 EM47

Characterisation of large deformation behaviour of starch gels using compression and indentation techniques

Chaiwut Gamonpilas[1], Maria Charalambides[1], Gordon J. Williams[1], Paul J. Dooling[2], and Simon R. Gibbon[1]
[1]Mechanical Engineering, Imperial College London, London SW7 2AZ, UK; [2]Wilton Centre, ICI Applied Research, Wilton, UK

Two types of starch gel have been studied in terms of their mechanical behaviour. Firstly uniaxial compression tests have been performed at various strain rates and various starch/water weight ratio. It was ensured that the effect of friction between the platen and the specimen was eliminated by using silicon oil as a lubricant and by testing cylindrical samples of various height/diameter ratios. The stress-strain curves were highly non-linear and were fitted to the Ogden rubber elastic models with two material parameters, namely the initial shear modulus (μ) and the Ogden constant (α). Even though the behaviour at small strains was rate independent for both gels, the stress and strain at failure increased considerably with strain rate. An alternative method to characterise the gels was investigated based on the indentation technique. A spherical probe of 6 mm diameter was used to indent the cylindrical samples at various strain rates. Similar to the compression tests, the response was found to be rate independent. An inverse analysis based on the Marquardt-Levenberg optimisation algorithm was used to predict the stress-strain response from the indentation tests. To enable this procedure, numerical simulations of the indentation using the Finite Element technique were performed. A database of indentation load-deflection was thus created as a function of the two material parameters. The optimisation relies on determining the set of material parameters which leads to a minimum error between the numerical and the actual indentation response. It was found that the predictions closely matched the direct measurements from the compression tests. The method was used on rigid gels as well as on non self supporting gels, ie those that were made with very low starch content. This indentation characterisation method can be used as a fast way of evaluating and/or monitoring the gels' behaviour.

Friday 11:25 De Anza I 💿 EM48

Characterization theory and technique for polymer melt under the superimposed vibration

Yue-jun Liu, Xiang-gang Li, and Yu-gang Huang
Key Laboratory Of New Material And Technology For Package, Hunan University Of Technology, Zhuzhou, Hunan Province 412008, China

The introduction of a vibration force field has a profound influence on the polymer formation process. However, its mechanism has not been explored clearly until now. By introducing a vibrating force field into the extrusion process of polymer melt, an experimental equipment of constant velocity type dynamic rheometer of capillary (CVDRC) was designed with which we were able to analyze in detail the whole extrusion process of a polymer melt. A set of experimental procedures was established, by which the dynamic rheological parameters of polymer can be acquired, and a set of dynamic rheological data processing methods was set up. Meantime, the characterization formula of polymer melt's rheological behavior in a vibrating force field was set up. The instantaneous value of capillary entry pressure, capillary volume flow rate and their phase difference were measured and analyzed, and the melt apparent viscosity and the first normal stress difference, which describes the viscosity and elasticity behavior of polymer melt in a vibrating force field , was obtained.

PL-2. Closing Plenary Lecture

Organizers: L. Gary Leal and Ralph H. Colby
Session Chair: Ralph H. Colby

Friday 12:00 Serra I PL2

Non-equilibrium mechanics of active gels and living cells

Fred MacKintosh
Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands

Much like the bones in our bodies, the *cytoskeleton* consisting of filamentous proteins largely determines the mechanical response and stability of cells. Such important cellular processes as locomotion, cell division, and mechanosensing are largely governed by complex networks of cytoskeletal biopolymers and associated proteins that cross-link these and/or generate forces within the network. In addition to their important role in cell mechanics, cytoskeletal biopolymers have also provided new insights and challenges for polymer physics and rheology. Biopolymer networks, for instance, exhibit strongly nonlinear rheology-in many cases stiffening by more than a factor of 100 when subject to shear strains of less than unity. In the cell, these polymer networks or gels are far from equilibrium in a way unique to biology: they are subject to *active* internal force generation by molecular motors. We describe recent theoretical and experimental results on active in vitro networks that demonstrate significant stiffening and non-equilibrium fluctuations due to motor activity [1,2]. We also show how fluctuations and dynamics of individual cytoskeletal filaments can be used to probe both mechanical properties and non-equilibrium activity in living cells [3].

[1] D Mizuno, C Tardin, CF Schmidt, FC MacKintosh, *Science*, **315**:370 (2007); [2] FC MacKintosh and AJ Levine, *Physical Review Letters*, in press; [3] CP Brangwynne, FC MacKintosh, DA Weitz, *PNAS*, **104**:16128 (2007).

Poster Session

Organizers: Jai A. Pathak and Nina C. Shapley
Tuesday, 5 August 2008   6:00 pm – 9:00 pm   *Serra I*
Reception   7:00 pm – 9:30 pm   *De Anza I*

Materials Processing

Characterising microstructured materials using a capillary rheometer PO1

Christopher I. Hicks, Emad Y. Arabo, and Howard See
School of Chemical and Biomolecular Engineering, University of Sydney, Sydney, Australia

The viscosities of a range of microstructured fluids were measured using a capillary rheometer, as a function of shear rate. Results were compared with those obtained using a torsional rheometer. With bread dough made from an Australian hard flour, it was found that the viscosity could be reliably measured using the capillary system up to a share rate of approximately $250\ s^{-1}$. Above this shear rate, the effects of stick-slip wall interactions become apparent. In addition, similar experiments have been carried out on microstructured polymeric materials, such as polypropylene undergoing crystallization.

Sensitivity analysis of two-dimensional viscoelastic film casting process PO2

Seung Won Choi[1], Dong Myeong Shin[1], Joo Sung Lee[2], Hyun Wook Jung[1], and Jae Chun Hyun[1]
[1]Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea; [2]IT & EM R&D, LG Chem, Daejeon 305-380, Republic of Korea

Frequency response method has been developed in this study to investigate the sensitivity of film casting process with respect to sinusoidal ongoing disturbances. Amplitudes of film thickness and cross-sectional area at take-up position to any sinusoidal disturbance have been obtained in two-dimensional film casting process, showing the resonant peaks along the frequency regime, where the frequencies at these points are closely related to the imaginary parts of the successive leading eigenvalues from the linear stability analysis. Effects of the process conditions - e.g., fluid viscoelasticity, aspect ratio, cooling, drawdown ratio, etc. - on the sensitivity as well as the stability in this system have been examined. Especially, the dichotomous behavior between extensional thickening and extensional thinning fluids has been elucidated by this analysis.

Stability of multilayer film blowing process PO3

Dong Myeong Shin[1], Seung Won Choi[1], Joo Sung Lee[2], Hyun Wook Jung[1], and Jae Chun Hyun[1]
[1]Department of Chemical and Biological Engineering, Korea University, Seoul 136-713, Republic of Korea; [2]IT & EM R&D, LG Chem, Daejeon 305-380, Republic of Korea

Multilayer films have good barrier properties. Due to this advantage multilayer films are widely used for packaging applications. Most of research results focus on the barrier properties not on the productivity or processibility, namely stabiliy and sensitivity. In this study, The stability analysis of a two-layer film blowing process has been conducted using a simple model in which the two layers consist of a Newtonian and a Phan-Thien Tanner fluid, respectively. These two fluids are chosen to investigate the relative influence of viscous and viscoelastic forces on the stability of the two-layer biaxial extension flow of the process. Using transient solutions of simulation model the effect of material properties and process conditions such as viscosity ratio, fluid viscoelasticity, flow rate ratio, draw ratio, and etc. will be presented.

Friction factors for flow of drag reducing solutions of micellar surfactant additives in straight circular pipes and conventional globe valves PO4

Martin Dostal[1], Jiri Sestak[1], and Vaclav Mik[2]
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Experiments were carried out in order to investigate pressure drops due to friction and form for flow of water with micellar drag reducing additives Arquad S-50, CTAB and CTAC which were prepared in various different concentrations. The rheological behavior of these solutions was studied on a Thermo-Haake coaxial cylinder rheometer Rheostress 600. Standard experimental data evaluation in the form of flow curves disclosed a pattern in which, in the low shear rate range, a nonlinear shear stress decrease with increasing shear rates was observed. For still higher shear rates, shear stress values approached asymptotically constant, shear-independent, values. Therefore, in the low shear rate region, experimental data were described with sufficient accuracy by means of the simple power-law model.

A closed-loop experimental stand consisted of a 2700 mm long stabilization section followed either by a 3000 mm long straight, stainless circular tube (15, 20, and 25 mm I.D.) or with a conventional globe valve.

Results are presented in the form $f=c.\mathrm{Re}_g^{-m}$, f being the conventional Fanning friction factor, Re_g the generalized Metzner-Reed Reynolds number, c a parameter depending primarily on geometry of the fitting interior and m a parameter depending on the slope of the f, Re_g relation in a double-logarithmic plot. In the laminar flow region, the exponent m was found to be 1 for flow in the pipes, whereas for the globe valve, it attained values lower than 1, indicating a possible influence of inertial forces. Also, it is worth to note that the pressure loss reduction in the lower shear-rate range in pipes occurs due to the pseudoplastic behavior of the solutions rather than due to the drag-reduction mechanism in the proper (Toms) sense of the word.

Effect of organoclay dispersion on the barrier properties of polypropylene/organoclay nanocomposites in film blowing process

PO6

Hyung Tag Lim, Kyung H. Ahn, and Seung J. Lee
School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea

Polypropylene(PP)/organomontmorillonite(OMMT) nanocomposites are attractive candidates for applications requiring good barrier properties because the high length-to thickness ratio of the individual platelets could lead to a dramatic decrease of the gas path length and gas permeation, resulting from direct passage blocking of the gas. To maximize the gas barrier properties of PP/OMMT, the clay should be exfoliated and orientated to the perpendicular direction of the gas flow. In this study, we investigate the effect of clay dispersion and orientation on the gas permeability of PP/OMMT nanocomposites in the film blowing process. The clay dispersed by the compatibilizer like maleic-anhydride- grafted polypropylene(PP-g-MA) as well as inomer like Surlyn® , and the degree of clay orientation are controlled by extension under the film blowing process. We control the morphology (clay dispersion and localization), the degree of orientation of the clays to the perpendicular direction of the flow. The effect of clay orientational direction on the rheological and mechanical properties of the nanocomposites will also be discussed.

Composites of polystyrene/wood fiber: Processing effect to creep resistance

PO7

Lorena Romero[1], Mónica E. Mendoza[1], Abel Gaspar[2], Sergio G. Flores[1], and Rigoberto Ibarra[1]
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In the present work the interaction PS/wood fiber in composites of fibers compatibilized with silane and non-compatibilized was studied in relation to their creep response by means of a dynamic mechanical analyzer (DMA).Two variables were evaluated, wood fiber content, and the process of elaboration of the composites: compression, extrusion and injection molding. A series of weight ratios PS/ wood fiber were prepared, 90/10, 80/20, 70/30 and 60/40. For the compatibilized series, silane in 1% wt in relation to the polystyrene weight was added. The creep tests were performed inside and outside the lineal viscoelastic region at 80 ºC. It was observed that the compatibilized samples obtained by injection molding showed a higher creep resistance than their counterparts. The previous signifies that the compatibilization system is efficient in conditions of prolonged stresses which improve the material dimensional stability. This behavior suggests that the high orientation of the fibers generated by the injection molding process, in relation to the extrusion and compression molding, promotes a higher superficial area of treated fiber to be in contact with the PS matrix, which enhances the adhesion and in consequence the resistance to creep.

Some unusual rheological responses of poly(vinylidene fluoride-co-hexafluoropropylene) solutions in dimethyl acetamide and their effects on the electrospinning process

PO8

Jae Sik Seo, Ki Hyun Lee, and Byoung Chul Kim
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The electrospun fluoropolymer webs have desirable physicochemical properties as medical and electronic materials. The rheological properties of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) in dimethyl acetamide (DMAc) were investigated to obtain preliminary data for electrospun webs. In the extremely dilute solutions, the intrinsic viscosity was decreased while its Huggins constant was increased with increasing temperature. In the concentrated regime, however, the dynamic viscosity of the solutions was increased and Bingham behavior got more dominant as temperature was increased at a given concentration over the temperature range of 30 to 70 oC. Increase of temperature and concentration of the solutions increased yield stress and relaxation time but reduced loss tangent. In spite of the increase in dynamic viscosity with temperature, the diameters of electrospun fibers were not affected by temperature and remained almost constant if other spinning conditions were identical.

Uniaxial extensional flow and rheological behaviour under large amplitude oscillatory shear as tools to understand and predict the development of melt flow instabilities during extrusion

PO9

Susana Filipe, Ernst Uttenthaler, Bernhard Knogler, Katrin Hofstadler, and Jens Reussner
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Relevant knowledge was gathered in what regards the influence of molecular structure and topology on the onset and amplitude of instabilities developed during extrusion. Apart some exceptions, the majority of the investigations were done in order to find rheological parameters under small amplitude oscillatory shear that could be sensitive towards changes in molecular character and thus, relevant indicators of higher, moderate or no tendency for the development of surface defects [1-4]. In a recent work, an experimental correlation was found between the non-linear behaviour under Large Amplitude Oscillatory Shear (LAOS) flow and the development of melt flow instabilities during capillary extrusion[5]. The dominance of extensional flows and the undeniable non-linear character involved during industrial processes, justifies a more in deep analysis of the rheological behaviour under uniaxial extensional flow and large amplitude oscillatory shear. It is crucial to understand the role of each type of flow on the type and magnitude of shark-skin, stick-slip and other defects typically developed in extrusion processes.

[1] S.-Q. Wang, Adv. Polym. Sci. 1999, Vol. 138, 228; [2] H. Münstedt, M. Schmidt, E. Wassner, J. Rheol. 2000, Vol. 44, 413; [3] M.M. Denn, Annu. Rev. Fluid Mech. 2001, Vol. 33, 265; [4] J. Doelder, R. Koopmans, J. Rheol. 2005, Vol. 49, 113; [5] S. Filipe, I. Vittorias, M. Wilhelm, Macrom. Mat. Eng. 2008, Vol. 293, 57.

Relationship between neck-in and viscoelasticity in an extrusion lamination process

PO10

Seiji Shiromoto[1], Masaaki Tsutsubuchi[1], Yoshiaki Togawa[1], and Toshihisa Kajiwara[2]
[1]Plastics Technical Center, Sumitomo Chemical Co., Ltd., Sodegaura, Chiba 299-0295, Japan; [2]Department of Chemical Engineering, Kyushu university, Fukuoka, Fukuoka 812-8581, Japan

In this study, experiment of extrusion lamination process using high-pressure process LDPE was performed. The non-isothermal viscoelastic simulation of the experiment was also carried out. The simulation results were in good agreement with experimental data. Neck-in behavior was investigated by using simulation results of the LDPE and the model fluids with different viscoelasticity. As a result, it was confirmed that neck-in was controlled by the ratio of planar to uniaxial elongational viscosity rather than the strain hardening of uniaxial elongational viscosity.

Surface migration of highly-branched polymeric additives PO11

Zhenyu Qian, Venkatachala S. Minnikanti, and Lynden A. Archer
Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, USA

Linear response theory and lattice simulation were used to study the effect of architecture of polymer additives on their surface tensions. A lot of typical molecular architectures, such as star, comb and dendrimer had been theoretically investigated and symmetric star architecture was proved to be the best candidate for surface migration. Two series of symmetric star polystyrenes with different molecular weight, which are 4-arm and 11-arm stars were then anionically synthesized to provide experimental evidences for architectural effect. Surface tensions were measured as a function of temperature in the melt and also as a function of molecular weight using a modified Wilhelmy plate technique. We find that through architectural changes alone it is possible to dramatically lower the surface tension of a molten polymer relative to a comparable molecular weight linear polymer. Later these symmetric star polystyrenes were mixed as model additives with their linear counterparts, and the surface tension of the star/linear blend system were measured. We found that the star branched polymer tends to segregate at the surface, acting as a surface active additive, and the surface tension of the blends drops a lot from that of the linear component at low star weight concentration. Finally, other than quiescent migration, the introduction of shear field dramatically accelerated and enlarged the surface migration of additives. This provides an opportunity for flow-induced migration to be achievable in polymer processing step.

Relevant aspects in modeling of micro-injection molding 💿 PO12

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Growing demands in the manufacturing of micro and precision components in plastics require new concepts for molding machines and micro molds on the one hand. On the other hand, a deeper understanding of the filling and solidification process in a micro mold is indispensable. In the framework of a research project granted by the German Research Foundation (DFG), the filling process of a micro spiral was analysed by modeling the compressible flow using pressure dependent viscosity and adjusted heat transfer coefficients. At the same time, experimental filling studies were carried out on an accurately controlled micro-injection molding machine. Based on the relationship between the injection pressure and the filling degree, essential factors for the quality of the simulation can be identified. It can be shown that the flow behaviour of the melt in a micro cavity of high aspect ratio is extremely dependent on the melt compressibility in the injection cylinder which needs to be considered in the simulation in order to predict an accurate flow rate. Moreover, the heat transfer coefficients between the melt and the mold wall vary significantly when changing cavity thickness and processing conditions. It is believed that a pressure dependent model for the heat transfer coefficient would be able to improve the quality of the process simulation.

Dynamic characteristics of plug-assist thermoforming process PO13

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Plug-assist thermoforming is a well known technique in polymer processing due to its interesting features. The dynamic value of driving-force for the stretching process is determined based on equilibrium equation. This amount of force is required for applying to a plug in order to stretch a sheet. It is used for calculation of the required theoretical work, and power of a plug-assist thermoforming process.

Pressure/flow performance of viscoelastic polymeric melts in cylindrical channels PO14

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One of the most widespread practical methods of polymer processing is the extrusion method that is based on pressing a polymeric melt through channels of the molding tool which have dif-ferent geometrical cross-sections. The basic performance of extrusion is based on the pressure/flow performance which sets functional correlation between volumetric flow rate of a poly-mer medium, pressed through a molding tool, and created pressure drop. Arguments of this cor-relation are the rheological parameters of polymer and the geometrical characteristics of the channel in which the polymeric melt flows. In this paper a viscoelastic model with a corrected strain energy function is implemented. The comparison of revealed theoretical expression in this paper with the experimental data for flow of polymeric melts in cylindrical channels with various cross-sections demonstrates a good convergence over a wide range of pressure gradient.

Complex Flows

Viscoelastic flows in journal bearings PO16

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In this study, flows between eccentrically rotating cylinders are computed using the commercial software POLYFLOW. These flows are directly connected to journal bearing lubrication. The addition of polymers to Newtonian oils for industrial purposes has resulted in shear thinning and changes in elastic properties of the materials, thus leading to complex behavior in such eccentric rotating geometries. Viscoelastic fluid flow in the annulus of rotating eccentric cylinders as a model of a journal bearing with steadily rotating journal is simulated by the commercial software POLYFLOW. Finite element method is used for solving the model equations. Evolution methods and elastic viscous split stress (EVSS) 4*4 Streamline Upwinding interpolation scheme for stress are applied for viscoelastic fluids simulations. Comparisons between the simulation results and the analytical solutions and experimental results for Newtonian, Carreau and Phan-Thien-Tanner fluids are consistent. Rheological characterization of lubricants can be particularly important in designing effective lubricants that control the friction and wear in their tribological applications. Rheological experiments for a bio-lubricant using different additives are performed and the viscoelastic constitutive equations able to describe the lubricants behavior are determined. Flow start-up and steady state flow for different viscoelastic fluids as lubricants models are studied. The transient evolution of load capacity and torque on the inner cylinder are presented. Load capacity, torque and coefficient of friction as a function of Weissenberg number are presented. A conclusion on the effects of the lubricant viscoelasticity on the journal bearing performances is given.

Shear banding: Counter rotation to produce symmetric stratification PO17

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Recent particle tracking velocimetric observations revealed [1] that entangled liquids such as polybutadiene [2-4], DNA [5] and wormlike micellar [6] solutions yield like a solid both during startup shear and after large step strain. In most of cases, the shear inhomogeneity was asymmetric, with the high-shear band close to the moving surface in a simple-shear cell. In this work, we compare velocity profiles under various flow conditions between two cases: a) cone-plate with one surface rotating and b) cone-plate where counter rotation takes place. The restoration of symmetric profiles has profound implications about the nature of deformation and flow in entangled polymers.

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This work is supported, in part, by a SGER grant from NSF (DMR-0603951) and a standard NSF grant (DMR-0804726).

Analysis of the edge fracture for several polymer melts PO18

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In former studies the phenomenon and the kinetics of the edge fracture of polymeric materials was investigated for steady rotational shearing in rheometers. However, this phenomenon is observed for oscillatory rotational shearing, too. In these experiments one can notice a fracture of the sheared melt at supercritical deformation amplitude and supercritical frequency as well. We investigate this critical state experimentally as well as theoretically. To determine the boundary between stable and unstable flow we rely on an equation originating from Tanners and Keentoks work on edge fracture during steady rotational shearing. In addition, we make use of several empirical rules combining first and second normal stress difference as well as a relationship between first normal stress difference and dynamic moduli for polymer melts. We validate the applicability of the derived equation for PS, PE and PP melts of defined molecular architecture.

Viscoelastic fluid flow through 3D square-square expansions PO19

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In this work we present an experimental study of the 3D laminar flow of a Newtonian, a Boger and a shear-thinning fluid through square-square expansions with expansion ratios of 1:2.4, 1:4, 1:8 and 1:12. Detailed visualizations of the flow patterns were performed using streak line photography and the velocity field of the flow was measured in detail using Particle Image Velocimetry (PIV). The experimental results obtained with the Newtonian fluid are compared with numerical predictions. The numerical code used is based on a Finite-Volume method and an excellent agreement is found between experimental and numerical results. For all expansion ratios, a Moffatt corner vortex is observed downstream of the expansion and an increase in the inertia of the flow leads to an enhancement of the vortex size. On the other hand, also for all expansion ratios studied, the viscoelastic fluid flow also reveals the existence of a corner vortex downstream of the expansion, which decreases in size and strength when the Deborah number is increased. The vortices in square-square expansions exhibit a three-dimensional structure evidenced by a helical flow, which is well predicted by numerical simulation in the Newtonian fluid flow case.

Response of viscoelastic fluids under combined oscillatory squeezing and shear flow PO20

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We propose a novel method to determine the rheological responses of viscoelastic fluids under combined oscillatory squeezing and shear flow, and provided a comprehensive theory for the interpretation of experimental data. PDMS (Polydimethylsiloxane) and PB (Polybutene) were used to investigate the behavior of normal stress and torque signal under oscillatory shear, oscillatory squeezing flow, and combined flow of both oscillatory squeezing and shear. It is observed that PDMS undergoes a transition with the increase of strain (e0) amplitude as is evidenced by different types of stress patterns. This transition is caused by the dramatic change of microstructure. With increasing strain (e0) amplitude, the normal stress curves exhibit two interesting features: a forward shouldering of the force signal, and a non-symmetry with respect to the zero value. Here, it is interesting to consider Fourier transform tools, in order to evaluate the non-linearity in the kinetics and in the force signal. This work was undertaken to further establish the use of oscillatory squeeze and mixed flow for measuring the rheological properties of fluids. It is expected to contribute to the productivity enhancement as well as to understanding the physics of complex fluid flows.

Flow visualization and numerical simulation of viscoplastic fluid displacements in eccentric annuli PO21

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In completion of oil and gas wells, zonal isolation requires proper cement placement with adequate bonding to the casing and formation. To help achieve a successful cementing operation, the cement slurry must be properly designed to enable effective displacement of the drilling fluid from the annulus between the casing and wellbore. This is a complex process, involving time-dependent displacement of non-Newtonian fluids in eccentric annuli. The rheology, flow rate, and interfacial mixing of these fluids have direct impact on the displacement efficiency. Reliable computational modeling of the dynamics of the displacement process is critical to proper pre-job design and post-job analysis of the cementing operation. Furthermore, experimental data are also required to validate numerical predictions. This paper presents a flow visualization study using a helical flow device with adjustable annular eccentricity and rotation of the inner cylinder. Displacement experiments were conducted with a variety of non-Newtonian fluids to simulate the cement slurry - drilling mud displacement process. The results obtained demonstrate that the profile and evolution of the moving fluid-fluid interface are strongly influenced by fluid rheological properties, flow condition, annular eccentricity, and inner pipe rotation. Displacement efficiency in highly eccentric annuli can be markedly improved by rotating the inner pipe, even at low speeds. The experimental data can be compared with, and used to validate, numerical simulations produced by a proprietary 3-D displacement model being developed by Halliburton.

Turbulent pipe flow of “rod-like” polymer solutions

PO22

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Previous studies have shown that “flexible” polymers, when added to a Newtonian solvent, exhibit significantly less frictional resistance to flow in the turbulent regime compared to the solvent alone [1, 2]. The limited literature on “rigid” or “rod-like” polymers has shown that these polymers are also capable of drag reduction but possibly to a lesser degree than flexible polymers [3, 4]. In the present study the drag reduction and turbulence structure of an aqueous solution of a rigid rod-like polymer, scleroglucan, was experimentally investigated in a 100-mm diameter 23-m long circular pipe-flow facility.

Shear, oscillatory shear and extensional rheology measurements were conducted on the polymer solution over a wide range of concentrations (0.0075%-0.5%). The critical overlap concentration, c^*, was found to be about 0.057%. Small-amplitude oscillatory shear measurements on semi-dilute solutions showed a decreased frequency dependence with increased polymer concentration indicating increased molecular structure with concentration. Capillary break-up extensional rheology (CaBER) measurements were used to study the extensional viscosity of the polymer solution where filament thinning was observed with a high-speed digital camera at 2000 frames per second. Due to instrument limitations, the measurements could only be achieved for solution concentrations well above c^*. In marked contrast to the behaviour of flexible polymers, which exhibit exponential filament thinning in time over a large range of the filament break-up process, Newtonian-like linear thinning was observed for this rigid polymer. However, the measured Trouton ratio (Tr) confirms that the polymer is non-Newtonian as $\mathrm{Tr} \gg 3$.

Pressure-drop measurements were conducted using a differential pressure transducer and compared to that of a Newtonian fluid flow for a range of concentrations. Due to solution turbidity at higher concentrations detailed velocity measurements were only possible at a concentration of 0.01% and comprised mean axial velocity and complete Reynolds normal stress data, i.e. u', v' and w', measured by means of a laser Doppler anemometer at three different Reynolds numbers, all in the turbulent regime. Two Newtonian control runs within the turbulent regime were also performed for comparison. The experiments here provide a benchmark data set, hitherto lacking in the literature, for modellers wishing to develop closures for such polymers (see e.g. [3] or [5]).

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Re-entrant corner flows of Oldroyd-B fluids in the natural stress basis

PO23

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We consider the steady planar flow of an Oldroyd-B fluid for re-entrant corners of angle π/α where $1/2 \le \alpha < 1$. Local to the corner we consider a class of similarity solutions associated with the inviscid flow equations which arise from the dominance of the upper convected stress derivative in the constitutive equations. This solution derived by Hinch (Hinch 1993, J. Non-Newtonian Fluid Mech. **50**, 161-171) with a core stress singularity that depends upon the corner angle and a radial distance r as $O(r^{-2(1-\alpha)})$ and a stream function behavior of $O(r^{\alpha(3-\alpha)})$. This outer solution is matched to inner regions at the wall for upstream boundary layers. The formulation is carried out in both Cartesian and natural stress basis with the latter presented, implicitly assuming flow in absence of a lip vortex. This work extends the results of Rallison, Hinch (Rallison, Hinch 2004 J. Non-Newtonian Fluid Mech. **116**, 141-162) finding a new core balance for the natural stress variable ν giving a consistent similarity solution. Essential features of this analysis are the matching of the core region to the wall boundary layers where the boundary layer equations are analyzed. The new results are concerned with the far-field boundary layer behaviour of the stream function and stress components. Numerical solutions for the parameter dependences are also given.

Evaluation of negative wake criteria in an associative polymer

PO24

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We present an experimental study of the motion of a solid sphere falling through a hydrophobic alkali-swellable associative polymer (HASE). The complex associative character of these polymer systems is modeled by constitutive equations to obtain an estimation of the material properties in extensional and simple shear flow respectively. Sphere-to-tube ratios from $a/R=0.0375$ to $a/R=0.15$ are investigated over a wide range of Weissenberg numbers.

Particle image velocity measurements are used to analyze the flow fields around the falling spheres. Measurements of the downstream velocity and position of the stagnation point are correlated to the values of Weissenberg number, Reynolds number, sphere-to-tube aspect ratio and concentration of the solution applied in order to quantify the magnitude and influence of the rheology in the flow behind the sphere.

Different criteria published in the literature are evaluated for negative wake generation and a real estimation of the extensional rate is proposed to readily quantify the influence of extensional properties of the fluid in the governing physical mechanism.

Re-entrant corner flows of PTT fluids

PO25

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We consider the local asymptotic behaviour for planar flow of Phan-Thien-Tanner (PTT) fluids around re-entrant corners, i.e. corners of angle π/α, where $1/2 \le \alpha < 1$. We assume the situation of complete flow around the corner with lip vortices implicitly assumed to be absent and consider the model in the PTT model regime $\kappa = O(1)$ in the limit of vanishing solvent viscosity. The asymptotic structure has been shown to comprise an outer core flow region in which the upper convected stress derivative dominates together with narrow boundary layer regions at upstream and downstream walls at which viscometric behaviour is recovered.

A preliminary analysis has derived a leading order solution in the core for which the stress singularity is $O(r^{-2(1-\alpha)})$ and which the streamfunction vanishes at $O(r^{\alpha(1+\alpha)})$, where r is the distance from the corner. This preliminary analysis considered the upstream boundary layer only and here we complete this by discussing the downstream boundary layer. Rather surprisingly, we now find a restriction on the validity of this solution being limited to the corner angles $2/3 < \alpha < 1$. This follows from the solution in the natural stress variables, the details of which we will present in the poster.

Investigation of vortical structures in bifurcations PO26

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The present paper is concerned with the experimental investigations and numerical modeling of the Newtonian and weakly elastic flows in branches. Two types of bifurcations are used: (i) a cylindrical bifurcation with a nominal diameter of 2.5 mm; (ii) a micro geometry with a square section of 0.7 × 0.7 mm. The work is directed to biofluid dynamics applications, respectively to the study of stenosis development in blood vessels. In both motions the flow is driven by pressure gradients. The tested samples are mineral oils and solutions of polyacrylamide dissolved in water at different concentration, below the entanglement critical concentration. The experiments are focused to the investigation of vortices development beyond bifurcation, in the branch characterized by the lowest flow rate. The aim of the study is to determine, for each type of the sample and geometry, the maximum (critic) Reynolds value which preserves the existence of the vortex. The results can be extended to the hemodynamics analysis of stenosis vessels; it is assumed that one can obtain a relation between the existence of stenosis on the wall of artery and the local Reynolds number value. The main goal of the paper is to observe the influence of elasticity of the vortex formation, and to establish a correlation between the value of critical Reynolds number and the Weissenberg number. The experiments, including flow visualization under microscope and rheometry of the samples are performed in REOROM Laboratory and the Interaction Matter - Field Laboratory from UPB. Numerical simulations of the corresponding flow fields are obtained using FLUENT, POLYFLOW and FEMLAB commercial codes (generalized Newtonian and viscoelastic rheological models), in cooperation with TU Darmstadt.

Extended separated representation of micro-macro models related to complex fluid flows PO27

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Recently, we proposed a new discretization technique (fully deterministic and based on a separated representation of the unknown fields) was applied for solving efficiently highly dimensional partial differential equation, some of them never until now solved. In particular we addressed the models related to polymer solutions (FENE, bead-spring-chains, ...) and melts (Doi-Edwars or Ottinger models), associative polymers, fiber suspensions, ... The interested reader can refer to [1]-[2] and the references therein. All the models considered in our former publications concerned rheological flows, where a homogeneous microstructure evolution was assumed. In the present work we focus on the solution of complex flows, where an extended separated representation involving physical space, time and the conformational coordinates is proposed and successfully applied. Two benchmark problems are here considered: (i) the converging flow of an associative polymer, where the flow kinematics is solved by using the stream-tubes method technique; and (ii) the driven cavity flow, involving a short fiber suspension, where the flow kinematics is solved by using a stabilized finite element method. In both cases the microscopic model is solved by applying the extended separated representation technique.

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Time dependent flow patterns in Couette-Taylor motion of pure viscous and weakly elastic polymer solutions PO28

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The work is concerned with the experimental investigations of the Couette -Taylor vortex flow regimes of the Newtonian and viscoelastic fluids between two concentric cylinders of finite length. The main goal of the research is to evidence the differences between the routes to turbulence of weakly elastic polymer solutions, in comparison to a pure viscous liquid. Weakly elastic polymer solutions in different concentrations of aqueous polyacrilamide have been considered in the Couette -Taylor flow and the development of flow structures for ramped input signals were observed in relation to the Newtonian patterns. For the sample A (lowest concentration, almost constant shear viscosity), the flow patterns exhibited a behavior similar to the Newtonian case: Taylor vortex flow, wavy Taylor vortex flow and turbulent Taylor vortex flow, with the remark that before the onset of the Taylor vortex flow regime, secondary flows were spotted in the fluid column (phenomena which is absent in the case of the Newtonian fluids). For the sample B (higher concentration, relevant shear thinning behavior), more significant differences were observed against the Newtonian case: the pre-Taylor secondary flows were present, followed by the Taylor vortex flow, standing waves and turbulent Taylor vortices. We also investigated the time dependence of the flow patterns around the first Taylor critical point: pre-Taylor secondary flows, wavy Taylor vortices and standing waves were considered for the samples under study (the recordings were made at constant Taylor numbers for a time period of 40 minutes). The pre-Taylor secondary flows exhibited time dependence: the structures are present periodically within the fluid column, even though at some moments of time they look much alike the time independent Taylor vortices. For the wavy Taylor vortices (sample A), the behavior is similar to the Newtonian case; respectively, at Taylor numbers above the Taylor vortex flow regime, the wavy Taylor vortices start as Taylor vortices, develop the wavy regime and return to zero azimuthal amplitude, and hence again to Taylor vortex flow. Therefore, the wavy flow regime seems to be unstable for a weakly elastic solution. As elasticity is increasing (sample B), the wavy Taylor regime is disappearing and is replaced in the way to turbulence by the standing waves (flow regime similar to Taylor vortices, but characterized by a lower cells height). One can conclude that the presence of elasticity significantly affects the transient flow patterns by replacing the wavy Taylor regime with standing waves.

Liquid-liquid displacement flows in a Hele-Shaw cell including viscoplastic effects PO29

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Visualization experiments were performed to investigate the phenomenon fingering during the displacement by a Newtonian oil of aqueous solutions of carbopol flowing through a parallel plate channel (Hele-Shaw cell). Applications include displacement of heavy crudes in oil reservoirs. The channel is 100 mm wide and 150 mm long, and the gap between plates is 1 mm. The plates are made of transparent glass to allow flow visualization. The Reynolds number is kept low for all cases investigated, to ensure negligible inertia. The apparatus was built in such a way that the interface is always flat at the startup of the flow. The main parameters that govern this flow are the viscosity ratio, the capillary number, and the yield stress. In the experiments, the interface shape is recorded as it proceeds along the cell for different flow rate values, and the conditions under which fingering occurs are determined.

Nonlinear pattern formation in viscoelastic Taylor-Couette flow PO30

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Three-dimensional and time-dependent simulations of viscoelastic Taylor-Couette flow of dilute polymer solutions are performed using a fully implicit parallel spectral time-splitting algorithm to discover flow patterns with various spatio-temporal symmetries, namely rotating standing waves, disordered oscillations and, solitary vortex structures referred to as oscillatory strips and diwhirls. A detailed account of the impact of flow transitions on molecular conformation and viscoelastic stress, velocity profiles, hydrodynamic drag force and energy spectra of time-dependent flow states is presented. Overall, predicted pattern selection and flow features compare very favorably with experimental observations. For elasticity number E, that signifies the ratio of elastic to viscous forces > 0.1, when the shear rate (cylinder rotation speed) is increased above the linear stability threshold, the circular Couette flow (CCF) becomes unstable to rotating standing waves which are characterized by a checkerboard-like pattern in the space-time plot of radial velocity, implying symmetry between inflow/outflow (I/O) regions. As the shear rate is further increased, perturbations that break the I/O symmetry are amplified leading to disordered oscillations and/or flame-like patterns with spectral mechanical energy transfer reminiscent of elastically-induced, low Reynolds number turbulence. However, when the shear rate is decreased from those at which such chaotic states are observed, the radially inward acting polymer body force created by flow-induced molecular stretching causes the development of narrow inflow regions surrounded by much broader weak outflow domains. This promotes the formation of solitary vortex structures, which can be stationary and axisymmetric (diwhirls, DWs) or time-dependent (oscillatory strips, OSs). The dynamics of the formation of these structures by merging and coalescence of vortex pairs and the implication of such events on instantaneous hydrodynamic force are studied. For O(1) values of E, OSs and DWs appear approximately at constant values of the We, defined as the ratio of polymer relaxation time to the inverse shear rate in the gap. As shear rate is decreased further, DWs decay to CCF although at We values less than the linear stability threshold. The flow transitions are hysteretic with respect to We, as evidenced by a plot of drag force vs. We.

Derivation of a shear band initiation criterion in nonlinear viscoelastic flow PO31

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Shear bands represent a phenomenon of coexisting regions of a different strain rate. These regions are usually separated by sharp interfaces. They belong to a wider class of material instabilities that emerge as abrupt local changes in behavior. Shear bands have been observed in various types of material media like granular materials, metals and plastics. They can occur in systems of complex fluids as well and have been found in various systems like worm-like micelles, liquid crystals and entangled polymer melts. It is now widely accepted that one of the most important triggering mechanisms for the onset of shear band is a relationship describing a non-monotonic stress and strain rate. During the process of deformation and viscoelastic flow such a relationship allows separation into two domains with different strain rates. This is understood to be the main reason for the onset of shear band formation where homogeneous steady ground state becomes unstable and the system spatially separates-bifurcates into regions with low and high deformation rate. During the process the traction and the traction rate remain continuous across the interface which separates both domains. Consequently, the condition of traction rate continuity across the band serves as a starting point in development of the corresponding shear band initiation criterion. A theoretical framework for the analysis of bifurcation of deformation into a highly localized pattern is well established and well understood for a standard case of incrementally linear constitutive equation where at a given state of stress and deformation the relationship between stress rates and strain rates is essentially linear and is defined by the corresponding tangent operator. However, if the constitutive relation connecting stress and strain rates is genuinely nonlinear, the derivation of instability criterion is not so straightforward since the structure of the resulting criterion depends directly on the chosen form of incremental nonlinearity. Consequently, such a criterion appears to be non-universal, and does not carry close resemblance with the corresponding material instability criterion of the incrementally linear case. In contrast to the classical case with incrementally linear constitutive relation where a derived universal structure of the bifurcation criterion yields a linear dependence in jumps of the velocity gradient, which makes the problem linearly solvable in the corresponding amplitude jumps, incremental nonlinearity induces a nonlinear relation for the amplitude jumps in velocity gradient across the shear band. Derivation for such kind of a system is illustrated for a certain subclass of viscoelastic constitutive equations of White-Metzner type. For this form of constitutive relation the shear band initiation criterion is given in an explicit form. We discuss certain non-generic features of established criterion and analyze the corresponding geometric structure.

Onset of vortex shedding from a circular cylinder settling in a power-law fluid PO32

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We investigate the dynamic sedimentation of a single circular cylinder in an infinite domain filled with a power-law fluid using a fictitious domain method. Our objective is to elucidate the role of power-law rheology on the onset of wake instability and vortex shedding. In particular, we examine the influence of the additional degree of freedom represented by the ability of the particle to move freely in the flow domain as opposed to the case of the flow past a fixed obstacle. In the numerical parametric survey, we consider both shear-thinning ($n < 1$) and shear-thickening ($n > 1$) fluids. Our results highlight the complex interaction between the two non-linear terms (viscous and inertial) in the momentum equations and show that the flow dynamics is more intricate for shear-thinning fluids than that for shear-thickening fluids. Possible mechanisms which shed some light on these trends are outlined.

On the accuracy of extensional rheological measurements using capillary thinning procedures PO33

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Capillary thinning experiments have recently gained popularity as a tool for determining the extensional rheology and relaxation time of a wide range of fluids, covering those of academic and industrial interest. In this presentation, the applicability of CaBER-like experiments is critically assessed by performing numerical experiments with a range of fluids - elastic, inelastic non-Newtonian and Newtonian - of known constitutive equation. In this manner, the apparent rheological properties may be compared from a naive measurement - treating the fluid as an unknown - with the rheological properties obtained from the constitutive equations. The techniques utilised in the simulation are finite element/volume discretisations with an ALE formulation, particle tracking for free-surface movement and a compressed mesh approach for domain adjustment. As well as demonstrating the applicability of the CaBER for measuring fluids under ideal experimental conditions, the effect of a range of experimental considerations is also discussed. In particular, the effect on the calculated extensional viscosity is explored of different fluid loading (e.g. cylindrical, convex or concave), alternative plate separation profiles (e.g. linear or exponential), and the influence of gravity. The overarching aim from this work is to achieve optimal design of experimental procedures and a high level of confidence in the rheometrical data derived therefrom.

Stability of shear-thickenning flow between rotating cylinders 💿 PO34

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The effects of nonlinearities on the stability are explored for shear thickening fluids in the narrow-gap limit of the Taylor-Couette flow. Here, a low-order dynamical system is obtained from the conservation of mass and momentum equations. In comparison with the Newtonian system, the present equations include additional nonlinear coupling in the velocity components through the viscosity. It is found that the critical Taylor number, corresponding to the loss of stability of the base (Couette) flow becomes higher as the shear-thickening effects increases. Similar to Newtonian fluids, there is an exchange of stability between the Couette and Taylor vortex flows. However, unlike the Newtonian model, the Taylor vortex cellular structure loses its stability in turn as the Taylor number reaches a second critical value. Naturally, one expects shear thickening fluids to result in inverse dynamical behavior of shear thinning fluids. This study proves that it may not occur as expected everywhere in the bifurcation diagram.

KEY WORDS: Shear thickening, Stability Analysis, Taylor-Couette Flow

Homogeneous Polymeric Systems

Structure-property relationships of LDPE PO36

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The structure-property relationship of a broad range of commercial LDPE resins produced by either tubular or autoclave processes were investigated. It was found from this study that some of the structure-property relationships that were established for the model long chain branched molecules and the sparsely long chain branched molecules are also applicable for the highly long chain branched molecules, such as LDPE, if the backbone Mw is used. The advantage of using backbone Mw over absolute Mw is that the Mw value is less affected by the level of LCBs, so that the melt properties of the molecules can be compared at a reference level. The difference between the molecular structures of tubular and autoclave LDPE resins were also evidenced.

Non-linear step strain of branched polymer melts 💿 PO37

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The Pom-pom model by McLeish and Larson (Journal of Rheology 42(81-110), 1998) is a highly successful molecular theory for describing the rheology of long chain branched melts. However, there is a long-standing puzzle in step strain: how can a model that is intrinsically non-separable recover empirical strain-time separation? We investigate the Pom-pom model in step-strain, comparing the qualitatively different behaviour of the single mode integral and differential orientation. Despite this difference when both models are used in a multi-mode form, their behaviour is shown to be comparable. Although neither integral nor differential model can predict exact time-strain separability, both can create a region in which the approximation is a very good one before the longest stretch time has been reached. By transforming to a continuous spectrum we find under certain assumptions, a parameter sub-space where an analytic damping function can be derived. We survey a range of materials produced by two different synthesis routes; high pressure polymerised LDPEs and metallocene catalysed HDPEs. Extracting non-linear

Pom-pom parameters from extensional data, we look for spectra that display time-strain separability. Despite the assumptions made in deriving the damping function, the parameter space can be successfully expanded to encompass a general long chain branched melt.

Is there elastic yielding in absence of edge effect? PO38

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Evidence has emerged rapidly to show that entangled polymeric liquids suffer elastic yielding after large step strain [1,2] and during large amplitude oscillatory shear (LAOS) [3,4]. Specifically, particle tracking velocimetric (PTV) observations reveal that there are macroscopic motions after shear cessation in entangled solutions that also display inhomogeneous deformation during LAOS. Could these results arise from edge effect at the meniscus? We have redesigned our experiments by modifying a standard cone-plate apparatus to ensure that the meniscus does not become unstable during and after shear. If the phenomena re-occur in absence of any conceivable edge effects, then the previous PTV studies can be placed on firmer grounds. Otherwise, all the new findings from recent PTV observations would be found to have been built on "thin ice". Thus, it is essential that such new experiments be carried out urgently.

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This work is supported, in part, by a SGER grant from NSF (DMR-0603951) and a standard NSF grant (DMR-0804726).

Hierarchical relaxation in star polymer melts PO39

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Using Neutron Spin Echo (NSE) spectroscopy and a labelling scheme unique to neutron scattering it is possible to observe different relaxation processes in polymer melts separately. In comparison to linear polymer melts stars are more confined due to the branching point. Following the concept of hierarchical relaxation the star arms have to fully retract to the star center before the whole star can move.

Using the contrast between protons and deuterons the branching point of a 3 arm polyethylene (PE) star has been labelled. Within the accessible time range of NSE the dynamic structure factor shows a clear transistion to a plateau, signifying the stronger confinement of the star center in comparison to a corresponding center labelled linear chain (‘2 arm star’). Shortening of one star arm to about only one entanglement length leads to the same topological confinement as for the symmetric star, reflecting a stronger effect of such a small branch than expected. These results are comparable to rheological experiments on the same system.

The process of arm retraction can be followed by observing the relaxation of 2 fully labelled arms of a symmetric 3 arm star. Deeper arm retractions are expected to be retarded due to the entropic barrier from the branching point. The measured dynamic structure factors of PE stars with various arm length have been compared with those of corresponding linear ‘2 arm stars’. Surprisingly no different relaxation behaviour was observed, indicating that the relaxation of the arms are not significantly suppressed by the branching point. Only for the smallest star a slowing down in the relaxation function has been observed.

Critical experimental techniques in broad frequency range characterization of monodisperse polybutadiene (PBD) PO40

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Two monodisperse linear PBDs with molecular weight of 78 kg/mol and 194 kg/mol were studied. The linear viscoelasticity of the samples were determined by small amplitude oscillatory and creep/recovery tests. Master curve with frequency range from 10^{-5} to 10^{9} rad/s was obtained at a reference temperature of 25 °C by time temperature superposition of the oscillatory data combined with the dynamic moduli which were inferred from creep compliance. The data obtained from different rheometers and test methods superimposed perfectly which can be used as the reference data for tube model evaluation.

To ensure data are reliable over the board range of frequency, several crucial but often being neglected experimental techniques were studied. We will present the proper methods to handle sample molding, thermal and oxidative degradation, normal stress build-up during loading the sample, frost on sample at low experimental temperature, as well as the method to build the master curve.

Shear modification and elongational behavior of two types of low-density polyethylene melts with different long chain branching PO41

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Rheological behaviors of two kinds of low density polyethylene (LDPE) melts with long chain branching are studied in terms of shear modification and elongational rheometry. One LDPE is made by vessel process and the other is made by tubular process. The combination measurements of GPC and intrinsic viscosity indicates that long chain branching of the vessel LDPE is longer and more complicated than that of the tubular LDPE. Zero shear viscosity and shear rate dependence of viscosity is similar in both LDPEs. On the other hand, transient uniaxial elongational viscosity shows different features in these LDPEs. The vessel LDPE exhibits more strain hardening than that of the tubular LDPE. This could be caused by pronounced stretching of molecular chain under the elongational flow and the suppression of chain contraction due to multi-branch points in the vessel LDPE. In addition, difference of shear modification behaviors in these LDPEs is more significant. Both LDPEs exhibit recovery of melt strength owing to annealing after kneading in an internal mixer. However, the magnitude of the recovery is much more prominent in the vessel LDPE than that in the tubular LDPE. This indicates that the vessel LDPE has more hierarchical branch structure than the tubular LDPE. We also measured transient biaxial elongational viscosity and damping functions under large step shear and biaxial strains. The uniaxial and the biaxial elongational viscosities and the damping functions for the step shear and the step biaxial strains will be compared and discussed.

Kinetics of shear-induced crystallization: Effects of shear rate and strain PO42

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The kinetics of shear-induced crystallization of an isotactic polypropylene was studied using a sliding plate rheometer at shear rates up to 200 s^{-1}. The rheological properties of the sample during crystallization were monitored by small-oscillatory oscillatory shear, which was applied after the sample was initially subjected to a short period of steady simple shear. The crystallization kinetics was also tracked by monitoring turbidity using an optical setup equipped with a bifurcated optical fiber. The relative importance of shear rate and strain on the enhancement/saturation of crystallization kinetics is discussed. To understand these data, the nonlinear shear stress growth data initially measured during the steady simple shear are also presented. The effect of pressure on shear-induced crystallization is also under study.

Chemical recycling of polyethylene terephthalate (PET) PO43

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Recycling of polyethylene terephtalate (PET) has been done for many years. The requirements for recycling post-consumer waste are very different than the requirements for recycling waste PET that is generated within the manufacturing operation. In post-consumer the main problems are consumer misuse and contamination, while industrial scrap often has high monomer concentrations and/or poor physical properties, but lower levels of contamination. Currently, chemical recycling is not viable because the recycled monomers are more expensive then the raw materials and the current processes are usually batch ones, which limits their usefulness. Nevertheless, there is clearly scope to try to overcome these drawbacks since chemical recycling can be the ideal for processing plant waste because the monomers are required at the site. If successful, this recycling of these monomers would offset the need to purchase them as raw materials and reduce effectively the cost of the process of recycling. The objective of this work is to develop a novel approach for the continuous selective depolymerization of PET to low molecular weight molecules using a twin screw extruder as reactor and ethylenoglycol as an agent of depolymerization and supercritical carbon dioxide ($ScCO_2$) as plasticizer. The reaction was followed collecting samples along the extruder. Characterization of the molecular weight and molecular weight distribution was performed by dynamic rheological measurements, intrinsic viscosity and gel permeation chromatography (GPC). The decrease of molecular weight achieved depends on the processing conditions, the amount of ethylenoglycol and supercritical carbon dioxide.

Interdiffusion of ring-shaped polystyrenes with high molecular weights PO44

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Time evolution of interfacial thicknesses between a cyclic polystyrene (c-hPS) / its deuterated counterpart (c-dPS) and a linear polystyrene (l-hPS) / its deuterated counterpart (l-dPS) bilayer films was investigated by dynamic secondary ion mass spectrometry (DSIMS) and neutron reflectivity (NR). Weight average molecular weights of samples are 115k and 50k, which are much larger than the critical entanglement molecular weight for linear polystyrene. For the case of molecular weights of both 115k and 50k, the interfacial thickness of (c-hPS/c-dPS) film was significantly larger than that of (l-hPS/l-dPS) film at any given annealing time, indicating that the diffusion constant of c-PS is constantly larger than that of l-PS. It can be explained in terms of weaker topological constraint coming from the entanglement for the c-PS than for the l-PS.

Effective pairwise potentials in entangled polymer networks PO45

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Whereas the 3D slip-link network model describes the entangled polymer dynamics reasonably, the thermodynamic expression of the model is still controversial [Y. Masubuchi et al., Modell. Simul. Mater. Sci. Eng., 12, S91 (2004)]. In the present work, a free energy for describing chain interaction in the 3D-network model is proposed on the basis of the local densities of Kuhn segments. In the model, each polymer is replaced by a series of Gaussian strands corresponding to primitive path segments between consecutive entanglements. The free energy is formulated as repulsive potentials defined for two Gaussian entangled-strands to represent overlapping of their Kuhn segments. It has been noticed that the behavior of the potential was in qualitative agreement with the earlier work by Flory-Krigbaum on the effective potential between polymer coils in solutions.

Effects of propylene glycol on the physical properties of poly(vinyl alcohol) solutions and films PO46

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The rheological properties of poly(vinyl alcohol) (PVA) solutions in dimethyl sulfoxide (DMSO) and the physical properties of PVA films were investigated in terms of propylene glycol (PG) content in PVA. As the PG content was diminished, the solutions showed higher viscosity and more noticeable Bingham behavior. The yield stress of the solutions was increased with increasing temperature and concentration. However, increase in PG content reduced it. 6 wt% PVA solutions containing PG more than 30 wt% gave rise to an abrupt reduction of dynamic viscosity and storage modulus over the frequency range 0.08 and 0.2 rad/s. Further they showed a sudden decrease of relaxation time. On the other hand, 12 wt% solutions did not exhibit this discontinuous change of rheological parameters with PG content. As the PG content was increased, the tensile strength of PVA films were decreased but elongation at break was increased. Thus, incorporating PG in PVA toughened the resultant films up to a critical PG content.

Toward a new universal model for polymer rheology based on group interactions

PO47

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Recent work [1-2] has developed a a dynamic monte carlo percolation grid simulation which can successfully predict the linear viscoelastic response of thermosets materials during the whole isothermal cure, including the power-law relaxation at gelation. The model is based on extension of the group interaction model [3] to incorporate connectivity and branching effects. This paper will discuss the usefulness of this viscoelastic model in describing thermoset polymer viscoelasticity and gelation behaviour and include new interpretations for network development from gelation through to vitrification for thermoset systems. Additionally the extension of this model to predictions of the viscoelasticity of branched thermoplastic polymer systems (hyperbranched polymers, long chain branched polymers and polydisperse polymers) will then be discussed with surprising results [including the successful prediction of viscosity dependence on molecular weight shifting from a power of 1.0 to 3.4, as seen experimentally for many thermoplastic systems]. In this way we hope to describe the potential of this energetic approach for developing a new universal model for polymer viscoelasticity.

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Descriptions on the thixotropy-loop tests by the simplified Mewis-Denn model

PO48

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The theoretical characterizations on the triangular-form thixotropy loop tests of a LDPE melt (Q200) were performed in the present paper by using the simplified Mewis-Denn model, which contains a modified upper convected Maxwell model and a kinetic equation. The simplified Mewis-Denn model, containing five parameters, was obtained by reducing the multiple relaxation mode of Mewis-Denn model to a single relaxation mode. The calculated results show that the simplified model can well describe the reported thixotropy loop experiments of the LDPE melt.

Rheological modeling of commercial polystyrene resins

PO49

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Commercial polystyrene resins may pose particular challenges for rheological modeling because of their relatively high polydispersity and low degree of entanglement. We have found discrepancies between the predictions of two double-reptation models and the corresponding linear viscoelasticity measurements of commercial polystyrene samples. The accuracy of the experimental data has been verified by conducting viscoelasticity measurements in different laboratories using different types of rheometers, and by showing that small distortions in chromatographic measurements cannot account for the discrepancies seen in the viscoelastic response. In addition, the discrepancies between predictions and measurements are shown to be systematic, suggesting that gaps in the theory are responsible for the mismatch.

Rheological and ultrasonic monitoring of the in-situ polymerization of cyclic butylene terephthalate

PO50

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Dynamic rheological measurements were used to monitor the in-situ polymerization of cyclic butylene terephthalate (CBT) oligomers. The material is a two-component system where the catalyst was pre-blended within the CBT oligomers. Following temperature sweep tests which revealed a temperature window for polymerization to take place, time sweep tests are conducted at different polymerization temperatures using the parallel plates configuration under constant stress and a constant frequency of 6.28 rad/s. Following the polymerization, the material is heated to 235 °C and a frequency sweep test is also done. The in-situ polymerization of CBT was also investigated under various conditions of temperature and pressure using a device that combines ultrasonic and volumetric measurements. A frequency of 2.7 MHz was used throughout the tests. In a typical ultrasonic monitoring experiment the CBT sample is heated at a rate of 2 °C/min to the polymerization temperature where it is held for a certain time under low or high pressure (30 to 400 bars). The sample is heated again to about 240 °C and cooled at the same rate to room temperature. From the measurements of sample volume, ultrasonic velocity and attenuation, a dynamic viscosity can be calculated and used to characterize the polymerization process. Melting and crystallization of the resulting PBT polymer are also identified. The results from both the rheological and ultrasonic approaches will be compared and discussed.

Elastic and viscous properties of linear and long-chain branched ethene/α-olefin copolymers in the terminal regime

PO51

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Several ethylene homopolymers and ethene/α-olefin copolymers synthesized by metallocene catalysts with butene, hexene, octene, dodecene, octadecene, and hexacosene as comonomers were characterized in linear-viscoelastic shear flow. Creep and creep recovery measurements were used to investigate the time dependence and to determine both the zero shear-rate viscosity η_0 and the steady-state elastic recovery compliance J_e^0. The well-known correlation between the zero shear-rate viscosity η_0 and the weight average molar mass M_w was found to be obeyed by all samples containing comonomer contents up to 29 wt.-%, too. This is somewhat surprising, as such a high comonomer content means that more than 25 wt.-% of the molar mass are not in the main chain and thus the number of entanglements should be significantly reduced. For the linear steady-state elastic compliance J_e^0 an increase with growing molar mass M_w (for constant molar mass distribution) was observed independent of the kind and content of the comonomer. The reasons for this molar mass dependence of J_e^0 are not clear, as J_e^0 independent of M_w was found for linear monodisperse polymers. However, to our knowledge this is one of the first studies so far for polydisperse polyethylenes with constant *MMD*.

For long-chain branched samples both an increase of the zero shear-rate viscosity η_0 and the steady-state elastic recovery compliance J_e^0 is found in comparison to the values expected from molar mass M_w. An increase of the degree of long-chain branching leads to a higher effect on the rheological behavior (for η_0 an inversion of this dependence is found for high degrees of long-chain branching). For low degrees of long-chain branching J_e^0 reacts more sensitively than η_0 on branching, while for high LCB-levels a greater sensitivity of η_0 was found. A normalization of η_0 and J_e^0 to the values expected for these quantities from molar mass M_w, η_0^{lin} and $J_e^0{}_{lin}$, respectively, was performed. A plot of these reduced quantities ($J_e^0/J_e^0{}_{lin}$ vs. η_0/η_0^{lin}) leads to a clear root function-like dependence.

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Heterogeneous and Self Assembled Polymeric Systems

Shear induced chain migration in flowing polymeric solutions: A molecular dynamics study PO54

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Mechanistic understanding of the flow behavior of dilute polymer solutions near a solid surface is of interest for development of applications such as manipulation of biological molecules in micro and nanofluidic devices. In this work, we have used molecular dynamics simulations to investigate the shear flow behavior of dilute polymer solutions in nanochannels. In particular, we focus on the cross-stream migration of the polymer chains in the flowing polymer solutions. The hydrodynamic interactions are governed by the intermolecular interactions in our model system. The polymer is represented by bead-spring chain model in our system and an explicit, atomistic model is used for the solvent. The dependence of the cross-stream chain migration phenomenon on the length of the polymer chains is studied by considering solutions containing a mixture of chains of different lengths. The effect of specific intermolecular interactions is captured by using both the standard Lennard-Jones (LJ) and the purely repulsive LJ (WCA) potential for characterizing the intermolecular interactions in the system. Simulation studies were also carried out in channels of different widths to quantify the effect of channel size on the cross-stream chain migration process. The chain migration phenomenon is driven by the hydrodynamic interactions between the chains stretched by the flow and the channel walls. This process is thus expected to be affected by the concentration of the flowing solutions. We have carried out simulations over a range of values of polymer concentrations to determine the effects of the concentration on chain migration process.

Self-assembly of benzylidene-D-sorbitol derivative under geometric confinement PO55

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1,3:2,4-di-O-methylbenzylidene-D-sorbitol (MDBS) is a small organic molecule that is capable of inducing self-assembly in a wide variety of organic solvents. In the present work, MDBS self-assembled in propylene carbonate (PC) and formed into MDBS/PC gel in a series of microchannels with its width varying from 20um to 80µm. We focus on the microchannel dimension and gelator concentration effects on the topological variations of MDBS/PC gel by using a combination of optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The distinct difference of the topological structures of MDBS/PC gel network is observed between un-confined and confined conditions when the microchannel width decreases. MDBS/PC gel with fibrillar network is self-assembled in the microchannel and its melting point is higher than that of MDBS/PC gel with sheaflike spherulite structure (with semi-diameter defined as D0) that is formed in un-confined condition when the width of microchannel is far less than D0.

Blend dynamics in interacting miscible polymer blends PO56

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Coupling of dynamic response between two blended polymers with huge dynamic asymmetry (large $?T_g$) may be observed if enough hydrogen bonding interactions are present. This behavior differs from the widely reported dynamic heterogeneity observed for weakly interacting/non-interacting blends. Hence, it is interesting to understand the influence of these favorable interactions on the viscoelastic properties. Blends of styrene-*co*-vinyl phenol (PSVPh) and poly(vinyl methyl ether) (PVME) were studied. Incorporation of styrene (PS) into the strongly interacting blends of poly(vinyl phenol) (PVPh) and PVME provides an effective way to modulate hydrogen bonding interactions in the system. The vinyl phenol content in PSVPh copolymers was varied to further explore the influence of hydrogen bonding on dynamic heterogeneity and blend dynamics. Oscillatory shear tests were performed to obtain the dynamic response of the blends as well as the PVME homopolymer over wide large temperature range. For each blend, linear viscoelastic master curves were created. The analysis indicates that time-temperature superposition (tTS) fails for some PS/PVME blends, whereas for different PVPh/PVME blends studied tTS was obeyed over a wide temperature range. For the blends of PSVPh copolymer with equal styrene and vinyl phenol units distributed randomly, tTS was successful indicating that the random presence of equal amount of styrene units was insufficient for dynamic response decoupling. A monomodal terminal relaxation process was observed for all the blends studied so far, and the relaxation time varied smoothly with the blend composition and temperature.

Component dynamics in polystyrene/4-pentyl-4'-cyanobiphenyl blend PO57

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Even if a polymer and a low mass compound (LMC) are homogeneously mixed, dynamically heterogeneous behavior generally appears due to the large difference in the glass transition temperatures (T_g) between the two components. In other words, segmental motion of polymer component and rotational motion of LMC component (both motions are essentially determinative of the glass transition) will not be cooperative. However, as the molecular size of LMC increases and becomes comparable to the segmental size of the polymer, the two kinds of motions might become cooperative. Based on this idea, we investigated the dielectric and viscoelastic relaxation behavior of polystyrene/4-pentyl-4'-cyanobiphenyl (PS/5CB) blend in the miscible region. Note that the size of 5CB (1.3nm) is comparable to the Kuhn length of PS (1.5nm). Since the dipole moment of 5CB is much larger than that of PS, only the motion of 5CB can be observed by the dielectric measurement. The experimentally observed dielectric spectra were bimodal. This result means the existence of two types of motion for 5CB in the blends. From the dielectric data we evaluated the two relaxation times, τ_{fast} and τ_{slow} corresponding to the fast and slow modes and compared them with the longest relaxation time τ_{L} of PS-chain evaluated by viscoelastic measurement. The τ_{slow} and τ_{L} had the same temperature dependence, and the value of τ_{slow} was very close to the segmental relaxation time of PS, which was estimated from the τ_{L} value. This means that the slow mode of 5CB is cooperative with the PS-segmental motion. On the other hand, the temperature dependence of the fast relaxation time (τ_{fast}) was weaker than that of τ_{L}. Therefore, it is suggested that the fast mode is ascribable to the 5CB motion not being cooperative with PS-segmental motion.

Rheology and adhesive performance of soft polymer networks PO58

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Soft polymer networks are commonly used as pressure sensitive adhesives (PSAs). This is due to their ability to flow and yet to resist flow. These contradictory requirements indicate that the mechanical properties are finely tuned, and that the types of deformation upon application are carefully considered. Two main mechanisms must be considered when studying adhesives that is; the debonding and bonding mechanisms. Linear rheology is used to study the debonding mechanisms to gain better understanding of the peeling process of the PSAs. A variety of PSAs are prepared by mixing a linear vinyl terminated polymer with a silane terminated f-functional cross-linker, with $f>2$. The stoichiometric imbalance, r (silane to vinyl ratio), the molecular weight of the linear polymer, M_n, and the cross-linker functionality, f, are used as adjustable parameters to tune the properties of the cross-linked networks. The adhesive performance was tested with 90 degree peel tests at three peel rates and thicknesses, and it was observed that the peel force varies with r, M_n and f and also the peel rate. The fundamental viscoelastic parameters that govern the PSA performance were used to state an empirical relation for the peel force. This relation combines the peel force with the loss tangent at the peel frequency and the equilibrium modulus, G_0, and forms a universal curve for each polymer/cross-linker system tested. It was found that the normalized peel force can be reduced by reducing M_n or increasing f at corresponding loss tangent. Non-linear rheology is used to analyze this dependency on M_n and f with relation to finite extensibility.

Spectacular transient effects in measuring the ultra-high viscosity of a chlorinated biphenyl PO59

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Low-shear-rate viscosity measurements were carried out on an ultra-high viscosity chlorinated biphenyl (CBP) (an Aroclor R) to enable reduced variables plots of acoustic high-frequency shear measurements at 40 MHz on a series of chlorinated biphenyls during the period of 1967-8. Although the final results were published, the spectacular transient memory effects encountered in measuring the viscosity went unreported; hence this presentation. Falling ball measurements were carried out on the CBP in a chemical hood using steel spheres ca. 1/2 inch in diameter with the CBP in a graduated cylinder of ca. two inches i.d. and ca. 24 inches in length. Measurements of position versus time were made over a period of two to three months! For the initial phase of motion, downward displacement of a sphere created a long trailing air path which eventually broke away from the sphere. Plots of position versus time indicated long term memory effects which eventually disappeared. However, as a sphere neared the bottom of the cylinder, constriction of fluid motion caused deviation from constant velocity, indicating that the sphere was sensing the end of the cylinder. The viscosity was calculated using the Faxen correction, which was significant for this geometry. Copies of photographs will be shown which demonstrate the visual extent of these effects, which are quite spectacular.

Viscoelastic behavior of aqueous solutions of hydrophobically-modified water-soluble polypeptides PO60

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Water soluble polypeptide, poly[N^5-(2-hydroxyethyl) L-glutamine] (PHEG), was hydrophobiocally modified partially along the main chain by long alkyl chains $-(CH_2)_{n-1}CH_3$ (Cn). Association and viscoelastic behavior of aqueous solution of these self-assembling polymers (PHEG-g-Cn, n = 12, 16 and 18) were investigated by means of steady-flow viscosity and linear dynamic viscoelasticity measurements. In the mixed solvent of water/ethylene glycol (EG), the main chain of PHEG-g-Cn changed its conformation from flexible random-coil to rigid α-helix with the increase in EG content of the solvent. When the solvent was pure water, the existence of associative alkyl chains induced a drastic increase in solution viscosity than PHEG homopolymer, probably because of formation of self-assembled large aggregates via intermolecular association. When EG was used as solvent, the steady-flow viscosity exhibited non-Newtonian behavior, suggesting a weak association strength of the alkyl chains in EG and a destruction of the aggregates under high shear rate. Concentration dependence of the viscosity for EG solution was similar to that for lyotropic liquid crystalline solutions near isotropic-anisotropic transition concentration, which may suggest an orientational ordering of PHEG-g-Cn chains in rigid α-helical conformation.

Rheological properties of aqueous solutions of sulfonated poly(ether ether ketone), polyetherimide and polysulfone PO61

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The solution properties of polymers used in fuel cell application were investigated using different rheological tools. Dynamic and steady shear measurements were carried out in an ARES rheometer at room temperature. In addition, intrinsic viscosity was measured in a viscometer. It was observed that degree of sulfonation (DS) and solution concentration has enormous effect on the rheological properties as revealed by the zero-shear viscosity, η_0, storage modulus, G', and loss modulus G". For PEI and PSU solutions, G' was found to be independent of frequency and the polymer solution behave like a gel (G' >> G"). The shear dependent of the dynamic viscosity increases with both degree of sulfonation and polymer concentration. The system of SPEEK behave like a liquid (G" > G') at very low frequency Different rheological models were used to correlate the effect of DS, polymer structure, polymer concentration and solvent on the model parameters. Solution viscosity of SPEEK obeyed Fuoss and Strauss equation and showed strong charge interactions common for polyelectrolyte solutions.

The authors are gratefully thankful to King Fahd University of Petroleum & Minerals (KFUPM) for financial support of this research.

Microencapsulation by coacervation: Designing rheological properties of the shell by employing polymer mixture-ionic surfactant interactions PO62

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Coacervation is the phase separation in colloidal systems into two liquid phases-the coacervate and the equilibrium solution [1]. It is a common method for microcapsules production. Coacervation is a unique microencapsulation technology because of very high payloads achievable (up to 99 %), and the controlled release possibilities based on mechanical stress, temperature or sustained release [2]. The concept behind microencapsulation by coacervation is the phase separation of one or many macromolecules from the initial solution and subsequent deposition of the newly formed coacervate phase around the active ingredient suspended or emulsified in the same reaction media. The key factor that determines barrier properties of microcapsules is the structure of the shell material.

In this paper, complex polymer mixture-ionic surfactant interactions were employed to obtain oil-content microcapsules with a coacervate shell of controlled rheological properties. Emulsions of sunflower oil in a solution of a nonionic polymer-hydroxypropylmethyl cellulose (HPMC), an anionic polymer-sodium carboxymethyl cellulose (NaCMC), and an anionic surfactant-sodium dodecylsulfate (SDS) of various concentrations were prepared. Complex HPMC-SDS-NaCMC interactions [3] took place in the continuous phase of the emulsions. The interactions brought about separation of HPMC-SDS complex from the solution in the form of a coacervate, which formed a shell around the dispersed oil droplets. Rheological properties of the coacervate shell were controlled by tuning the interactions taking place in the continuous phase. In this way, coacervate microcapsules with the shell of the controlled properties were obtained. The microcapsules in the dried form were produced by spray drying. Properties of the microcapsules (oil content, stability etc.) depended on the shell structure.

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Rheology and self-assembly of heterogeneous methylcellulose PO63

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Methyl Cellulose (MC) is produced commercially in a heterogeneous manner. This results in what is commonly believed to be a blocky structure that undergoes self assembly in aqueous solution at moderately elevated temperatures. Rheology indicates that a network structure is formed on heating. The nature of the interactions that form the physical network junction points is still under debate. As the system forms the physical network, the optical properties change from a clear to a cloudy solution, in extreme cases separating into polymer and water rich phases. This phase separation can be seen on the nanoscale by SAXS, showing that there is no dominant size scale in this range, similarly SALS also shows no dominant size scale. However optical microscopy reveals textures that would seem to indicate a spinodal structure. Rheology and SAXS indicate that the network evolves over time, rheology and scattering studies show that at temperatures 10 – 20K below the typically quoted gel point the network is already forming. This would suggest that gel structure is kinetically limited, as in most studies to date a constant heating rate has been employed, resulting in the gel structure being pinned at the gel temperature.

Polyurea segmented multi-block copolymers: Structure and dynamics PO64

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While Polyurea segmented multi-block copolymers are widely used as impact-resistant coatings, the molecular underpinnings of these applications are not well understood. Due to inter-segmental repulsion that renders the segments thermodynamically incompatible, such copolymers exist in a micro-phase separated state, comprising “hard” and “soft” phases. We study the mechanical properties and rheology of a Polyurea copolymer (containing 19.8 % hard segments by mass) by measuring its stress-strain behavior at large strain rates (between 100 inverse s and 1000 inverse s) and by oscillatory shear rheometry, respectively. Polyurea shows elastomeric mechanical response over a wide temperature range, as the rigid domains physically cross-link the soft domains. The modulus increases (“strain-rate hardening”), while the residual strain in samples stretched to failure decreases with increasing strain rate. To elucidate how structure controls mechanical and rheological behavior, we study the micro-structure of these materials by Small-Angle X-Ray Scattering (SAXS). SAXS on undeformed specimens reveals two clear scattering intensity peaks. The higher wave-vector peak characterizes semi-crystalline hard segments with long period (lamellar size)on the order of 6 nm, while the lower wave-vector peak arises from micro-phase separated domains of spacing on the order of 70 nm. Polyurea specimens quasi-statically stretched to failure show anisotropic scattering, while samples stretched to failure at large strain rates show isotropic scattering. These results suggest that deformation effects on morphology are controlled by rigid domain response over the deformation time-scale. As more time is allowed during deformation, greater molecular reorganization and alignment take place, yielding anisotropic scattering and large residual strain in failed specimens. In the limit of infinite extension rate, no molecular reorganization is possible, and such failed specimens consequently exhibit identical structure as undeformed materials, pronounced strain-rate hardening in modulus and low residual strain.

Micro and macrorheology of cross-linked Pluronic hydrogels: Anomalous behavior at the cmc PO65

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In aqueous solutions, triblock copolymers of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO-Pluronic) self-assemble into a number of known aggregation states depending on concentration. In dilute concentration regimes, they form independent core-shell micelles, whereas highly concentrated PEO-PPO-PEO solutions instantaneously form a thermo-setting gel upon heating. The multimicelle structures can be reinforced by the formation of chemical cross-links between the polymer chains. The resulting cross-linked micelles have been shown to be stable upon dilution and can withstand environmental change and shear forces without structural deterioration. Such synthetic hydrogels are seen as ideal candidate matrices for the controlled release of bioactive molecules and for the encapsulation of living cells. This paper reports the outcomes of a study of the sol-gel transition corresponding to the cross-linking reaction of diacrylated-F68 (DA-F68) Pluronic polymer chains, utilizing a redox initiation system. The formation of a covalent network was characterized using both conventional macrorheology and particle tracking microrheology. We describe in particular the anomalous behavior observed for solutions at the critical micellization concentration (cmc). All experiments were conducted at room temperature over a range of concentrations, from 5 to 20 wt. %. Prior to initiating the redox reaction, using shear rheometry, we confirmed that no gel structure existed for all solutions. We also conducted microrheology experiments to confirm the value of the cmc for end-functionalized pluronic copolymer solutions. The resulting cmc (5 wt. % at 25°C) was found to be equal to that observed for the F68 aqueous solutions, suggesting that the end-group functionalisation did not change the aggregation state prior to crosslinking. After adding the redox initiators, the formation of a network as a function of time was monitored, using both macrorheology and microrheology. Above the cmc, the following behaviours were noted: 1.) The concentration of each initiator affects the induction time and the duration of the reaction. 2.) The cross-linking density was highly sensitive to the Pluronic concentration, assumed to be due to the final gel structure being determined by the initial packing state of acrylated Pluronic macromers, which is highly dependent at a given temperature, on the polymer concentration. Microrheology interestingly showed that the mean square displacement (MSD) of the particle tracers as a function of time showed anomalous behavior at a concentration of 5wt. % (i.e. at the cmc). At this concentration, after the covalent network was formed, the hydrogel gradually lost its integrity ('melted') with time and eventually displayed liquid-like behavior. The solution did not recover the gelled stated thereafter. The mechanism at present is unknown but thought to be linked to an induced phase inversion of the pluronic micelles upon crosslinking. Above this concentration, no such transition was observed

Characterization of disentangled polymers obtained from solutions PO66

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Current theories stipulate that flow of polymer melts is due to restricted diffusion in a topological tube in which macromolecular chains reptate; the incidence of the inter-molecular forces between conformers on their mobility is convoluted in the definition of the tube characteristics (diameter, renewal time), and is also reflected in the value of the monomeric friction coefficient, which varies with (T-Tg), but not with M (Tg is a function of M). The tube diameter is associated with Me, the molecular weight between entanglements, and the terminal relaxation time scales with (M/Me)^3.4 . In the present study, we vary M, Me and Tg for a series of polar (PMMA) and non-polar (PS) melts to determine the coupling laws between inter-molecular forces and network entanglement density (rau/Me). For a series of well characterized polymer grades, of various molecular weight (for PS), or Tg (for PMMA, by varying the tacticity and/or the content of EA co-monomers), we vary Me in a controllable manner by swelling in a Theta-solvent, quench-freeze in liquid nitrogen, and remove the solvent by vacuum evaporation, below Tg. Disentanglement of the polymers is varied between 10% and 100% (full dissolution). The dried disentangled samples are produced in sufficient quantity to create testing samples for dynamic rheometry (G', G"), thermal analysis (DSC), and XRD. Other tests will also be reported. Up-quenchs followed by time sweeps in isothermal conditions, at constant w, permit to study the kinetics of re-entanglement, and to deconvolute the influence of inter-molecular coupling and network entanglement density on reptation.

Gelation of regenerated fibroin solution PO67

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Silk fibroin is a high molecular weight multiblock ampiphillic protein known for its ability to form high strength fibers. It is also biocompatible; silk sutures have been traditionally used for many centuries. Recently, there has been much interest in making silk hydrogels for applications ranging from tissue engineering to controlled delivery.1 Fibroin gels are formed from aqueous fibroin solutions by changing one or more of its state variables such as pH, temperature and ionic strength. Since microstructure of firboin gels is the key to developing successful products, we have probed the gelation of aqueous fibroin solutions derived from Bombyx Mori silk using light scattering and rheological techniques. In this work we present dynamic light scattering results and small amplitude oscillatory shear (SAOS) results during isothermal gelation of aqueous fibroin solutions.

On the role of chain defects in governing the microstructure and rheology of thermoplastic polyurethanes PO68

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We have synthesized a series of thermoplastic polyurethanes containing pendent alkyl side chains on the hard segment. We have probed the microstructure of these thermoplastic polyurethanes using SAXS, FTIR, DSC and rheology over a wide range of temperatures. In this work we show that the shorter side chains create defects in hard segment packing and also modulate the hard-soft segmental interactions thereby affecting the microphase separated structure of the polymers. Longer side chains create more interesting microstructures.

Effect of hyaluronic acid on the self assembling behaviour of PEO-PPO copolymers in aqueous solution PO69

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The influence of Hyaluronic acid (HA) on the self assembling properties of Pluronic (PEO-PPO-PEO block copolymers) blends has been studied with the aim of engineering thermosensitive and mucoadhesive polymeric platforms for drug delivery. The gelation temperature (Tgel), viscoelastic properties and mucoadhesive force of the systems were investigated and optimised by means of rheological analyses. Pluronic micellar radius was evaluated by Photon Correlation Spectroscopy (PCS). Moreover in order to explore the feasibility of these platforms for drug delivery, the optimised systems were loaded with acyclovir and its diffusion properties studied in vitro. By formulating Pluronic /HA platforms, at specific concentrations, it was possible to obtain a thermoreversible gel with a Tgel close to body temperature. The addition of Low Molecular Weight Hyaluronic acid did not hamper the self assembling process of Pluronic just deleting the gelation temperature of few Celsius degrees. Furthermore the HA presence led to a strong increase of the Pluronic rheological properties thus indicating possible HA interactions with micelles trough secondary bonds, such as hydrogen ones, which reinforce the gel structure and consequently improve its rheological properties. These interactions could also explain the PCS results which show, in systems containing HA, aggregates with hydrodynamic diameters values much higher than those of Pluronic micelles. The mucoadhesion experiments showed a rheological synergism between Pluronic/HA and mucin dispersion which led to a change of the flow behaviour from a quite Newtonian one of the separate solutions to a pseudoplastic one of their mixture. In vitro release experiments indicated that the optimised platform was able to prolong and control the acyclovir release for more than 6 hours.

Bio-Rheology

Time dependency of non-linear rheological properties of colloidal gels in biopolymer solutions PO71

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The time dependency of the apparent yield stress of colloidal silica networks in biopolymer solutions has been investigated using shear stress overshoot tests. Samples were pre-sheared at a fixed strain rate and allowed to equilibrate for a set amount of time, teq. A step-strain-rate was then imposed on the sample causing it to yield and the resulting overshoot stress was recorded for various teq and applied strain rate values. The thixotropic restructuring time was calculated for the colloidal gels as a function of particle concentration in two different biopolymer solutions, CMC and Xanthan. The magnitude of the overshoot stress was found to increase significantly upon aging in both cases, and the restructuring time varied from 30min to several hours depending on particle concentration and on the nature of the background fluid. The observed variations are explained by the change in mobility of particles in different biopolymer solutions which has a profound effect on the viscoelastic recovery of the colloidal silica network formed in each case.

Tuning of tissue engineering hydrogel material properties PO72

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Synthetic extracellular matrix hydrogels can be used for three-dimensional cell culture, wound repair, and tissue engineering. Thiol-modified hyaluronic acid and thiol-modified gelatin can be cross-linked into biocompatible materials and used to aid the development and repair of cells and tissues. The material properties of these hydrogels contribute to their usefulness in a given application. For example, the stiffness of a gel used to aid in bone reconstruction must be much higher than that of a gel used to prevent abdominal tissue adhesions. In addition, the physical properties of materials used as tissue engineering scaffolds help determine cell phenotype and stem cell differentiation. Hydrogels with a wide range of stiffness have been synthesized from a few components in variable concentrations and characterized rheologically. The dependence of oscillatory shear modulus on these composition variables will be discussed.

Preparation and shear modulus of polyacrylamide gels as nerve cell culture PO73

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In the recent years, physical interactions between cells and their mechanical environment have been recognized for their influence on cellular functions, such as differentiation, motility, and growth. The importance of this phenomenon on neural cells is being investigated here in order to evaluate the optimal mechanical environment for their maximum growth. We prepared polyacrylamide gel as a culture medium for the nerve cell growth. Since we hypothesize that the shear modulus of the medium, which is fully saturated with water, plays an important role in the cell growth, we prepared gels having different shear modulus by varying the ratio of the polymerizing agents and the thickness of the medium was controlled by molding. It is the key issue to determine the shear modulus of the gels to study the effect of the modulus on the nerve cell growth. However, because the physical properties of the gels should be measured when those are saturated with water, but there should be no water layer on the surface to prevent slip in rheometers, new techniques were developed to dissolve these issues. This poster will present those rheological techniques, preparation of the gels, and the effect of shear modulus of the gel medium on the growth of nerve cells.

Effect of DNA sequence and DNA chain conformation on DNA assisted dispersion of single wall carbon nanotubes in aqueous medium PO74

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Oligonucleotides with alternating G and T base sequence is shown to be excellent molecules to disperse and debundle single wall carbon nanotubes in aqueous medium. In This study we report dispersion of SWCNTS with range of of oligonuecleotides with different base sequence including polyA, poly(AC), Poly(GT) and Poly(T) and with number of bases ranging from 10 to 30. The characterization of the SWCNTs dispersion is carried out using UV-vis-NIR spectroscopy and photoluminescence spectroscopy. The relative ability of different types of oligoneucleotides to disperse SWCNTs can be related to the chain conformation of oligonucleotides. The chain conformation of Oligonucleotides will be studied using circular dichroism spectra and small angle neutron scattering.

Cell attachment on new fibrous PET structures for vascular grafts under controlled shear stress PO75

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Nonwoven fibrous structures made from polyethylene terephthalate (PET) fibers with diameter in the 1-10 µm range showed promising results as vascular graft, with adequate biocompatibility, attachment and biomechanical features. While the ability of human brain endothelial cells (HBEC) and human aortic smooth muscle cells (AoSMC) to attach and proliferate on such PET fibrous structures under quiescent conditions has been already demonstrated, additional testing under simulated blood flow conditions remains to be performed to ascertain the cell attachment under such constraints. The measuring chamber and the associated spindle of an Anton-Parr rheometer have been modified to accommodate for visual inspection of the cell attachment under controlled shear conditions at human body temperature. The fluid being sheared has been chosen to mimic closely the viscoelastic properties of human blood, while maintaining optical clarity to enable visibility of the cells attached to the PET structure using on-line microscopy. Sterilization of the blood analogue components, xantham gum and glycerol, was necessary for the biocompatibility with human cells, and the impact of the sterilization step was evaluated with regard to the end-rheological response. We report here the development of the optical/rheometry platform as well as the rheological results related to the blood analogue with respect to composition and sterilization. Preliminary results regarding the cell attachment on the PET graft under a wide range of shear stresses are also reported.

Designed textures from plant material PO76

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Different processing conditions to disrupt vegetables and decompose plant cell wall material will be utilized to investigate the influence of concentration, particle shape and size distribution of insoluble cell wall material on product rheology. Furthermore the partitioning of soluble cell wall polymers in the final product as a function of processing conditions and their influence on the microstructure of processed vegetables will be determined.

Plant food dispersions are mixed systems formed of a continuous phase (serum) and a dispersed phase (pulp). The serum is a liquid phase containing different pectic materials, sugars, salts and organic acids. The pulp is formed by cell wall materials and other parts of the plant such as skin and seeds. The heterogeneity in size, shape and composition makes it difficult to analyse the rheological properties of these products.

In the past it was thought that the main component having an effect on the rheological properties of these materials were the soluble solids in the continuous phase, mainly the pectic substances. However nowadays it is known that the insoluble solids and even more the ratio soluble-insoluble is an important parameter determining the rheological properties. They are defined as shear thinning materials with a yield stress.

Different measurement systems have been used to characterise the viscoelastic properties of the plant food dispersions. A comparison between the two preferred geometries, these are Couette geometry with rough surfaces and a vane with the same dimensions, was performed in order to select the measurement system which will give reproducible results. The vane has been widely used in the literature as the best geometry to characterise the rheological properties of materials with a yield stress. The comparison has been carried out on systems with different particle size and concentrations.

Different heating and shear processes, including high pressure homogenization, have been applied on three vegetables and fruit (carrot, broccoli and tomato). The rheology and microstructure of the resulting dispersions have been characterised. Oscillatory small deformation measurements were carried out on the samples after a pre-shearing and a resting step. The apparent viscosity has been measured on shear rate sweeps. The microstructures have been characterised by confocal scanning laser microscopy (CSLM) and scanning electron microscopy (SEM). The different botanical origins lead to different ways in which the material is disrupted having a significant effect on the final mechanical properties of the products.

Rheology and gelation temperature of aqueous gelatin and sodium alginate solutions PO77

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The rheology and gelation of biodegradable polymers, such as gelatin and sodium alginate, are of particular interest in the processing of films in the pharmaceutical industry. Constant stress temperature ramps were used to determine the thermotropic gelation temperature (T_{gel}). The effect of operating parameters, such as stress and cooling rate, and formulation parameters, concentration and pH among others, on the gelation temperature will be presented. The steady-state rheology above T_{gel} was experimentally measured. Time-temperature superposition and concentration shifting were used to obtain master curves for the steady-state viscosity. It was found that simple phenomenological models may be used to describe the master curves.

Rheological studies of polylactide degradation PO78

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Polylactide (PLA) is a biodegradable polymer which is synthesized from lactic acid which, in turn, is produced from renewable natural plant sources. Polylactide has been known for many decades and is becoming an increasingly popular material for packaging, medical and engineering applications. Therefore the importance of degradation studies of polylactide under processing and end use conditions can not be overestimated. Numerous, sometimes contradictive mechanisms had been proposed to describe polylactide degradation. In this work we aim to shed more light on the most important degradation factors (including temperature, oxygen, humidity, amount of residual oligomer and catalyst) using a rheological technique. We have found that in the absence of oxygen, zero shear viscosity, decays following a single exponential until reaching a limiting value. In the presence of oxygen this single exponential decay is accompanied by a linear term related to the oxygen. These observations indicate the existence of two different degradation mechanisms which can easily be quantified using rheological studies. Additionally, by performing multiple frequency sweeps over many hours under different atmospheres we have obtained the entire relaxation spectra of the polymer at different stages of degradation. This information will be combined with known techniques for estimating MWD of polymers from LVE properties allowing further detailed analysis of degradation mechanisms. Finally, torsion measurements on solid samples will be performed to study the degradation at temperatures between the glass transition and the melting point which represent some end use conditions.

Characterizing the non-linear rheology of biopolymer networks using inertio-elastic oscillations PO79

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Accurately characterizing the non-linear rheological properties of materials is an important challenge. Although there exist a variety of methods to probe non-linear properties, there is no consensus regarding their unique advantages. We demonstrate the usefulness of using inertio-elastic oscillations to measure non-linear material properties. Inertio-elastic oscillations occur naturally in rotational rheometry as a consequence of a material's elasticity and the inertia of the rheometer's bearing. It is well known that these oscillations can be used to effectively characterize linear viscoelastic properties. We demonstrate that extending this technique to non-linear deformations provides accurate measurements of non-linear material properties. Our experiments are performed on fibrin networks, which are well-characterized, and have dramatic non-linear properties that are biologically significant. To verify the accuracy of non-linear measurements from inertio-elastic oscillations, we compare these results to other standard methods of probing non-linear rheology, namely a pre-stress differential test, a geometric interpretation of large amplitude oscillatory shears, and an extension of the linear viscoelastic moduli to the non-linear regime. Our measurements suggest that inertio-elastic oscillations provide the most straightforward method of distinguishing between non-linear elasticity and dissipation at any given non-linear stress.

Superdiffusive motion with fractional power-law exponents PO80

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The spontaneous random motion of microbeads bound to the cytoskeletal network of living cells is a non-Brownian process. The mean-squared-displacement (MSD) of the beads as a function of lag time shows a sub-to-superdiffusive transition that arises from the interplay of uncorrelated noise, dominating at short time scales, and persistent traction forces, dominating at longer time scales. The fractional power-law exponent of the superdiffusive bead motion in the range from 1-2 is unexplained, however. We propose an analytically solvable model for the cytoskeletal dynamics that accounts for superdiffusive behavior with fractional power-law exponents. The cytoskeleton is described as a network of elastic, force-generating springs (stress fibers) undergoing gradual changes of rest length and stiffness due to ATP-driven processes. In addition, new fibers emerge spontaneously, generating an increasing and finally saturating prestress that is coupled to the reinforcement of focal adhesions. The fiber growth process is catalyzed by enzymes which constitute a limited, shared resource of the cell. We demonstrate that superdiffusion with a fractional power-law exponent arises naturally by a multiplicative noise process. Our model accounts quantitatively for the MSD data and the exponential distribution of prestress in mature stress fiber populations.

The measurement of thickened liquids used for the management of dysphagia PO81

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Dysphagia is a condition where an person has difficulty in swallowing. This can lead to reduced dietary intake, dehydration and malnutrition and also aspiration of material into the lungs and asphyxiation. Regular fluids require excellent muscle control and accurate timing between the swallowing system and the breathing system. Using thickened fluids slow the act of swallowing and by doing so enhance safe swallowing. A common method of thickening drinks is to use a powdered thickener, but this can lead to problems in ensuring that the consistency of the degree of thickening appropriate to an individual is maintained by those making up the fluids. The degree of thickening can be time dependent and also change with different beverages (sometimes the manufacturers indicate different amounts of thickener for different drinks, but often they do not). There is also no assurance that the thickness of thickened liquids is consistent across commercial manufacturers. In this field viscosity is typically measured using a Line Spread Test, with the resulting viscosities being described by such terms as nectar- honey- or pudding-thick. This test is also prone to many variations in operating conditions and so cannot provide accurate reproducible data.

In this paper we have used conventional rheology (dynamic oscillatory using a couette cell) to provide quantitative measurement of the development in thickness of various beverages as a function of time. A frequency of 50 s-1 was used as this is commonly associated with the swallowing process. It was found fruit juices typically required less thickener and milk more to achieve the same thickness. The thickness of the beverages reached a plateau after about 15 minutes. Pre-prepared commercial thickened fluids were used as viscosity standards to determine the actual viscosity corresponding to the various thickness levels. In other studies comparing the Line Spread Test and oscillatory rheology we have found that whilst some correlation between the methods exists, the Line Spread test fails to distinguish variations in yield stress between different formulations. These therefore highlight the need for a more formal definition of viscosity in this area and application of rheological techniques in this area.

Characterizing microstructure of biofilm formed from *Pseudomonas aeruginosa* using particle tracking microrheology PO82

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Biofilm is complex aggregate of microorganisms surrounded by the slime they secrete. It is composed of bacteria, void and extracellular polymeric substances (EPS). Bacteria induces biofilm by producing extracellular polymeric substances at surface. Because biofilm prevents flow of material, people are paying more attention to removing biofilm from the surface, for example, that of medical devices like catheter and prosthetics. To remove biofilm effectively, understanding developing mechanism and mechanical properties of biofilm is essential. There have been studies on measuring mechanical properties of biofilm using conventional rotational type rheometer. However, in this case, the microstructure of biofilm could be destroyed during oscillation. Also, with this kind of bulk rheology the heterogeneity of biofilm structure cannot be characterized, nor the developing process of biofilm cannot be observed. Therefore, to overcome these disadvantages particle tracking microrheology was suggested as a novel method. Biofilm was induced directly from bacteria which is attached to glass surface. During developing biofilm, fluorescence particles were added to biofilm and the particles which were dispersed in biofilm were tracked on the microscope. Rheological properties of biofilm such as elasticity, modulus and heterogeneity could be evaluated in developing process using the movement of particle. As a result the modulus from particle tracking microrheology was less than that from conventional rheometer. Additionally, the effect of flow rate of nutrient that supplies bacteria with oxidation and food was considered on developing process.

Alkali and acid solubilization effects on rheological properties of horse mackerel muscle proteins 💿 PO83

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Surimi is a wet concentrate of myofibrillar proteins that has been processed to remove bones, fish oil and fish flavour, the process consumes a large amount of water and typically results in a yield of as low as 20% to 30%. In order to improve this efficiency another method has been proposed based on the protein solubilization, when fish muscle proteins are solubilized by acid or basic treatments followed by centrifugation and isoelectric precipitation, most sarcoplasmic proteins can be recovered in addition to the myofibrillar proteins. Therefore, this technique results in higher protein recovered than the conventional surimi process, and allows significant reduction of concentration of fish lipids in the recovered protein, the reduction in membrane lipids enhances final product oxidative stability. Proteins are solubilized by adjusting the pH of a protein water mixture away from the isoelectric point of the proteins targeted for recovery myofibrillar proteins. For acidic solubilization the final pH is 2 to 3, and for alkali solubilization is 10 to 11. The aim of this work is to evaluate the influence of the acid and alkali solubilization in the viscoelastic properties of raw surimi and gels made from horse mackerel (Trachurus trachurus) muscle. Samples of this study were the following: surimi A and gel GA, and surimi B and gel GB elaborated by acid and alkali solubilization respectively, both methods A and B with 4% sorbitol + 4% sucrose as a cryoprotectant and neutralized at pH 7. Rheological properties were analysed using a Bohlin CVO and RS600 Haake rheometers. Stress and frequency sweep tests showed that raw surimi paste from method B presents higher viscoelastic moduli, lowest values of phase angle and minimum viscoelastic moduli dependence with frequency than surimi A. These results are in agreement with the fact that the recovered protein from alkaline treatment could show less lipid content than those from de acid treatment, allowing this way, an increase of protein-protein interaction that could explain the greater firmness and hardness of samples B, showing a more compact network structure. Starting from temperature sweep test at a constant frequency, since viscoelastic moduli behaviour with temperature, it could be deduced a less protein denaturation in surimi B. From static (creep and recovery) and dynamic tests (stress and frequency sweep), gels developed from alkali solubilization resulted in higher gel strength and more rigid network than those from acidic pH. The less structural quality of GA gels is likely due to the more protein denaturation and the more lipid content on the raw surimi as compared to alkali treatment. This superior effect on gelation of alkaline processing is consistent with the findings of others who noted alkali-processed surimi made from Pacific whiting, croaker or catfish, produced gels with higher breaking force and deformation than surimi prepared by acid process.

Blended solutions of celluloses from different biological origins 💿 PO84

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Solution properties of celluloses from different biological origins were investigated mainly in terms of rheological properties in 8 wt% LiCl/amide solutions. The solution viscosities were proportional to the a-th power of the polymer concentrations. The exponent, a, were 3, 4, and 7.5 for the solution from bacterial, wood and cotton, and tunicate cellulose in the semi-dilute regions, respectively. These celluloses were blended to get solutions having various molecular weights and molecular distributions of the polymer. The high molecular weight component, tunicate cellulose: $M_w = 4.13 \times 10^6$, had remarkable effect on the long-time region of the viscoelastic functions of the blends. The weight fraction dependence of the zero-shear rate viscosity of the blends can be expressed by a linear mixing relation based on Ninomiya theory. The zero-shear rate viscosities of the blends are proportional to the 5/2-th power of the weight-average molecular weight calculated from a linear combination of that of each component. This indicates that the zero-shear rate viscosity of the cellulose blends depends strongly on the molecular weight but scarcely on the molecular distribution.

Winged helix transcription factor CPCR1 controls fungal arthrospore formation in *Acremonium chrysogenum* PO85

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The filamentous fungus *Acremonium chrysogenum* is exploited industrially for the production of the ß-lactam antibiotic cephalosporin C. The fungus is cultured worldwide and yields around 2,500 tons of cephalosporin derivatives annually. In the production of cephalosporin C by *A. chrysogenum* on an industrial scale, the fungus is being cultivated in a complex medium with dextrose and different plant oils as the major carbon sources. The alternative carbon sources, such as methyl oleate, soybean oil, and rice oil, are used for commercial cephalosporin C production to minimize catabolite repression. There have been few studies of the effect of alternative carbon sources on cephalosporin C systhesis, and it is not clear how plant oils affects physiological characteristics of *A. chrysogenum*. *A. chrysogenum* produces four morphological cell types that represent stages in the growth cycle: hyphae, arthrospore, conidia, and germilings. In the ß-lactam producer *A. chrysogenum* the differentiation into athrospores coincides with the maximum rate of cephalosporin C biosynthesis. However, the molecular mechanisms controlling hyphal fragmentation and arthrospore formation remain mostly undefined. The biosynthesis of cephalosporin C consists of six enzymatic steps, which are catalyzed by six enzymes. The transcription level of the biosynthesis genes greatly controls titres of antibiotic production. Interestingly, in *A. chrysogenum*, no comparable amplifications of structural genes were detected in strains with increased cephalosporin C production level. Therefore, transcription factors seem to be important mediators of internal and external parameters affecting ß-lactam biosynthesis. Recently, transcription factor CPCR1 involved in secondary metabolism has functionally characterized from *A.chrysogenum*. The CPCR1 protein binds to regulatory sequences in the promoter region of the cephalosporin C biosynthesis genes pcbAB-pcbC. In this study, morphogenesis, transcription factor CPCR1 and biosynthesis genes (pcbAB and pcbC) were investigated for CPC production. During cultivation of *A. chrysogenum* in the culture media containing linoleic acid, significant differentiation into arthrospores were observed by image analyzer in submerged batch cultures. The biosynthesis genes which produced CPC biosynthesis enzymes were expressed at exponential phase, respectively. However, amount of CPCR1 bound to regulatory sequences site, were higher than control during early exponential phase. Therefore, it was demonstrated that linoleic acid was first known regulator of transcription factor CPCR1 in *A. chrysogenum* and that the CPCR1 protein bound in promoter sequence of cephalosporin C biosynthesis genes. However, biosynthesis genes were not directly involved in cephalosporin C production by linoleic acid in *A. chrysogenum*.

Ocean rheology and plankton biology PO86

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The mechanical properties of the air, the land and the sea determine the rates of most environmental processes. Seawater, an aquatic solution of inorganic salts and dissolved organic matter (DOM), also contains colloidal and particulate organic matter (OM). Leaving aside important standard measurements of Newtonian viscosity, the rheology of ocean waters can be divided into three components: 1 bulk (or compression) rheology; 2 2D rheology of surface films, in either compression or shearing, principally at the air-sea surface; 3 constant-volume rheology of the bulk phase (in shearing, elongational/squeezing, conduit-flow and turbulent deformation).

As well as providing insights into the molecular structure of seawater, bulk viscoelasticity determines the propagation of sound. Alemán et al (2006, J Non-Newt Fluid Mech, 133:121) reviewed ocean bulk viscoelasticity, so this presentation will concentrate on components 2 and particularly 3.

The physical properties of the surface film are modulated by the hydrophobic, bipolar and buoyant components of exopolymeric secretions (EPS) mainly of phytoplankton. It influences air-sea gas exchange, ripple and gravity-wave production, and entrainment of air-bubbles down into the sea and both spray and aerosols up into the atmosphere.

Except for the major salts, the bulk phase of ocean waters is dilute (typically =~6 g m^{-3} DOM). Its measured viscoelastic excess shear modulus G_E (i.e. excess to that provided by the solvent) is likewise small, typically =0.5 mPa even in exceptional phytoplankton blooms. We have measured differences in G as small as 10^{-7} Pa (Jenkinson, 1993, Oceanol. Acta, 16:317). The dynamic viscosity of the aquatic phase (water and salts) is within a factor of 2 of 1 mPa·s. So in calm surface waters of an Adriatic summer or in vast parts of the ocean interior, where shear rates are typically c. 10^{-3} s^{-1}, G equal to 0.5 mPa represents a 500-fold increase.

Viscosity in the ocean is heterogeneous, shown by visible marine organic aggregates (MOAs) and transparent exopolymeric particles (TEP), stained for acid polysaccharides. Cm-scale variation in viscosity associated with more diffuse OM has been measured (Seuront et al 2007, Biogeochem, 83:173). Sinking of MOAs modulate removal of C fixed from CO_2 by phytoplankton towards burial on the seabed. Rheology-mediated floc break-up modulate this biogeochemical C flux. Rheology also modulates rates of encounter between plankton predators and prey as well as between sexes, either by making it harder to swim or by changing the characteristics of turbulence.

Special aspects of ocean rheology include: 1) coral mucus and reef dynamics; 2) mucus events particularly in the Northern Adriatic, 3) the killing of fish by algal mucus reducing gas exchange at their gills in harmful algal blooms and in algae-rich intertidal organic fluff. We will show in a poster how we investigated the last topic with ichthyoviscometers.

Flow-induced morphologies of highly concentrated collagen solutions PO87

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Collagen molecules form a major part of the extracellular matrix where they are assembled into ordered fibrous networks. When placed in a low pH solvent molecular collagen solutions spontaneously transition at a critical concentration from an isotropic state to a liquid crystal. These liquid crystalline solutions exhibit a distinct rheological behaviour which is characterized by tumbling and flow-aligning effects. For instance, at intermediate shear rates in steady state flow the first normal stress difference becomes negative due to the so called tumbling of the rodlike collagen molecules. The relations between flow and morphology development were used to induce homogeneously aligned cholesteric bands by means of a flow-controlled deposition process. For this purpose collagen solutions of different concentrations were injected into thin flow-channels installed within polymer matrices. The morphology, in particular the degree of orientation and the thickness of the bands is mainly influenced by the flow rate, the line speed of the used robotic arm and the concentration of the collagen. Furthermore, the channel width plays an important role in terms of confinement effects and desiccation rate. The produced three dimensional collagen substrates can be used as templates for many bodily tissues.

Suspensions and Colloids

Deformable particles in dilute suspensions: A numerical investigation of particle segregation and the depleted layer PO89

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Particle deformation affects the flow properties of suspensions, as seen for instance in microcirculatory blood flow. Deformable red cells migrate toward the center of vessels, creating a cell-depleted layer of plasma near the vessel walls. In the microcirculation, this effect leads to a reduction of the blood viscosity relative to the bulk. Previous experimental studies in microchannels demonstrate that manipulations of this effect can aid in plasma separation. A more detailed understanding of the underlying mechanisms may aid in the development of even further clinical and diagnostic applications.

We present a numerical study designed to investigate the phenomenon of the particle-free layer in more detail. Deformable particles and drops are known to migrate away from a channel wall in a shear flow. Deformation also introduces irreversibility into the hydrodynamic interactions between particles in shear flow, causing a migration across streamlines. A numerical investigation of the flow of deformable particles through a channel shows that the competition between wall migration and cross-stream diffusivity creates a particle-free layer near the channel wall. The governing parameters for the thickness of this layer are the particle deformability, volume fraction, and the ratio of particle size to channel size. We extend the study to include multiple particle species with varying size and deformability, and investigate the effect of added parameters including the particle size ratios and volume fraction ratios. Under certain conditions, the addition of particle species may enhance the segregation of particles by size and deformability.

The application of melt linear viscoelastic properties in determining the role of organoclay's modifier on microstructure development of PP/PA6/organoclay nanocomposites PO90

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Effect of Organoclay's Modifier on distribution selectivity of organoclay in the blend components and microstructure development of nanocomposite blend samples was studied. The PP/PA6/PPgMA/Organoclay samples with the same composition (68/17/10/5) but varying in organoclay modifier (Cloisite15A, Cloisite30B) and prepared by diffrent feeding order were considered. The nanocomposite samples were prepared by the melt compounding consisting of the melt blending and melt intercalation process in a laboratory internal mixer. The XRD results showed greater extent of melt intercalation for PP/Organoclay nanocomposites containing Cloisite 15A compared to the samples with Cloisite 30B while a reversed trend was found for PA nanocomposite samples with these two organoclays. A prounounced low frequency nonterminal behavior in storage modulus along with viscosity upturn were observed for the blend nanocomposites containing Cloisite 15A whose extent increased by the presence of compatibilizer whereas a behavior similar to simple blends (PP/PA6) was found for blend nanocomposites with Cloisite 30B. These results indicated that in the case of PP/PA/Cloisite15A samples, although a portion of organoclay can be preferentially distributed in PA dispersed droplet, a fraction of organoclay in the form of tactoids or individual platelets may also be conveyed into interphase and/or in the PP matrix; the process which can enhance organoclay intercalation and improving the microstructure development. However, in nanocomposites samples containing Cloisite30B due to strong affinity between PA and Cloisite30B, the organoclay will mostly remain in PA droplets and could hardly transfer into PP matrix even in the presence of compatibilizer. SEM results showed smaller PA particle size in PP/PA6/ Cloisite15A nanocomposite samples compared to that in PP/PA simple blends and PP/PA6/ Cloisite30B. This could be attributed to interfacial enhancing between PA and PP matrix caused by Cloisite15A. The hindrance effect of highly aspect ratio platelets in reducing the coalescence of droplets could also play a role in decreasing PA dispersed phase. It was demonstrated that the order of feeding play a significant role in determining the nanocomposite blend morphology and the extent of microstructure development in PP/PA/Organoclay nanocomposite samples.

The bulk viscosity of concentrated suspensions PO91

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Suspension flows can lead to variations in particle volume fraction, thus making the particle phase compressible on a macroscopic scale. The stress in such a flow is characterized by an effective bulk viscosity (κ_{eff}) in addition to the effective shear viscosity of the suspension. The bulk viscosity of a suspension of particles relates the deviation of the trace of the macroscopic or averaged stress from its equilibrium value to the average rate of expansion. The equilibrium stress is the sum of the fluid pressure and the osmotic pressure of the suspended particles. Variations in particle volume fraction can be modeled by having a compressible fluid expand uniformly at a constant rate, causing the particles suspended in it to move apart. The rigid particles cannot expand, and create a disturbance flow that contributes to the total mechanical pressure in the system, thereby changing the effective bulk viscosity.

Explicit formulae have been derived to compute the bulk viscosity for all volume fractions of suspended rigid particles and for all expansion rates. To leading order in volume fraction (ϕ) it is shown that the particles contribute $4/3\eta\phi$ to the effective bulk viscosity, where η is the shear viscosity of the fluid. At higher concentrations the expansion flow drives the suspension microstructure out of equilibrium and is resisted by the thermal motion of the particles which acts to restore the particle microstructure. The hydrodynamic forces between particles including the strong lubrication interactions near contact play an important role at high concentrations. The bulk viscosity of concentrated suspensions with full hydrodynamic interactions is determined via direct simulation by adapting the Stokesian Dynamics paradigm to allow for a uniform rate of expansion. Brownian Dynamics simulations are performed to calculate the bulk viscosity of concentrated suspensions at the other extreme of no hydrodynamic interactions for comparison.

Rheological influence of synthetic zeolite on cement pastes PO92

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Self compacting concrete (SCC) is characterised by the capability to be compacted into every corner of a formwork without vibrating systems and only by means of its own weigh, therefore it must have proper flowability under a low applied stress (related to the weight) and adequate viscosity to avoid large particle segregation, maintaining a good "stability". These characteristics are strictly related to the rheological properties of the cement adopted in concrete preparation and they are usually obtained by means of proper additives such as superplasticizers, viscosity modifying admixture and fine materials. The requirement for increased fine content in SCC is usually met by the use of limestone, dolomite, fly ash, silica fume, glass or quartzite filler. However, recently, the use of zeolite, both synthetic or natural, is becoming interesting due to the high performances that they seems able to give to SCC. Concrete properties are strongly affected by characteristics of the fresh cement paste that is the continuous phase dispersing larger aggregates. Therefore, aiming to characterise mechanical properties of final concrete is relevant to know rheological properties of the base cement paste. In this work cement paste for SCC preparation were prepared by using, as additive, synthetic zeolite 5A in different amounts; cement samples were characterised by dynamic tests in linear viscoelastic conditions and complex modulus as frequency function was analysed by the weak gel model, aiming to relate fundamental rheological parameters to zeolite content. It was found that weak gel parameters, interactions strength A and network extension z, are qualitatively related to macroscopic properties like workability or apparent yield stress and an optimal zeolite content was found as a good compromise between high viscosity (relevant to avoid coarse particle sedimentation) and proper flowability (necessary to ensure the flow without vibrating systems). Experimental data obtained by using zeolite were compared to rheological properties of cement paste prepared using traditional additives such as silica fume or limestone, confirming the positive effects of zeolite. Finally, concrete properties were studied by traditional empirical tests and their results were compared to cement paste rheological parameters obtaining a good correlation.

Electrical dependence on dynamic strain for CB/SEBS and GP/SEBS composites PO93

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Carbon black (CB) and Graphite (GP) were embedded in poly(styrene-ethylene/butylene-styrene) (SEBS) to form CB/SEBS and GP/SEBS composites. The electrical and dynamic mechanical properties of the composites at different concentrations were examined and compared. The electrical resistivity of the composites decreased dramatically by increasing the CB and GP content, at 8% and 14%w, respectively. It was found that CB composites present lower resistivity and percolation threshold than GP composites. The dynamic modulus during dynamic strain sweep decreased upon increasing strain amplitude in composites with particle concentration up to the electrical percolation threshold, showing the Payne effect. During the in situ correlation between resistivity and dynamic storage modulus the resistivity increased at deformations higher than 1%, for CB composites this change was bigger than for GP composites. The composites close to the electrical percolation threshold showed the biggest change in the resistivity.

Influence of water content on the flow behavior of PVC Plastisols PO94

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Plastisols are suspensions of mainly poly-vinyl-chloride (PVC) particles in a hydrophobic plasticizer with a particle volume fraction of about 50%. Chalk particles are often added as a cheap filler. Plastisols are used as stone-chipping and corrosion protection. To process plastisols their rheological properties have to be adjusted in a given range. An unsolved problem therefore is the strong variation of the rheological properties between apparently identical batches. Using a simplified but relevant formulation it could be shown that the rheological properties of plastisols are extremely influenced by the water content. For example, the yield stress increases by a factor of one hundred when 0.5% water is added. The influence of water content on viscosity and yield stress was correlated with the particle size distribution and the agglomerate structure of the filler. We found neither the particle size distribution nor the structure of the agglomerates are the primary reason for the extreme influence of water content on the rheological properties of plastisols. The water is insoluble in the hydrophobic plasticizer and we assume an adsorption of water on the contact area between adjacent PVC particles and thus an increase of the contact forces between the particles. The extreme influence of the water content on the rheological properties of PVC plastisols opens new possibilities to control yield stress and viscosity, both quantities are essential for processing of plastisol formulations.

Rheology of nanoparticles suspensions in hydroxypropylcellulose (HPC) solutions PO95

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The effect of nanpoparticle shape and concentration on the rheology of isotropic and liquid crystalline solutions of hydroxypropyl cellulose (HPC) has been studied experimentally. Multi-walled carbon nanotubes (MWCNT) were dispersed by ultrasonification in HPC/m-cresol solutions, while commercial aqueous colloidal nanosilica suspensions (LUDOX) were mixed with HPC in water. The liquid crystalline phase behavior was identified by rheological measurements of the viscosity and optical microscopy of the solutions. Scaling arguments for the steady-state viscosity and the dynamic viscoelastic moduli will be presented. The effects of dispersion methods are also addressed.

Direct visualization of structural rearrangements in sheared confined colloidal suspensions PO96

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Our recent study on confined hard-sphere colloidal suspensions demonstrates that glass transition can be observed `sooner' as film thickness approaches a critical value while volume fraction remains constant. In this talk, we present a new study of the rheological properties of strongly confined colloidal thin films by using a home-designed micro-rheometer interfaced with a confocal microscope. We visualize the shear-induced structural relaxation at a single particle level and measure the rheological properties of confined colloidal thin films between two surfaces at narrow gap spacing ranging from 50 μm to 1 – 2 μm. Recently, we have observed and quantified the unique rheological properties of our confined colloidal thin films. For a volume fraction of $\phi = 0.53$, we observe plastic rearrangements at low strain amplitudes yet shear thickening behavior at higher strain amplitudes. To the best of our knowledge, we provide the first direct experimental evidence and quantification of structural rearrangements which govern shear thickening in colloidal systems. Additionally, we characterize the patterns, size and lifetimes of dynamical heterogeneities in the limit of low strains undergoing plastic deformation, and correlate their behaviors to the measured rheological properties of our confined suspensions.

Strings microstructures in sheared suspensions of spheres in viscoelastic liquids PO97

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Solid suspensions are widely used in industrial applications. Examples are the manufacturing of filled polymer composites, paints and coatings. The addition of particles leads to a change in the rheological properties of the fluid as well as in the flow fields. Many experimental results show that particles suspended in a non-Newtonian fluid can arrange themselves into various structures. In particular it is reported that the formation of particle strings or cluster depend on the imposed flow and on the nature of the suspending fluid. This work is focused on the investigation of string formation in a simple shear flow. In such a flow, experimental observations show that the particles align along the flow direction and then they chain one to each other. We have implemented a finite element code to simulate the behaviour of such a suspension in order to verify the stability of these structure formations. The rigid-body motion is imposed on the particle surface through constraints, i.e. the force and torque-free conditions are automatically satisfied. The analysis is carried out for a Newtonian fluid and for different viscoelastic medium in order to study the impact of the nature of the fluid on the structure formation.

Extensional flow and electric conductivity of carbon nanotube dispersed system 💿 PO98

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The carbon nanotubes were mixed with photopolymer and acetone by using an ultrasonic homogenizer, and then the acetone was vaporized from the dispersed system. Silver micro particles were added to the photopolymer in order to generate high electric conductivity. The diameter of the carbon nanotubes added were a few nanometers, and the characteristic scale of the silver particles is 1 to 5 micrometers. The shapes of the silver micro particles added were spheres and flakes. The temporal change in the electric conductivity was measured under a shear flow by using an electric resistance meter and a parallel plate rheometer. The volume fraction rates of the carbon nanotubes and the silver micro particles were changed, and its influence on the electric conductivity was investigated in this dispersed system. The dispersed system was solidified under the extensional flow by an ultraviolet light. The break-up surface of the stretched filament was observed by a scanning electron microscope. The orientation and the dispersion of the carbon nanotubes were discussed.

Rheological properties of binary suspensions TiO_2/Al_2O_3: Effect of ionic strength 💿 PO99

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Ceramic coatings are usually appreciated for their resistance to wear and to corrosive and thermal damage. Since ceramic dielectric materials are brittle, if the applied stress exceeds their breaking strength, they will crack. This situation depends upon the ceramic material, the thickness size, the termination materials, and defects within the ceramic structure. It is well known that ceramic coatings obtained from binary systems, such as titanium dioxide and alumina enhance their mechanical properties. Colloidal processing techniques are widely accepted to provide a powerful route to improve the reliability of ceramic materials. However, particle aggregation is still a particular problem encountered during the colloidal treatment, especially when two or more powder particles having different isoelectric points (IEP) coexist in suspension. Electrostatic attractive interactions are more likely to occur between particles when the surfaces are dissimilar, so mutual aggregation of the components of mixed suspension systems is a principal factor determining their rheological properties, which are related to the green micro-structural development and subsequent sintering behavior of the product. Although much is known about the role of ionic strength in promoting flocculation or stabilization of colloidal particles in slurries, this role is not always easy to quantify, especially for the oppositely charged ceramic oxide particles. Nevertheless a relevant study about the effect of electrolyte on rheological behavior will be beneficial for understanding the phenomena and the trends that occur in such a multicomponent situation, since the rheological behavior of colloidal systems is a function of the range and magnitude of the interparticle forces. Thus, the aim of the present work is to compare the influence of ionic strength on rheological properties of TiO_2/Al_2O_3 suspensions at different volume fractions, and solid particle composition (1:1, 2:1, 1:2). The relative ratio of titania to alumina particles is important in determining the dispersion of the binary suspension with salt addition. In the case of systems containing the same number fraction of dissimilar oxides, the colloidal stability is mainly governed by the aggregation, as can be seen from the higher values of the stress in the flow curves and the yield stress values compared with those obtained in 2:1 and 1:2 situations. An attempt to provide a clearer picture concerning the stability determined by delicate balance between the van der Waals, and electrostatic, as well as the possible mechanisms of this balance tuned by environmental conditions has also been made.

Simulation of particulate suspension system under electric field PO100

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The effect of electric field on the hydrodynamics of charged particle system was studied by self-consistent particle simulation. Under weak external electric field region, motion of charged particles can be expressed by electrophoresis. Combining the microscopic particle dynamics and the macroscopic flow simulation self-consistently, the fluid-particle interaction was taken into account. External electric field was obtained by solving Laplace equation of electric potential. As we impose different electric potentials on the boundary of the simulation domain, various non-uniform electric fields were prepared. The hydrodynamics induces local and global structures of particles, which were analyzed by 2D Fourier transform and 3D pair distribution function. We investigated the relation between structures of particles and external electric field. Also, we applied the external electric field to the contraction flow, and the vortex of contraction flow was suppressed and enlarged by various electric fields. The electric field makes electrophoresis of charged particle and changes the hydrodynamics. We present probabilities to control vortices of contraction flow by external electric field.

Shear induced brush deformation of soft colloids: Hybrid mesoscale simulations and Rheo-SANS experiments PO101

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The deformation of a soft colloid by external shear fields crucially depends on its "degree of softness"and the applied Weissenberg number. ($Wi = \gamma \tau_c$, with γ the applied external shear rate and τ_c the characteristic internal relaxation time of the deformable particle.) Here we compare results obtained with multiparticle collision dynamics simulations (MPC) and Rheo-SANS experiments for dilute solutions of regular star polymers (the limiting ultra-soft colloid). To achieve large Weissenberg numbers we use high M_w polybutadiene (PB) star polymers dispersed in a PB oligomer matrix. We found excellent agreement between theory and experiment with respect to onset and amount of shear induced brush deformation for star polymers with varying functionality f. Moreover, from MPC simulations we found that with increasing functionality star polymers exhibit a crossover in their flow properties from those of linear polymers to a novel behavior, which resembles the tank-treading motion of elastic capsules [1].

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Rheological properties and transfer phenomena of nanofluids PO102

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This study focused on the synthesis of stable nanofluids and investigation of their rheological properties and transfer phenomena. Diamond/ethylene glycol nanofluid, alumina/transformer oil nanofluid and silica/water nanofulid were used in this study. The diamond nanofluid and alumina nanofluid were produced by mixing the nanoparticles with base fluid before sonication. The silica nanofluid was synthesized by sol-gel process. Rheological properties of diamond nanofluids were determined at constant temperature (25^{o}C) using a viscometer and a rheometer. For the convective heat transfer experiment, alumina nanofluid passed through the plate heat exchanger. CO_2 absorption experiment was conducted in a bubble type absorber containing silica nanofluid.

Diamond nanofluid showed non-Newtonian behaviors under steady-shear flow except the case of very low concentration of solid nanoparticles and had viscoelastic properties which were dependent on concentration of nanoparticle. At the highest shear rate, the relative viscosity increased with concentration of nanoparticle.

The heat transfer coefficient of alumina nanofluid was higher than that of basefluid. One possible reason is that nanoparticles migrate to the center of pipe quite slowly and concentration of nanoparticles at the wall side is higher than that at center of pipe. Therefore, the thermal conductivity at wall side increases with increasing addition of nanoparticles.

Silica nanofluid showed that both average CO_2 absorption rate during the first 1 minute and total absorption amount enhanced than those of base fluid. The stably suspended nanoparticles creates a mesh-like structure. That structure arrangement cracks the gas bubble and increases the surface area at constant surface tension. It makes CO_2 absorption rate increased. From Kelvin equation, difference of pressure between inside and outside of bubble increases as bubble size becomes small. Large difference of pressure made solubility increase. Therefore, both CO_2 absorption rate and total absorption amount enhanced in nanofluid.

Impact and spreading of a particle-laden drop on the solid substrate PO103

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We present a numerical simulation technique of the impact and spreading of a particulate droplet on the solid substrate in 2D. The motivation is industrial inkjet printing that has become an acceptable technology for delivering a small amount of materials to a desired position in wide variety of applications such as the flat-panel display, PCB and manufacturing DNS chips. We consider the impact and spreading of a droplet that just after hits on a flat solid surface. We used a fixed Eulerian mesh for the entire computation. Inertia is applied on an initially stationary droplet just for one time step for acceleration to achieve a certain initial velocity. We used the 2nd-order Adams-Bashforth / Crank-Nicholson method to solve the Navier-Stokes equation and employed the level-set method with the continuous surface stress for description of droplet spreading with interfacial tension. The distributed Lagrangian-multipliers method has been combined for the implicit treatment of rigid particles and the discontinuous Galerkin method has been used for the stabilization of the interface advection equation. We focus in this work on 2D droplet problem on a solid surface. We investigated the droplet spreading by the inertial force and discussed effects of the presence of particles on the spreading behavior using an example problem. We present droplet spreading and recoiling on the solid surface. We report reduced oscillation and spread for the particulate droplet, compared with d droplet of pure fluid.

This work was supported by the grant No.R01-2006-000-10267-0 from the Basic Research Program of the Korea Science & Engineering Foundation, 2nd stage of BK21, and NURI project

3D Monte Carlo simulations of internal aggregate structures in a colloidal dispersion composed of rod-like particles for application of large magneto-rheological effect PO104

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We have treated a suspension composed of ferromagnetic rod-like particles with a magnetic moment normal to the particle axis in order to investigate aggregation phenomena of such a suspension by means of cluster-moving Monte Carlo simulations. In the present study, we have considered a three-dimensional mono-dispersed model system composed of such rod-like particles. Internal structures of self-assembled clusters have significant influences on rheological properties of such a suspension under circumstances of an applied magnetic field. Hence, these self-assembled clusters have been discussed quantitatively in terms of radial distribution, pair correlation, etc. Rod-like particles tend to aggregate to form raft-like clusters along the magnetic moment direction more significantly with magnetic particle-particle interactions. In such raft-like clusters, the direction of each particle axis has a tendency to incline in parallel formation, but is not so parallel as in a two-dimensional dispersion. For the case of strong magnetic particle-particle interactions, sufficiently long raft-like clusters are formed along the magnetic field direction, even if the influence of an external magnetic field is of the same order of that of the thermal energy. However, rod-like particles in such clusters do not necessarily incline in significantly parallel formation along a certain direction. Self-assembled tube-like clusters are formed when magnetic particle-particle interactions are much more dominant than the rotational Brownian motion under circumstances of rod-like particles inclining in a certain direction.

SAXS studies on the agglomerative silica suspension under shear PO105

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The rheological properties of colloidal suspensions depend to inter-actions between solid particles and medium. Within such suspensions, the particles form a network above a certain volume fraction. And this structure will be broken under shear. In this study, the agglomerative silica suspension were studied using rheometry and small angle synchrotron X-ray scattering (SAXS) experiments under shear and static conditions. SAXS measurements under shear were performed at beam line BL08B2 of SPring-8 in Japan. A three-dimensional paracrystal theory has been used. Comparing the scattering profiles obtained for the silica suspension, the sizes of the paracrystals were calculated and it was decreased with the increase of the shear rate. The theory combined with the change of the paracrystals size also was adopted to explain the rheological properties of colloidal suspensions.

The concentration effect on the rheological behavior of bauxite slurry PO106

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The rheological behavior of mineral settling slurries is a complex and an important matter for minerals industries. Several processes, as milling, dewatering and pumping, are affected by rheological properties. In this work, a bauxite slurry was analyzed using a rotational rheometer, with cylindrical and vane geometries. It was observed that the slurry behavior inverted, changing of thixotropic to rheopetical, as the concentration increased. The flow resistance decreased abruptly as we could observe in flow curves, at lower shear rates. The mineral characterization was performed using X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF) and particle size distribution (PSD). The advantages and limitations in using both geometries are discussed.

Rheological behavior of an epoxy resin with hollow glass microspheres PO107

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Since the end of the 1970s there has been a strong increase in the use of composites consisting of hollow glass microspheres in resin matrices in underwater structures. With the increasing research and exploitation of offshore natural resources, these composites began to be used in more sophisticated structures such as pipelines and hulls of mini-submarines for deep underwater inspection. This present paper reports the results of a study on the rheological behavior of an epoxy resin and hollow glass microsphere system. Glass microspheres, with different diameters and densities, were used. The system was composed by 100 parts of an epoxy resin diglycidyl ether of bisphenol-A (DGEBA), 13 parts of a triethylene tetramine (TETA), as a hardener, and glass microspheres. The present work provides an equation to relate the system viscosity and the microsphere volume fraction, and studies the influence of microsphere volume fraction, type of microsphere, hardener mass fraction and temperature - independent variables - on the viscosity and gel time - dependent variables - of this system. A full factorial design 33 was carried out, considering microsphere volume fractions of 10, 30 and 50%, types K46, S22 and K15 of microspheres from 3M Company, hardener mass fraction equals to 5, 13 and 20%, and curing temperatures equal to 30, 60 and 90oC. Gel time was considered here as the time when the resin system viscosity reached 5.000 Pa·s. All linear and quadratic terms of the analyzed factors were statistically important, at 5% of significance. When the microsphere volume fraction, the hardener mass fraction and the curing temperature increases, the gel time decreases. The most important variable was temperature, followed by hardener mass fraction and microsphere volume fraction.

Spatio-temporal behavior of dipolar nano-rods under shear: Shear induced polarization PO108

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The flow properties of nano-rods are strongly affected by the dynamical behavior of molecular alignment. A theoretical description can be made by an relaxation equation [1] of the order parameter tensor. For plane Couette flow geometry the model leads to a rather complex orientational and flow behavior [2]. Depending on the model parameters and the boundary conditions various types of flow like shear banding can occur. To describe suspensions consisting of dipolar nano-rods that can form clusters with an effective polarization the relaxation equation has to be extended. In [3] the coupling of the orientation and the dipole moment was investigated for the bulk system. The additional dipole moment strongly affects the orientational dynamics. In this contribution we study a spatially inhomogeneous tensor model. In the plane Couette flow geometry nano-rods without dipole moment can show a pulsating local spurt effect [4]. That is connected with strong gradients of the orientations. Here we show, that for dipolar nano-rods this strong gradient gives rise to a dynamical polarization of the fluid, even if in the equilibrium the fluid has no average dipole moment.

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Thermal conductivity and rheological properties of nanofluids PO109

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Nanofluid is a colloidal suspension of nano-sized particles dispersed in conventional heat transfer fluids. Nanofluids show the increase of thermal conductivity compared with conventional heat transfer fluids such as water and ethylene glycol. The enhancement of thermal conductivity of nanofluid depends on particle size, particle shape, properties of particle and base fluid and volume fraction of particles. And rheological properties of nanofluid are also related to the above factors strongly. Thermal conductivities of nanofluids containing alumina (D=44 nm, D/L=10nm/70nm) and titania(D=50nm, D/L=25nm/75nm) in water (or EG) were measured by using the transient hot-wire method. The experimental result shows that the increases in the thermal conductivity and the viscosity with the concentration of nanoparticles have strong similarities regardless of the shape of nanoparticles. Especially the thermal conductivity and the zero-shear viscosity of the nanofluid made from rod-like particles have the same functional form from dilute to semidilute regimes. The present results will shed light on the elucidation of the mechanism of the heat transfer enhancement of nanofluids.

Yielding in concentrated suspensions of plate-like (kaolinite) particle PO110

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Kaolin is the clay mineral which has a plate-like geometry and surface charge heterogeneity such that the face of a kaolin particle has a negative surface charge, but the edge shows a pH dependent charge profile. Because of the shape and the complex surface charge, concentrated kaolin suspension exhibits complex time dependent nonlinear rheological behavior. In this study, the effect of the change of microstructure under shear on the nonlinear rheological behavior of concentrated kaolin suspensions was investigated. A stress controlled rheometer (AR-G2) and a strain controlled rheometer (ARES) were used for oscillatory stress sweep, oscillatory strain sweep. In these experiments, the linear visco-elastic response of the kaolin suspensions was observed to be very short. While G' and G" both increased as a function of time, the strain decreased as a function of time irrespective of whether the applied stress was less than or greater than the vane yield stress in the oscillatory stress sweep. In the oscillatory strain time sweep, the shear stress and G' increased as a function of time. From these results, it can be inferred that the inner structure of the kaolin suspension is changed by shearing, even under conditions where the applied stress is less than the yield stress measured by the vane technique.

Interactions between aggregated particles in Stokes flow PO111

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The study of aggregating systems in a fluid suspension often uses the *collision efficiency* as a rate parameter governing the probability of particle-particle adhesion. This is the probability that a given particle, moving past a second particle because of a differential in weight or electric charge, will adhere irreversibly to the second particle. It is typically calculated using the interaction between two spherical particles for simplicity.

Many naturally or industrially occurring particles may be roughly spherical, or well approximated as such; but when two such particles collide, the resulting doublet is far from spherical. In order to continue calculations after aggregation has begun (for instance using population dynamics) it is desirable to have an empirical rule for selecting the effective radius of such a doublet aggregate.

In this paper we investigate the interaction between an isolated sphere and an aggregated doublet, using both an "exact" iterative technique (based on the method of reflections) and the Stokesian dynamics truncation. We compare the two methods briefly to demonstrate the accuracy of Stokesian dynamics for a three-sphere system. Finally we present heuristics for radius selection if our three-sphere system is to be reduced to two spheres of differing radius.

Dynamic and steady shear properties of reversibly cross-linked guar solutions and their effects on particle settling behavior PO112

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The rheological properties of reversibly cross-linked guar ($Mw = 2.2\times10^6$) with borate ion at different crosslinker concentrations were investigated by using a small amplitude oscillatory sweep and steady shear rate measurements. The polymer concentration was fixed at 0.003 g/ml which is above the overlap concentration ($c^* = 0.0005$g/ml) of the guar solution. Four different boron ion concentrations of 31, 62, 93 and 125 ppm were used in this work. The cross-linked solutions exhibit both shear thinning and elastic characteristics under oscillatory and steady shear measurements even at crosslinker concentration as low as 31 ppm. The complex viscosity-frequency data are satisfactorily described with a Carreau-Yasuda type equation. The dynamic results agree qualitatively with the trend of a single time constant Maxwell model. By using the Cox-Merz rule, the first normal stress coefficient (Ψ_1) and the first normal stress difference (N_1) of the samples can be estimated from the dynamic shear data. A transparent Couette cell was used to study sedimentation behavior of particles suspended in the reversibly borate cross-linked guar solutions under simple shear conditions. Dynamic settling results reveal that both shear thinning and elasticity of the suspending fluid can affect settling rate, defined as the motion of the suspension-supernatant interface with time. For a lightly crosslinked sample, the settling rate increases rapidly with increasing the imposed shear rate; by contrast, the settling rate decreases for a highly crosslinked sample. The opposed behaviors with respect to shear rate of these settling phenomenon can be attributed to the differences in the network structure induced by ionic interaction between polymer chains, and the associated manner in which elasticity is developed under imposed shear. Full-field images of the Couette during a settling experiment show clearly the development of a non-homogeneous particulate structure during sedimentation in a highly crosslinked sample. Extended particulate structures form in the direction of gravity for the zero-imposed shear experiment (static settling), and in the shearing direction for the dynamic settling experiment. Such microstructures are not found with a Newtonian suspending fluid where sedimentation is commonly found to be in homogeneous fashion.

Rheological behavior of silica suspensions in aqueous solutions of associating polymer PO113

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Associating polymers are hydrophilic long-chain molecules containing a small amount of hydrophobic groups. In aqueous solution, the associating polymers in which the hydrophobes are incorporated as terminal groups form flowerlike micelles beyond a critical micellar concentration. When the polymer concentration is increased, two flowerlike micelles are connected by bridging and finally a three-dimensional structure of transient network is constructed over the system. Then, the aqueous solutions are viscoelastic fluids. The additions of small amounts of associating polymer cause the viscosity increase of silica suspensions. The intrinsic mechanism is the flocculation by polymer bridging. In general, polymer adsorption is essentially irreversible, because the polymer chain may attach to the surface at several points and may not be able to desorb simultaneously from all sites. The bridges between particles are not broken in a quiescent state, but progressively broken in shear fields. As a result, the flow of flocculated suspensions is shear-thinning. The shear-thinning profiles observed for suspension containing associating polymer at low concentrations can be explained by the irreversible bridging. For suspensions prepared with associating polymer solutions in which the associating network is developed, the viscosity decreases, shows a minimum, and then increases with increasing particle concentration. The flow changes Newtonian flow from shear-thinning at this time. The viscosity decrease may arise from the breakdown of associating network due to adsorption of polymer chains onto the silica surfaces. In these suspensions, the excess polymer chains can remain as nonadsorbed coils in solution phase. The adsorption sites on the silica surfaces may be fully occupied by segments of hydrophilic backbone. But the chain adopts a conformation with the hydrophobes extending into solution. The dangling ends of the adsorbed chain can make aggregation by associating interactions with hydrophobes of nonadsorbed chains. Thus, the particles can be connected by the multichain bridging. Since the associating interactions are very weak, the particle-particle bonds are forming, breaking, and reforming by thermal energy. Since the dynamic structures of flocs are not influenced by shear rate, the flow is Newtonian. As the particle concentration is increased, the polymer concentration in solution is decreased and finally all polymer chains are adsorbed on the surfaces. Then, the viscosity shows a minimum. Beyond this point, the partial coverage of particle surfaces with polymer takes place and strong interactions between particles are generated by polymer bridging. Since the stable suspensions are converted to highly flocculated systems, the viscosity is increased and the flow becomes shear-thinning. The concentration effect of silica particles on the viscosity behavior of suspensions can be explained by a combination of viscosity decrease in solution due to polymer adsorption and viscosity increase due to flocculation.

Electrorheology of poly(ethylene glycol) suspension PO114

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The electrorheological (ER) effect is defined as a reversible change of viscoelastic properties on the application or removal of electric field. When DC high electric field is applied to poly(ethylene glycol) (PEG) particle suspension, chain networks between two parallel plates can be observed with the naked eye and yield stress is detected. However, the ER effect of PEG suspension is different from that of general particle suspensions. For example, when the stress becomes higher than some value, the plate started rotating fast, chain networks are broken, and the shear rate increases suddenly, i.e. PEG suspension shows yield stress but does not behave as a Bingham fluid. Furthermore, a lot of particles aggregates at the negative electrode and yield stress did not change even though particle was added.

Thus, PEG suspension shows unique ER effect, but ER study of PEG suspension is not done well. We studied molecular weight (MW), temperature, and particle size distribution dependences of ER effect for neat PEG suspensions. PEG3k (MW = 3,000) and PEG20k (MW= 20,000) were crashed by ball mill, and the others were crashed by homogenizer. In particular, PEG1k (MW = 1,000) and PEG1.5k (MW = 1,540) were crashed with cooling. Crashed samples were sifted out by a sieve (75 µm mesh). In the case of MW > 3,000, yield stress of high molecular weight PEG becomes weak and that of PEG2M (MW = 2.0×10^6) disappears. It can be thought that low molecular weight PEG has many end groups and interparticle interaction becomes strong.

However, the yield stress of PEG1k and PEG1.5k suspensions were much weaker than that of PEG3k. The melting point of low molecular weight PEG is close to room temperature (~310K for PEG1k and ~320K for PEG1.5k) and these are soft compared to the higher molecular weight PEG. Therefore we measured temperature dependence of ER effect for PEG3k at 293-323 K, and the yield stress became higher as temperature became higher. Although PEG3k softened, yield stress was not decreased.

For PEG1k and PEG1.5k, the rate of small particles (< 10 µm) was much lower than that of others and particle size distribution was narrow. So we sifted out PEG3k by a sieve (20 µm mesh) and measured ER, yield stress disappeared (but particle chain networks were observed). Small sieve makes powder which has narrow particle size distribution and chain network becomes weaker than powder which has wide distribution.

Force induced microdiffusivity of colloidal particles PO115

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In constant force microrheology the velocity of the probe particle fluctuates owing to interactions with the surrounding medium. On long time scales, this fluctuating velocity gives rise to a diffusive motion of the probe particle. We study this diffusive motion as the Peclet number, Pe - the ratio of the strength of the external driving force, F^{ext}, compared to thermal forces, kT/a - is varied. Here, kT is the thermal energy and a the probe size. At small Pe Brownian motion dominates and the diffusive behavior characteristic of passive microrheology is recovered. At the other extreme of high Peclet numbers the motion is still diffusive, and the diffusivity becomes 'force-induced' scaling as F^{ext}/η, where η is the viscosity of the solvent. Specific calculations are performed for a probe particle of size a immersed in a background of colloidal bath particles of size b. The diffusive motion becomes increasingly anisotropic as the Peclet number is increased - motion parallel to the direction of forcing exceeding that transverse. The 'force-induced' microdiffusivity is compared with the analogous 'shear-induced' diffusivity found in macrorheological measurements.

Structure, dynamics, and rheology of biphasic colloidal mixtures PO116

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We investigate the structure and dynamics of biphasic colloidal mixtures composed of coexisting attractive and repulsive microspheres by confocal microscopy. Attractive gels formed in the presence of repulsive microspheres are more spatially homogeneous and, on average, contain fewer interparticle bonds per particle than their unary counterparts. The repulsive microspheres within these mixtures display heterogeneous dynamics, with some species exhibiting freely diffusive Brownian motion while others are trapped within the gel network during aggregation. We also characterize the rheological properties of biphasic mixtures under both shear and compressive flow. Remarkable differences are observed in the volume-fraction dependent elastic properties relative to pure colloidal gels. This novel route for tailoring gel structure and bulk properties provides a new paradigm for designing concentrated colloidal inks for direct-write assembly of 3-D structures.

Rheological/morphological study of PS/CNT nanocomposite electrospun fibers PO117

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This work depicts rheological characteristics of Polystyrene (PS)/Carbon Nanotube (CNT) nanocomposite solutions and their incidence on the morphological properties of final electrospun fibers. Nanocomposite fibers were obtained through electrospinning of PS/Di-Methyl Formamide (DMF) solutions containing different concentrations and types of Carbon Nanotubes. CNTs were dispersed by sonication followed by continuous mixing. Viscometry technique was employed to evaluate the rheological properties of the initial solution. The morphology of the fibers at different concentrations and types of CNTs was studied using Scanning Electron Microscopy (SEM) and Optical Microscopy. Correlation between initial CNT dispersion and final fibers morphologies was obtained using viscometry results and optical microscopy of initial solutions. The results obtained show that beads presence in the fibers are due to nanoparticles agglomerations. A styrenic copolymer (Styrene-Butadiene-Styrene, SBS-Kraton) was employed as a compatibilizing agent to improve CNTs dispersion instead of chemical modification. Addition of copolymer affects both final fiber morphologies and CNT dispersion condition.

Rheology modification in mixed shape colloidal dispersions PO118

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We report the results of a comprehensive study of the rheological properties of a series of mixed colloid systems where the shape of one of the components has been varied systematically. Specifically we have measured the oscillatory, transient (creep) and continuous steady shear flow behaviour of a 2.5 wt% dispersion in water of a well-characterised hectorite clay modified by the addition of a series of aluminasol colloidal particles whose shape varies systematically from rod (boehmite) to platelet (gibbsite) to sphere (alumina-coated silica), all having essentially the same smallest dimension which is similar to that of the hectorite. The mixtures and the pure components show the same general behaviour, displaying a complex 'yield space' transition from an elastoviscous gel at low applied stresses to a viscous, weakly elastic, shear-thinning liquid at high stresses. The unifying theme of this work is that the addition of 0.25 wt% of the minor component in all cases results in dramatic enhancements to the dispersion rheological properties. At the same time the magnitude of this effect depends on the shape of the particles. Shear moduli, low stress viscosities and effective yield stresses all increase in the additive order rods < platelets < spheres, with enhancements for the latter being up to a factor of 500 and typically 20. At the same time the critical failure strains for the gels decrease in the same order – the strongest gels are also the most fragile in this sense. The poster summarises the physicochemical factors underlying this behaviour and gives the basis of a simple qualitative model. While no complete explanation or model can be proposed at this stage, the study provides a quantitative model-system baseline for mixed colloidal dispersions already used for industrial applications (e.g., oilwell drilling fluids) and suggests ways in which such fluids may be optimised and controlled.

Effect of composite ceramic paste velocity profile on extrudate microstructure PO119

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Composite ceramic materials prepared from the homogeneous mixture of basic components having the optimal properties exhibit high mechanical strength. Preparation of composite ceramic body having a high and uniform density in the body volume is necessary precondition of proper technological processing of the mixture. Uniform microstructure and optimal particle distribution along with their orientation in the matrix volume are necessary for the anisotropic particles to have a positive effect. The objective of work was to indicate the possibilities of controlling the microstructure in composite ceramic body at extrusion process in relation to the resulting mechanical properties of the final material. The method of mathematical modeling for the flow of composite ceramic paste through an extruder die was used to express the effect of forming parameters on the arising microstructure of composite body. The orientation of the anisotropic particles can be influenced by the character of velocity field at the flow of composite ceramic paste through the circular extruder die. The velocity field established at flow of ceramic paste can be described by a mathematical model of the non-Newtonian liquid flow provided its constitutive equation is known. The parameters of this mathematical function can be generally determined from the dependence of shear stress on the shear rate obtained by capillary viscometer method. The velocity profiles of the flow of ceramics paste through the circular extruder die were calculated from a mathematical model and compared with experimentally determined profiles. The assumption about the influence of the velocity field on anisotropic particle orientation during paste flow was confirmed by a comparison of the evaluated anisotropic particles distribution with the corresponding shear rate profiles. A mathematical model of the paste flow allows controlling the conditions for reaching various required orientations of particles ranging from randomly oriented structure within the entire bulk up to structure having oriented particles at the surface layer of the body. The model enables to control preparation of composite ceramic materials to suit specific applications. The various orientations of the particles and their combinations enable control over directional mechanical strength of composite ceramic materials.

Enzo-rheology: Investigations of high-solids biomass slurries for bio-refinery applications PO120

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The enzymatic digestion of cellulosic biomasses, such as corn stover and switchgrass, to create biofuels, such as ethanol, is economically competitive only when working at high solids fractions. Therefore, the production of cellulosic ethanol involves working with high-solids slurries, which are notoriously difficult to transport due to their high viscosity, requiring large, powerful pumps. As a result, it is particularly important to understand the rheological properties of these slurries. In this work, we examine the rheology of high-solids biomass slurries as a function of the critical variables for biorefining. Acid hydrolyzed corn stover slurries were investigated and found to exhibit properties characteristic of soft solids, including an apparent yield stress and shear thinning behavior. Rheological properties were examined using vane-in-cup and parallel plate geometries. To avoid slip, a serrated cup was used with the vane, and roughened surfaces were used for the plates. Squeeze flow experiments were also conducted to further characterize the slurries' rheology. Shear thinning behavior and an apparent yield stress on the order of 1000 Pa were observed, and the Herschel-Bulkley model was used to characterize the data. Rheological properties of the slurries were also measured during enzymatic hydrolysis. Interestingly, preliminary measurements suggest that viscosities do not decrease monotonically with the degree of cellulose conversion (digestion time). An attempt was made to correlate the slurries' rheological properties with the enzymatic hydrolysis of cellulose and the molecular interactions between the slurry particles. Thus, "enzo-rheology" combines enzyme kinetics, rheology and microscopy to capture the breakdown of fibrous cellulosic biomasses and the processability of the slurries.

Shear induced alignment of multi-walled carbon nanotube dispersions via small angle x-ray scattering 💿 PO121

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We report small-angle x-ray scattering studies of shear-induced alignment of multi-walled carbon nanotube (MWCNT) dispersions. Uncured epoxy was used as a viscous, Newtonian suspending medium, and samples were prepared from 'aligned' MWCNTs using methods previously reported (Rahatekar et al., J Rheol 40:599, 2006); here we emphasize measurements on rather dilute dispersions. Flow-induced alignment was studied in both the flow-gradient (1-2) plane, and the flow-vorticity (1-3) plane using, respectively, annular cone and plate and rotating disk x-ray capable shear cells. Small-angle x-ray scattering patterns were rendered anisotropic under application of shear flow. Measurements in the 1-2 plane indicate that the average MWCNT orientation direction is intermediate between the flow and gradient directions. Transient studies of structure evolution were done performed at low shear rates where high flux synchrotron radiation enabled sufficiently rapid data acquisition. These results are complemented with mechanical rheological characterization to help understand the relationship between rheology and MWCNT alignment during shear flow of these samples.

Rheology measurements of a biomass slurry: An inter-laboratory study PO122

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The conversion of biomass, specifically ligno-cellulosic biomass, into fuels and chemicals has recently gained national attention as an alternative to the use of fossil fuels. Current biochemical conversion processes in research and development typically use high concentrations of water and hence low concentrations of biomass solids. Increasing the concentration of the biomass solids has a large potential to reduce the cost of conversion. These concentrated biomass slurries have highly viscous, non-Newtonian behavior that poses several technical challenges to the conversion process. A collaborative effort to measure the rheology of a biomass slurry at four separate laboratories has been undertaken. The biomass slurry is dilute-acid pretreated corn stover provided by the National Renewable Energy Laboratory. A comprehensive set of rheological properties were measured using several different rheometers, flow geometries, and experimental methods. The tendency for settling, water evaporation, and wall slip required special care when performing the experiments. The rheological properties were measured at different solids' concentration up to 20% insoluble solids where the viscosity is on the order of 10^5 Pa-s. The slurry was found to be strongly shear-thinning, thixotropic, and to have a significant yield stress. The elastic modulus was found to be almost an order of magnitude larger than the loss modulus and independent of frequency. The results of this work will be useful in the development of biochemical conversion processing steps that operate at high solids' concentration.

Stress relaxation of carbon black filled rubbers under various deformation modes PO123

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The nonlinear stress-strain behaviors of filled elastomers are significantly time-dependent. The understanding of the time-dependent nonlinear elasticity of filled elastomers still remains incomplete. In this study, the stress relaxation behaviors under various types of deformation (equibiaxial stretching, pure shear and uniaxial stretching) have been investigated for carbon black filled styrene butadiene rubbers (SBR). The curves of the stress relaxation components $\Delta\sigma_\mathrm{i}(\lambda_1,\lambda_2 t)$ (=$\sigma_\mathrm{i}(\lambda_1,\lambda_2 t)$ - $\sigma_\mathrm{i}(\lambda_1,\lambda_2 t_{eq})$ where :t_{eq} is the equilibration time) along the principal axes (i = 1,2) under various deformations at a certain principal ratio (λ_1) were reduced to a single curve by the vertical shifts with arbitral degrees in the double logarithmic plots of $\Delta\sigma_\mathrm{i}(\lambda_1,\lambda_2, t)$ versus t. The similar superposition was also successful for various λ_1 (λ_1 = 1.1 - 2.5). These results indicate that the time-dependence of $\Delta\sigma_\mathrm{i}(\lambda_1,\lambda_2, t)$ is independent of the type of deformation, principal ratio, and principal axis. Thus the stress relaxation components are described by a separable form of deformation- and time-dependent terms. The normalized relaxation function $\psi(t)$ that decays from unity to zero corresponding to the beginning and end of stress relaxation is more useful than $\mu(t)$ for further analysis: $\psi(t) = \Delta\sigma_\mathrm{i}(t) / \Delta\sigma_\mathrm{i}(t_i)$. It is of significance that $\psi(t)$ universally describes the time dependence of stress for all types of deformation. This simplifies the full description of the time-dependent nonlinear elasticity of filled elastomers: The form of the strain energy density function considering the time effect $\mathrm{W}(\lambda_1, \lambda_2, t)$ (=$\mathrm{W}(t)$) is simply expressed by $\mathrm{W}(t) = (\mathrm{W_i} - \mathrm{W_{eq}})\ \psi(t) + \mathrm{W_{eq}}$. The functions $\mathrm{W_i}$ and $\mathrm{W_{eq}}$ are the strain energy density functions in the short and long time limits, respectively, that can be estimated from the stress-strain data under various deformation modes in the corresponding time regions.

Development and validation of a mixed rheological model for magneto-rheological suspensions PO124

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The paper presents a rheological model for magneto-rheological suspensions in variable magnetic field. Our model blends a pseudoplastic behaviour (Cross model) for small shear rate values with a shear-thinning behaviour (Herschel-Bulkley model) for large shear rates. Blending the two models is achieved through weighting functions (e.g. 1-tanh(x) and tanh(x), respectively) such that a smooth transition between the two type of behaviour is insured. The mixed model is validated against experimental data for MRF, within a range of $10^{-6}...10^3$ 1/sec for shear rate and 0...2 A current intensity in the coil of the Physica MCR300 magnetorheological cell. The main advantage of this new model is that there is no need to incorporate a yield stress at very low shear rate. As a result, it can be easily implemented in commercial codes for flow simulation (e.g. FLUENT), to be used for analysis of magneto-rheological devices. We present such a numerical example for basic shear flows.

Relationship between the rheological and the adhesive properties of cementitious pastes PO125

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We consider the adhesive properties of mortar pastes using the probe tack test. This test is widely used to characterise polymer adhesives, but much less exploited in the case of granular pastes. The tack test consists of measuring the evolution of the normal force required to separate, at different controlled pull off velocities, two plates between which a thin layer of tested material is sandwiched. Here, the general behaviour of the pull off force is the following: it rises, passes through a maximum, and monotonically decreases as soon as the material starts to rupture. The adhesive properties are characterised through two different parameters: the maximum value Fmax of the pull off force and the characteristic time of its decrease tau_r (related the rupture dynamics). These two parameters are related to the rheological behaviour of the pastes, including the yield stress, the fluidity index and the consistency. The influence of the dosage rate of water-soluble polymer additives is considered. Fmax increases when the pull off velocity is increased. This is expected and related to the viscous dissipation effects. The sensitivity of Fmax to the velocity is found to increase with the polymer content. At very low velocities Fmax is found to be almost independent upon the velocity and correlates with the yield stress. This indicates that in this low-velocity regime the origin of the adhesive force is essentially due to the cohesion properties of the paste. Changing the pull off velocity, different rupture modes are observed. At relatively high velocities the rupture mode of the paste is liquid-like, consisting of a single column whose average diameter decreases until full rupture. By decreasing the velocity the number of columns increases, and at sufficiently low velocities a transition to a solid-like (fragile failure) rupture is observed.

Identification method of the tribological properties of concentrated complex fluids PO126

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The identification of the tribological properties of concentrates géo-matérials remains still a way of very open research. Since the shear velocity range is wide, little of data are available. This set of themes of research interests, for example, the problems of excavation of grounds, clay material or cement paste based material extrusion, but also the problems of industrial fishings to the trawl in contact with sea-beds. The rheological behavior of studied materials is generally plastic, visco-plastique and this behavior evolves. The homogeneous character or not, the ability of drainage and consolidation makes the analysis to the interfaces more complex. For relatively low shear velocity ranges and levels of strong pressure, the results available with squeeze flow, ram extrusion, back extrusion technique, ... inform in a relevant way about the tribological behavior of such materials. However, with the aim to widen the prospects for analyses by integrating a high range of shear velocity, a high pressure level and by controlling the effect of roughness, we developed a measurement technique pawn on plan covering a shear velocity range between 0 and 2 m/s. This experimental process and the techniques of experimental data processing make it possible to integrate the rheological behavior and its evolution during the characterization. The sample, in a pasty but fluid state, is conditioned in the shape of a cylinder of cross section circular of weak twinge. One of the end of the sample is placed in contact with an indeformable wall whose movement and roughness are controlled. On the opposed face, a normal loading is imposed and modulated for a given shear velocity. The originality of our technique is due to the possibility of identifying the contribution in friction of the generator of the cylinder for a different given shear velocity and roughness. With this intention, we developed a harmonic system which makes it possible simultaneously to manage the problem of friction on two surfaces of the sample in contact with mobile walls. In this article, we present the architecture of the slotted measuring section as well as the methodology of data processing experimental and the calibration of the system. In a last part, we have the results of tribological characterization of concentrated liquid-solid mixtures composed of materials taken in marine environment (Bay of Quiberon - South of Britany - FRANCE). These materials are sand-muddy natures and a granular behavior is prevalent. For this type of mixture, our results show that the properties of friction obey the law of Mohr-Coulomb. The mixtures tested present a weak cohesive character. Finally the dynamic coefficient of friction is analyzed like a function the shear velocity for imposed conditions of roughness. The results are finally compared with the results obtained in quasi static condition.

Rheology of polyurethane nanocomposite films containing different nanofillers prepared from homogeneous aqueous solution polymerization PO127

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Polyurethane-urea nanocomposites containing reactive diamino-polyhedral oligomeric silsesquioxanes (diamino-POSS) and nanoclay, Cloisite 30B were prepared via environmentally-friendly homogeneous aqueous solution polymerization. The effect of the nanofillers (diamino-POSS and Cloisite 30B) on the viscoelastic, mechanical, morphological and optical properties of polyurethane-urea was investigated as a function of concentration. The POSS and Cloisite 30B were found to be strongly reacted with only the hard segments of PU (urea segment), while the soft segment was not affected by the presence of the nanofillers. This experimental fact was confirmed by the increase in the Tg of the hard segments with increasing concentration of POSS and clay as measured by DSC. Similar rheological measurements performed on the samples in the glassy and rubbery states (-70 to 150 oC) revealed that the storage elastic modulus increased and tand shifted systematically to high temperatures with increasing concentration of the nanofillers only in the high temperature range (i.e., the range of the Tg of the urea segments), while the modulus and tand changed significantly at low temperatures (i.e., the range of the Tg of the soft segments). For the PU/POSS nanocomposite films, the microphase separation temperature of polyurethane (TMPS) was found to be concentration independent when the POSS concentration is 6wt%, however, the TMPS shifted by 30 oC to higher temperature at 10 wt% POSS. In addition, the TMPS was found to be nearly concentration independent for the PU/clay nanocomposite films. For both systems (PU/POSS and PU/clay), the viscoelastic material functions were found to be well described by the time-temperature-superposition principle in a lower temperature range than the TMPS for a given concentration. At higher temperatures the principle just mentioned was no longer valid for all the samples. Furthermore, the TEM microphotographs confirmed that the reacted clay was exfoliated in the PU matrix while the nanoscale size of the POSS in the PU/POSS nanocomposite showed many interaction zones between the hard and soft segments and consequently a finer nanomorphology compared to that of pure PU.

Onset of the rheological fluid behavior in high concentrated suspensions PO128

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The paper is concerned with the rheological modeling of high concentrated suspensions of rigid and deformable particles in Newtonian or weakly elastic liquids. The tested samples are characterized by particles volumic concentration of minimum 40%, the medium dimension of the particles being in the range of 5 to 20 microns . The samples under investigations are emulsions of oil in polyacrylamide-water solutions and normal blood (suspensions with deformable particles), respectively solder pastes and magnetic fluids (suspensions with rigid particles). The dynamics associated to all these samples, which can be included in the category of soft matter, can be qualitatively separated into a deformation process and a fluid motion. The main goal of the study is to investigate, both from experimental and theoretical point of view, the threshold between the two rheological behaviors. In particular, we are interested to model the onset of the shear motion and to determine if the fluid behavior is related to a particular value of the shear stress (i.e. yield stress) or to a critical value of the strain. The wall deplation phenomena associated to the onset of samples flow is also a subject of study in this work. The transitory rheometry of samples is correlated with visualizations during the shearing of the micro-structure in the vicinity of the moving wall and with the local pressure fluctuations recorded on the surface at rest. The proposed continuum model for the modeling of fluid behavior of high concentrated suspension is a differential constitutive relation with time and structure dependences of the objective derivatives for the extra-stress, respectively stretching. The experimental investigations are performed in the Field-Matter Interaction Laboratory with a novel set-up based on high performance rotational rheometer and special designed optical devices. The first results of our investigations evidence the correlation between the formation of shear banding structure in the gap and the onset of flow recorded on the rotational geometry of the rheometer. The proposed constitutive model is capable to reproduce properly this transitory rheological regime, respectively the existence of shear bands simultaneously with the oscillations of stresses and shear rates at the walls. The study is expected to produce value results capable to offer general insights for the flow rheology of high concentrate rigid or deformable suspensions in liquids.

Coupling between contact line movement and evaporation-induced coating in colloids suspensions PO129

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Coating is usually achieved by the drying of a suspension or a solution. Despite the simplicity of drying experiments, the resulting coating or patterning is not straightforward. As in the famous example of a coffee drop, particles accumulation is usually observed during the drying of water solutions. This accumulation is due to the pinning of the contact line to the deposit that is forming and to the singularity of the evaporation rate at the contact line.

We investigate this phenomenon by imposing a velocity to the contact line of colloidal suspensions and polymer solutions. A capillary growth is performed in a Hele-Shaw cell partially immersed in a tank. The drying is achieved with an air flow whose temperature, humidity and velocity are carefully controlled. The contact line is moved by changing the thank level. Thanks to the use of the capillary growth phenomenon, we are able to measure with a very good precision the contact line position and then the pinning force.

First experiments have been performed with a colloidal suspension of silica particles (diameter = 80 nm). The following results have been obtained: At high velocities, the pinning is completely suppressed and the resulting coating is uniform, whereas at smaller velocities, we observe a periodic pinning that leads to very regular patterns. For the studied colloidal suspension in the stick-slip regime (velocities on the order of 10^{-6} to 10^{-4} m/s), we find that the pinning force is proportional to the evaporation rate and to the particle volume fraction, and is inversely proportional to the imposed velocity. However, independently of the experimental conditions, we show that the pinning force is directly proportional to the characteristic slope of the deposit shape, measured a posteriori using AFM experiments. This result leads to the conclusion that the pinning is of geometric origin. Then it is the growth of the deposit characteristic tilt angle that governs the amplitude of stick-slip phenomenon. A phenomenological law for this growth has been determined independently, and accounts for the scaling laws described above.

These experiments are currently performed on polymer solutions. Given the strong dependence of polymer solutions viscosity with solvent content, the corresponding results should lead to some discussions on the role of the rheological properties in the vicinity of a moving contact line.

Squeezing flow of suspensions: Flow regime evaluation from energy approach PO130

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Suspensions containing solid particles, such as fibers, spherical and non-spherical elements, are commonly encountered in industrial processes and products. The flow of concentrated suspensions or granular media is complex and largely influenced by the physical properties of particles, the interaction variety between particles and shear rate. This may induce different flow regimes. The behaviour of concentrated suspensions and granular mixtures is generally investigated from simulations and rheological measurements. Here, the squeezing flow geometry is used to investigate the properties of concentrated suspensions. The suspensions presently investigated consist in idealized system of smooth hard spheres dispersed in a yield stress colloidal gel. With such a material, following the solid volume fraction, the material rheological behaviour ranges from purely viscoplastic fluid to granular media. During the squeezing action, the material structure evolves with energy variation due to particle displacement and interaction. The goal of our study is to identify the effect of energy evolution on the flow properties of suspensions and detect granular contact evolution. The proposed study consists on an energy approach based on the analysis of the global squeeze force and sample height with time. The squeeze force is decomposed in a combination of an average force component and a fluctuating one. This local fluctuating component is investigated from Fourier analysis as a function of solid volume fraction and compression velocity. Results are studied in terms of evolution of the energy distribution during compression and allow the flow regime modification to be evaluated.

Low shear viscosity of concentrated suspensions in salt-free media: Water hydrolysis and CO_2 influence PO131

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An increasing interest is being devoted to the study of the rheology of concentrated suspensions, not only for the arising of new available theoretical models, but mainly because most of the suspensions usually found in industrial applications are concentrated. The rheological behaviour is a key factor regarding quality and control processes of these materials. However, very few theoretical results have been presented for the case of concentrated suspensions that have no ions different than those stemming from the colloidal particles (the added counterions, that counterbalance their surface charge), the H^+ and OH^- ions from water hydrolysis and the ions produced by the atmospheric CO_2 contamination.

We call this kind of systems "suspensions in salt-free media", in the sense that they are deionized all the possible and there is not other salt added during the preparation, although there are actually some ions in it. Striking condensation counterionic effects, which appears in suspensions in salt-free media, can considerably affect the rheological behaviour. In addition, understanding rheology in salt-free suspensions can be applied for the study of suspensions in non-aqueous solutions.

In this contribution, we show some theoretical results corresponding to the electroviscous effect of concentrated suspensions of spherical particles in salt-free media with the only presence of the added counterions, the water hydrolysis ions and the CO_2 ions. In particular, we have studied the influence on the electroviscous coefficient of the surface charge density, the particle volume fraction and the type of added counterions. The water hydrolysis and CO_2 dissociation are described by local chemical reactions which, coupled with the integro-differential Poisson-Boltzmann equation, allow us to find the correct ionic distributions and electric potential around the particles.

The structure control of catalyst layer for polymer electrolyte fuel cell by the preparation condition of catalyst particle suspension ⊛ PO132

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The catalyst layer for polymer electrolyte fuel cell was manufactured by the coating of suspension consisting of polymer electrolyte solution and catalyst particles. Many researchers noted the importance of the structure control of the catalyst layer. In this work, paying attention to the dispersed state of particles in a suspension, the effect of the mixing time in a preparation of suspensions on the structure and performance of the catalyst layer were investigated. As mixing proceeded, the suspension viscosity increased gradually and attained a steady state at the mixing time of 2h. However, the viscosity increased again when the mixing time became much longer. The catalyst layer was manufactured by coating the suspensions on a Teflon sheet and drying in a nearly saturated vapor of the drying solvent. On the surface of the catalyst layer, the aggregate of catalyst particles was observed at a short mixing time. The aggregate became small and its number was reduced till the viscosity became steady. At the condition of excessive mixing time, the cluster, which is quite different from aggregate, could be observed and it suggested re-agglomeration of catalyst particles connected by polymer electrolyte. The inner structure of the catalyst layers manufactured by these suspensions was evaluated by mercury porosimetry. From the pore size distribution, the crack and the void between catalyst particle aggregates were found in a catalyst layer. The size and volume of the crack was decreased gradually as the mixing time increased and it may attain steady at enough long mixing time. On the other hand, the volume of the void increased up to a steady value for the mixing time less than 2h, though its size was almost constant for each suspension. Finally, we prepared the MEA by hot pressing the catalyst layer onto both sides of polymer electrolyte membrane and measured the cell voltage and corresponding current density. The catalyst layers from the suspension with the mixing time less than 4h had almost the same cell performance, although the catalyst layers from the suspension with shortest mixing time had a higher cell voltage than others. This is probably because the catalyst particle aggregate may be broken and the crack was filled by polymer electrolyte when hot pressing. However, at an excessive mixing time condition, the cell voltage became small compared to that of short mixing time particularly at a high current density region. This indicated that poor dispersion of polymer electrolyte and catalyst particles accompanied with re-agglomeration of catalyst particles was deteriorated the performance.

Surfactants, Emulsions and Foams

Multiscale modeling of lamellar mesophases PO135

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An important objective in rheological modeling is to be able to predict the macroscopic rehological properties of a complex fluid from a knowledge of the constituents. It is not possible to span the length scales from the molecular to the macroscale using one simulation technique, and it is necessary to use a hierarchy of simulations comprising the molecular, mesoscale and the macroscale continuum simulations. In this analysis, we analyse how the parameters in the coarse-grained simulations can be obtained from the results of the microscopic simulations for a lamellar mesophase. First, we identify the parameters in the mesoscale simulation based on minimising a free energy functional, and show how they can be obtained from a molecular simulation. Then we analyse how information from the mesoscale simulation can be used to fix the parameters in the macroscale simulation. It is shown that the linear response results predicted theoretically at the mesoscale are in agreement with the simulation results.

Numerical modeling of ferrofluid droplets in magnetic fields ⊛ PO136

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The motion of a hydrophobic ferrofluid droplet placed in a viscous medium and driven by a magnetic field is investigated numerically. The governing equations are the Maxwell equations, momentum equation and incompressibility. Initially, the drop is spherical and placed at a distance away from the magnet. The numerical simulation uses a volume-of-fluid algorithm with a continuum-surface-force formulation for an axisymmetric geometry. The time taken by the droplet to travel through the medium and the deformations in the drop are investigated and compared with experimental studies. The results are of interest in developing a treatment for retinal detachment. A small amount of ferrofluid is injected into the vitreous cavity of the eye and guided by a permanent magnet inserted outside the scleral wall of the eye. The drop travels toward the side of the eye, until it can seal a retinal hole. The time taken for the drop to migrate is thus an important quantity which needs to be predicted, and be relatively short for the feasibility of this procedure.

Rheology and tribology in drilling fluid performance PO137

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Traditionally, great consideration has been given to the rheological characteristics of oilfield drilling fluids. With implications in hole cleaning, pump power, and wellbore stability, this has been done for good reason. However, as the drilling fluids are additionally expected to serve in the wetting and lubrication of the bit/rock interface as well as the lubrication of the potential contact points between drillstring and wellbore, the tribological properties of such fluids are also of interest.

A series of water and invert emulsion drilling fluids were characterized using standard rheological methods for the industry. The same fluids were then analyzed using a novel tribology chamber for the rheometer. Tribological measurements were found to provide differentiation in fluids where little rheological difference had been observed. Additionally, tribological differences were observed in the use of different industry standard additives for improved lubricity of the fluids. Tests were also conducted using a variety of surfaces, including steel/steel and steel/Teflon combinations.

Viscoelastic properties of POSS-styrene nanocomposite blended with polystyrene PO138

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Polyhedral oligomeric silsesquioxane (POSS) are hybrid nanostructures of about 1.5 nm size.(Si) based polyhedral nanostructures are attached to a polystyrene (PS) backbone to produce a polymer nanocomposite (POSS-styrene). Due to its chemical compatibility, it is suggested that POSS-styrene can act as a nano-reinforcement to polystyrene. We have solution blended POSS-styrene with commercial high molecular weight polystyrene and studied the rheological behavior and thermal properties of the neat polymeric components and their blends. The influence of POSS- styrene concentration was investigated and the concentration was varied from 3 wt % up to 20 wt %. Thermal analysis studies suggest that there is phase miscibility between the POSS-styrene nanocomposite and the polystyrene matrix. The rheological characterization showed that the time-temperature superposition principle applies to all blends. The viscoelastic spectra showed a terminal regime and a rubber-like regime. Moreover, the POSS- styrene acts as a lubricating agent to the PS matrix, i.e., there is a reduction of melt viscosity (and rubber moduli) as the concentration of nanofiller increases. The flow activation energy of blends increased gradually with respect to the matrix as the POSS-styrene concentration decreased. POSS-styrene increased the fractional free volume

Coalescence of polymeric drops in a polymeric matrix via head on collision in the presence of insoluble surfactants: Effect of surface diffusivity PO139

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Boundary Integral simulations are used to study the coalescence via head on collision of two viscous drops in a biaxial extensional flow in the presence of block-copolymers which act as insoluble surfactants. The equation of state used, based on mean field theory, is specific to polymeric surfactants. The surface diffusivity is changed within a range appropriate for block-copolymer surfactants. It is shown how small changes in surface diffusivity can greatly alter the coalescence efficiency at low capillary number (measured in terms of non dimensional drainage time), Ca=O(0.001-0.01). Comparisons are made with experimental data [1]. This enable to provide a probable explanation for the experimental finding of a discontinuous transition in the coalescence process that occurs for low surface coverage as the capillary number is increased and the drainage time independence with surface concentration that occurs for higher surface coverage [1].

Simulations are also used to study the coalescence process at higher capillary number, Ca=O(0.01-0.1). In this range, simulations for clean interface drops show that the film drainage is halted [2], whereas in the presence of surfactants coalescence is possible for some range of surface concentration. In particular, contrary to intuition, the critical capillary number for coalescence increases for low surfactant concentration; instead, the film drains and coalescence is possible for high surfactant concentration. This last finding is also very sensitive to surface diffusivity changes.

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Varying blending protocol to realize high-dispersed phase immiscible polymer blends PO140

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Block copolymers, termed compatibilizers, are often added to immiscible polymer blends to improve blending. It is well-known that blending is improved due to a decreased interfacial tension and the ability of the compatibilizer to suppress droplet coalescence. The focus of this work is to exploit the ability of compatibilizers to suppress coalescence to create unusual morphologies in immiscible polymer blends. High dispersed phase morphologies and drop-in-drop morphologies (double emulsions) and were created using specific mixing protocols on blends of poly(dimethyl siloxane) (PDMS) and polyisobutylene (PIB) compatibilized by small amounts of a PIB-PDMS diblock copolymer. Previous work has shown that for this system the compatibilizer suppresses coalescence only if PIB is the continuous phase.

We show that for a specific mixing protocol, a double emulsion is formed when the compatibilizer loading is 0.1%. However, if the compatibilizer loading is increased to 1%, a high dispersed phase morphology is formed using the same protocol. Morphologies with dispersed phase volume fractions up to 70% were created, even when the component viscosities were well-matched. The blends with these morphologies show interesting rheological behavior, e.g. very high viscosities.

Furthermore, under high-stress, rapid mixing, the high dispersed phase blends undergo a phase inversion to simple droplet-matrix blends where the majority component forms the matrix phase. Similarly, when vigorously mixed, the double emulsion sub-drops “leak” from the outer drops, thus reverting to a simple droplet-matrix morphology. We were able to use rheology as a probe to effectively determine whether or not these two, very different transitions in morphology had occurred.

Viscoleasticity and crystalization of PC/mPP nanoblends prepared via in situ polymerization and compatiblization 💿 PO141

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Nanostructured PC/mPP blends with different concentrations have been produced via a simple and versatile method of in situ polymerization of macrocyclic carbonates in the presence of a maleic anhydride polypropylene (mPP). The current method showed that the dispersed phase is phase-separated into a nanostructured morphology of an average diameter as small as 150 nm. The rheological characterization of this system was investigated over a wide range of temperature, shear frequency and, concentration. The viscoelastic behavior of the pure components and blends of concentration less than 40 wt% PC can be well described by the WLF equation. A dramatic decrease in the storage modulus versus temperature at 240 oC for blends of composition = 40 wt% PC was observed and may be related to the order-disorder transition of the formation of graft copolymers of PP-g-PC during the in situ polymerization and compatiblization process. The isothermal real-time crystallization kinetics of mPP in the blends with different concentrations was investigated rheologically by monitoring the variation in the elastic modulus, G' with crystallization time at different crystallization temperatures. The crystallization kinetics of mPP based on Avrami analysis was accelerated dramatically with increasing concentrations of PC in the blend. This last finding may be attributed to the fact that the nanoscale dispersed phase can act as a nucleating agent for the crystallization process.

A theoretical analysis of the technique of micropipette aspiration for deformable particles PO142

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The aspiration of deformable particles such as capsules and giant vesicles into micropipettes is a standard technique for characterizing membranes. In a typical experiment, a large capsule or vesicle is first captured into a fine micropipette by applying a negative pressure from within. Using video microscopy to monitor the shape of the aspirated entity for different incremental suction pressures, a variety of membrane properties such as area compressibility modulus, bending rigidity and rupture tension may be inferred. The theory that underlies the interpretation of the raw geometrical data from the images to yield these membrane properties appears, however, to be oversimplified. In particular, the region of pinning between the membrane and the pipette calls for more careful analysis. In this poster, we investigate through theory and simulation the shape of an aspirated vesicle as a function of the differential pressure applied across the vesicle, and compare these predictions with experiment.

Flow-induced breakup of attractive nanoemulsions PO143

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Using rheological small angle neutron scattering (Rheo-SANS), we study how an applied steady shear alters the structure of nanoscale droplets in jammed networks of attractive nanoemulsions. Monodisperse silicone oil-in-water nanoemulsions, stabilized by the anionic surfactant sodium dodecylsulfate, are prepared by ultracentrifugal fractionation, yielding an average droplet radius of 40 nm. Relative to thermal energy, the interaction potential of the droplets is tuned from repulsive to attractive. In the absence of shear, we observe the hallmarks of slippery diffusion-limited aggregation: a strong fractal power-law rise in the intensity, I, toward low wavenumbers, q, and clear nearest-neighbor correlation peaks at high-q. However, when high shear stresses are applied, the emulsion's viscosity shear-thins, the scattering is anisotropic, and the low-q intensity drops significantly. These trends are interpreted in terms of shear-induced de-gelling of the attractively jammed networks through disaggregation of nanodroplets.

Thermo-gelation of surface-modified polyethylene microgels from fragmentation and immiscible blends 💿 PO144

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Polyethylene microgels were created by swollen-state grinding and ultrasonic fragmentation of bulk crosslinked polyethylene in squalane [Polym. Eng. & Sci. 48 (2), 329-339, (2008)], and by the extraction of crosslinked-polyethylene micro-domains from an immiscible blend of linear low-density polyethylene (LLDPE) and polystyrene (PS). The blend morphology has been found to agree with results by Teh and Rudin [Polym Eng. & Sci. 31 (14), 1033-1042, (1991)], where discrete polyethylene micro-domains are dispersed in a polystyrene matrix when the blend composition is 9:1 w/w. Polystyrene - polyethylene melt-viscosity ratios from approximately 5:1 to 1:1 were attained by varying the blending temperature. Crosslinking of the polyethylene micro-domains in the blend was achieved either by exposure to an electron beam, or by in situ peroxide curing during the blending process. For blends containing a block copolymer compatibilizer (styrene-ethylene/butadiene-styrene), the micro-domains comprise a core-shell microgel with a polyethylene core and a polystyrene outer shell. These particles tend to be smaller than those in blends void of the compatibilizer. Suspensions of both conventional polyethylene and core-shell microgels in squalane exhibit non-reversible thermal gelation upon cooling where both G' and G" increases by up to three- and two-orders in magnitude respectively when probed using small-angle oscillatory shear. We propose that this phenomenon is attributed to weak short-range interactions among the particles, which cause agglomeration at low stress levels. Surface terminal chains on conventional polyethylene microgels can co-crystallize forming inter-particle bonds upon cooling, while the core-shell microgels can form polystyrene-rich phases that act as bridges between particles upon cooling due to the low affinity of the polystyrene shell towards squalane. However, these interactions are mild enough that the systems may be reverted to its original state by applying higher shear stresses at elevated temperatures, making the system pseudo reversible.

Highly entangled liquids under extensional flow

PO145

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Highly entangled systems such as wormlike micellar fluids and monodisperse polymer systems exhibit spatially inhomogeneous shear-banding structures under imposed deformation. Rheological equations of state that are capable of describing these fluids include the new class of microstructural network models developed by Vasquez, Cook and McKinley (2006). The VCM family of models incorporates breakage of the micelles, and non-local effects arising from coupling between the stress and the microstructure. This leads to a set of differential equations describing breakage and reforming of two micellar species (a long species "A" and a shorter species 'B') in addition to reptative and Rousian stress-relaxation mechanisms. In filament stretching experiments designed to measure the extensional rheology of wormlike micelle solutions it is observed that the elongating filaments suddenly rupture near the axial mid-plane at high strain rates [Rothstein]. This newly observed failure mechanism is not related to visco-capillary thinning observed in viscous Newtonian fluids. The VCM model, in homogeneous extension, has a normal stress versus extension-rate curve which is non monotone and which is believed to be the basis of this fracture mechanism. We apply linear stability analysis to the two-species VCM model under homogeneous uniaxial extensional flow and find a purely elastic instability along the decreasing portion of the stress/strain-rate (extensional) curve. Further work examines the spatially inhomogeneous extension to further understand the rupturing mechanism.

Rheological studies of a phase-separated thermoplastic/thermoset blend

PO146

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Epoxy/poly(epsilon-caprolactone) (PCL) blends are known to undergo polymerization induced phase separation (PIPS) when cured with 4,4'-diamino diphenyl sulfone (DDS), owing primarily to a shift from inter- to intramolecular hydrogen bonding that occurs during crosslinking. Interestingly, a diverse array of morphologies spanning 50 υm to ca. 500 nm can be generated via PIPS, depending on system composition as well as crosslinking temperature. It was found that, with relatively high PCL content, an epoxy-rich phased that forms during crosslinking adopts the form of discrete spherical particles dispersed in a continuous PCL matrix. Rheologically, we found that the epoxy particles of such a morphology serve as physical crosslinks that integrate linear PCL chains and restrain the blend from macroscopic flow at temperatures exceeding the melting transition of PCL. Consequently, the rheological response is that of a lossy elastomer. Our rheological and morphological studies of this material system will be presented to reveal unique viscoelastic properties and their microstructural origins.

Rheology and simultaneous imaging of colloid-stabilised emulsions

PO147

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As the elastic properties of colloid-stabilised emulsions arise not only from interfacial tension, but also from interparticle interactions, the rheology of these Pickering emulsions promises great diversity. Using colloidal particles to stabilise emulsions, instead of molecular surfactants as in conventional systems, has the additional advantage that the surface chemistry of the colloids can be modified in a controlled manner.

Our emulsion system consists of water droplets in dodecane, stabilised by fluorescently labelled poly(methyl methacrylate) (PMMA) particles with a diameter of the order of a micron. The relatively large size of the colloidal particles allows individual imaging and particle tracking in confocal microscopy. Adding a different dye to the water even allows separate imaging of the particles and the dispersed phase. By combining a rheometer with a fast confocal microscope, we can characterise emulsions under shear and/or normal stress in three dimensions and in real time.

For dilute Pickering emulsions under simple shear, we have observed that stresses associated with the flow are insufficient to deform the droplets. However, during squeeze/pull tests, involving appreciable normal loads, the droplets deform considerably. At high normal strains, the emulsions start looking like liquid-liquid foams. Shearing conventional foams typically leads to bubble deformation and, at high strain, to T1 rearrangements. In exciting, initial experiments on shearing our liquid-liquid foams, droplet deformation and rearrangements do occur, but we also observe break-up and formation of particle-laden interfaces between deformed droplets.

Investigation on drop formation process by CaBER ‘hanging drop’ experiments

💿 PO148

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Drop formation is a physical process of significant importance to a number of technologies (1), and has been a subject of research by both industry and academy (2, 3). In this paper we use a commercial apparatus, the Capillary Breakup Extensional Rheometer (CaBER) from Thermo-Fisher Scientific, in an unconventional way, and present the CaBER "hanging drop" experiment as a possible tool for studying drop formation.

Conventional use of CaBER is to study extensional flow properties of viscoelastic fluids. In such an experiment a liquid is placed between the two cylindrical plates, separated for a few mm from each other. Then the upper plate is moved in the vertical direction to create an unstable liquid filament that undergoes the Rayleigh instability. The filament thins, and eventually breaks up. The dynamics of the thinning of the liquid filament is being observed, from which extensional flow parameters can be extracted.

In the CaBER 'hanging drop' experiments a microsyringe is used to place a drop of liquid onto the upper plate to create the hanging drop. The initial distance between the two plates is large enough and the hanging drop does not touch the lower plate. The volume of the drop is sufficiently small (up to a couple of tenths of microliters), so that surface tension of the liquid successfully overpowers the gravity and the formed hanging drop has a more or less, hemispherical shape. Then, the upper plate is suddenly moved in vertical direction, at a given speed, to reach the maximum distance the instrument allows. Inertial and gravity forces resist the sudden movement of the drop, caused by its adhesion to the moving plate. Thus, the continuous extension, deformation and movement of the drop takes place. The drop movement and the shape evolution are monitored by a high speed video camera. The drop movement and the shape evolution depend on experimental conditions (i.e. the drop volume, the speed of the upper plate movement) and on the physicochemical properties of the liquid. We employ the CaBER "hanging drop" experiments to study the inertia-visco-elasto-capillary force balance in relation to the drop formation process. Some qualitative results are presented.

Basaran, O.A. (2002). Small-scale free surface flows with breakup: Drop formation and emerging application. AIChE Journal 48 (9), 1842-1848; Tirtaatmadja, V., McKinley, G.H. and Cooper-White, J.J. (2006). Drop Formation and Breakup of Low Viscosity Elastic Fluids: Effects of Concentration and Molecular Weight, Phys. Fluids 18, 043101; Wijshof, J. (2007). Drop formation mechanisms in piezo-acoustic inkjet, Oce Technologies B.V.

Three-dimensional numerical simulations of a rising bubble in a viscoelastic FENE-CR model fluid PO149

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Three-dimensional, dynamic, computational results are presented for the problem of a gas bubble rising in a viscoelastic fluid. In this study, viscoelastic fluids are modeled by the Chilcott-Rallison model (FENE-CR), and a gas-liquid system with realistic physical properties are considered: e.g. the density (liquid/bubble) ratio is on the order of ~ 850. The numerical simulations are carried out by a sharp interface method based on a coupled level set/volume-of-fluid (CLSVOF) method which combines some of the advantages of the volume-of-fluid (VOF) method with the level-set (LS) method. The governing equations based on the CLSVOF method for incompressible viscoelastic two-phase flows are solved through a hydrodynamic scheme with formal second-order accuracy. Dynamic adaptive mesh refinement is used to focus on the cusp region, which exhibits large curvature. The physical properties used in the study presented here cover a wide range of Eötvös numbers; for large Eötvös numbers, the corresponding Newtonian system would exhibit largely deformed bubble shapes. From the computational results presented here, it is shown that the dynamic motion of a rising gas bubble in a FENE-CR fluid largely depends on the FENE-CR model parameters and the Eötvös number. In particular, a study is made that highlights interesting findings regarding cusp formation.

Ageing of casein micelles PO150

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Owing to their good solubility, surface activity, heat resistance, and water-holding properties, caseins are excellent emulsifiers and hence are used as ingredients in a wide range of formulated food emulsions such as ice-cream, coffee whitener, cream liqueurs, and whipped toppings. Caseins are a family of phosphoserylated proteins which exist in bovine milk as large colloidal particles (10^8 Da, ~ 200 nm diameter) historically called casein micelles.

The formation of casein micelles in aqueous solution may have considerable influence over either/both the formulation characteristics or the final qualities of casein-based products. However, details of the structures adopted by the casein in native buffer solution and the relationship between the extent of aggregation, gelation and ageing of casein micelles has not yet been fully elucidated. As such, we present here a study on the self-assembly of casein in buffer solution in order to determine the rheological and microstructural properties of the resulting soft matter.

The rheological response of the casein samples as a function of concentration has been investigated using a controlled-strain rheometer. Dynamic Strain Sweep (DSS) experiments of concentrated samples indicate liquid-like behaviour for all strain amplitudes. Three distinctly different aged states are apparent in the non-linear rheology data, obtained by subjecting the sample to a constant shear rate as a function of time. The form of the stress response upon ageing, irrespective of concentration, is that of a spontaneous increase of stress at very short times (< 1 s), followed by a plateau with fine structure superposed and lastly a sharp increase in stress of several orders of magnitude. A plausible explanation for this form of the stress response is that a local transient "caged" or "jammed state" occurs, where the casein micelles are intermittently rearranged by a simultaneous breaking and forming of the micelles. This is followed by a subsequent highly connected aged or three-dimensional gelled state where the system is arrested by collective, long-range and micelle interactions. As a function of concentration, this gelled state occurs at a more moderate shear rates.

Shear-banding in concentrated emulsions PO151

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Emulsions are widely encountered in food systems. Droplets of oil are stabilized in an aqueous continuum by a series of emulsifying agents, which reside at the oil-water interface. Emulsions are complex fluids, whose rheological pattern are always considered in relation with the properties and interactions of the droplets constituting the colloid. While speculatively it is believed that the emulsifying agent and the oil define the internal fluid structure of the emulsion, the manner in which these controls are achieved is not widely investigated. Here, we focus on the role of caseinates, the major family of milk protein, as a major controlling agent in determining emulsion stability, microstructure and physicochemical characteristics using food-grade oil (soybean oil).

The phase diagram of, for example, the oil-rich emulsion region (50 – 55 wt%) of the soybean oil-water-sodium caseinate system shows a number of macroscopic behaviours. This indicates that within a seemingly ambiguous emulsion domain, different classes of emulsion exist. The behaviour can be classified into four types. At low sodium caseinate content, the emulsions destabilize in one day. At higher sodium caseinate content, the emulsion has good stability over a period of several days. With further increases of sodium caseinate content, the observed emulsion stability is reduced again, with the rate of serum separation at the bottom of the sample now greatly increased. Once the caseinate concentration reaches a high value, a strong emulsion droplet network is produced which can reorganize only slowly, and is hence the system is much more stable to serum separation.

A classical rheology study of the oil-rich emulsion region was performed in a cone-and-plate geometry. The system does not exhibit a smoothly rising stress in the steady state flow curve. Instead a plateau is observed for shear rates between 0.1 and 1 s^{-1}. Our data, thus, raise the question of the definition of a global flow curve for such concentrated systems. Such apparent inhomogeneities have been observed previously in oil-in-water emulsions as evidenced by Dynamic Light Scattering (DLS) [1]. To investigate the existence of a plateau region further we have used a NMR velocimetry technique: rheo-NMR [2]. The results of the rheo-NMR experiments reveal the presence of shear banding. That is, there is a subdivision of the fluid into two regions of distinctly different, but locally constant, shear rates. The structural differences of these two shear states have been examined using cryo-electron microscopy.

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A look behind the salt curve: An examination of thickening mechanisms in shampoo formulations PO152

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Shampoos are viscoelastic materials, demonstrating both viscous (liquid-like) and elastic (solid-like) flow properties. They consist of worm-like micelles - equilibrium structures strongly dependent on composition variables. The interactions between micelles are responsible for the viscoelastic behavior of shampoos: entanglements, branching points, and adhesive contacts thicken these systems, while reptation (disentanglement through snake-like motion), breaking of the micelles, and sliding of contact points are the principal mechanisms of stress relaxation.

Control of both the strength and the lifetime of constantly changing micellar interactions are necessary to dictate low-shear viscosity and shear-thinning behavior of shampoo systems. In this work we examine the mechanisms by which these parameters can be controlled, enabling more efficient design of thickeners for shampoo systems.

The thickness of a shampoo can be altered by several means: variation of concentration of the principal surfactant; addition of salt; or addition of thickeners. In this study we find that the characteristic shape of the well-known "salt curve", in which the viscosity of a surfactant solution is highest at an intermediate salt concentration, is due to variation in the "relaxation time" (i.e., how long the structures remain intact and entangled), and not variation in the strength of micellar networks (i.e., density of entanglements and junctions). Further, we reveal a correlation between relaxation time and the average number of entanglements per micelle.

Betaines and alkanolamides, commonly used commercial thickeners, dramatically increase the peak relaxation time, shifting this maximum to lower salt levels. Intercalating into the micellar structure, they screen the repulsive force of the anionic headgroups, generating more entangled micelles. Note that betaines do not simply act as salts, shifting the salt curve maximum to lower levels of sodium chloride: their addition also increases the volume fraction of surfactant in solution and may have other effects on the micellar structure as well. The addition of PEG-distearate introduces a salt-independent relaxation mechanism. Presumably this component creates transient crosslinks between nearby worm-like micelles. In contrast to the salt effect, incremental addition of PEG-distearate thickens a shampoo through an increase in modulus, with no changes in relaxation time observed.

Theoretical model of viscous friction inside steadily sheared foams and concentrated emulsions PO153

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We describe a theoretical model of viscous friction in steadily sheared foams and concentrated emulsions, which includes several contributions. The first contribution [1] comes from energy dissipated inside the *transient planar films*, formed between two neighboring bubbles/drops, which slide along each other in the shear flow. This contribution predicts that the foam viscous stress, τ_V, should scale with $Ca^{1/2}$, in good agreement with experimental results by various authors. As usual, $Ca=(\mu G R_{32}/\sigma)$ is the capillary number,G is shear rate, R_{32} is mean bubble size, μ is viscosity and σ is surface tension of the foaming solution. Second, the effects of the *meniscus region* around the planar films and of the *surface forces* (electrostatic, van der Waals, etc.) acting between neighboring bubbles/drops, are considered [2]. The calculations show that the effect of meniscus region is not very significant, whereas the surface forces could be important in emulsions, due to the relatively small thickness of the emulsion films (often comparable to the range of surface forces). In contrast, the surface forces are usually negligible in sheared foams, because the dynamic foam films are thicker than the extent of surface forces. An additional contribution to the macroscopic viscous stress, created by *surface dissipation* of energy, was found for bubbles/drops exhibiting high surface viscosity [2]. The model allows one to describe also the viscous friction inside a single layer of bubbles - configuration encountered with bubble monolayers in 2D-foam rheological measurements. New explanation of the onset of foam/emulsion jamming at low shear rates is proposed, by considering the dynamics of the films, formed between neighboring bubbles and drops. The model predictions are verified with various experimental results.

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Thermal, morphological and rheological properties of rigid polyurethane foams as thermal insulating materials PO154

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The polyurethane foams (PUFs) were prepared by polyether polyols, polymeric 4,4'-diphenylmethane diisocyanate (PMDI), silicone surfactants, amine catalysts and cyclopentane as a blowing agent. Solid and liquid type fillers were used as a nucleating agent to decrease a cell size of the PUFs as well as improve the thermal insulating properties of the PUFs. The PUFs were prepared by adding solid and liquid type fillers in the range of 1 to 3 wt%. For the liquid type fillers, the cell size of the PUFs showed minimum and found to decrease compared the PUF without adding fillers. Also, thermal conductivity of the PUFs with adding fillers showed minimum. For the solid type fillers, cell size and thermal conductivity of the PUFs were observed to decrease with the filler content up to 3 wt%. From these results, it is suggested that the thermal insulating property of the PUFs can be improved by adding fillers as a nucleating agent. Also, storage and loss modulus of the PUFs will be presented to study gelling points of the PUFs.

Localization of topological changes in two-dimensional foams PO155

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Foams flow through discrete topological changes. In the cylindrical couette geometry, these topological changes are expected to become localized near the inner wall [1] resulting in both flowing and stationary regions of the foam. We employ Surface Evolver simulations to show that in simple shear, these events can localize in any region of the foam and that the width of the localized region depends on the square-root of area-disorder [2]. Furthermore we examine the properties of a localized foam. The transition from no localization to localization causes the bubbles to rearrange in such a way that a simple one-dimensional measure of structural disorder (known as the linear intercept method [3]) is maximized in the localized region. Using this measure we can determine the localized region of the flow at any instant. This measure succeeds where more obvious methods, such as the local area-disorder, fail. We also measure the orientation of the topological changes in the localized region and we will describe its dependence on both the area-disorder and liquid fraction of the foams.

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Interacting free-falling obstacles in two-dimensional foam: Simulation and experiment PO156

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The motion of two circular discs falling through a two-dimensional foam due to gravity is investigated through simulation and experiment. This is a variation on the well known Stokes experiment, a useful configuration in which to study the properties of liquid foams, from the discrete bubble-scale behaviour to the continuum case and in particular the transition from an elasto-plastic solid to a viscoelastic fluid. We use the Surface Evolver to calculate the film network and bubble pressure forces on the discs. We look at two different orientations for the initial placement of the discs in the foam: side by side and directly above each other and track their motion through the foam. In the first orientation, a rotation of one disc about the other is seen when the initial separation between them is small, while the interaction reduces considerably when this distance is increased. The initial separation between the discs is varied to investigate whether the foam screens the interaction. The area of the discs is also an important factor: when placed directly above each other, smaller discs are more likely to move closer together than larger discs. We aim to reproduce these results experimentally for a quasi-two-dimensional foam between two glass plates.

Granular Materials and Aging

Modeling collective failure and stick-slip in granular systems PO158

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When a sheared dense granular system reaches a certain critical state, failure mechanisms (e.g. frictional sliding and rolling at contacts and buckling of particle columns) may suddenly occur in a collective and coordinated manner. These failure events, especially those involving force chains, are known to be responsible for the sudden and periodic drop in shear stress in stick-slip events. Numerous models have been proposed to capture stick-slip (e.g. spring-block models), yet a key mechanism remains unaccounted for in all of these models except in discrete element simulations. This mechanism is that of confined buckling of force chains - a mesoscopic event that involves collective and coordinated failure at contacts, dominated by relative particle rotations, in jammed particle clusters. Mounting evidence from both experiments and discrete element simulations suggest that this failure mechanism is the key event that drives stick-slip. Here, we present predictions from a new class of cellular automata models. The elementary cell in these models consists of an axially loaded force chain that fails via buckling under lateral confinement from surrounding weak network neighbors. The rule governing the dynamics of the system is deterministic, and derived from a direct consideration of this buckling process within the framework of structural mechanics. The extent to which these CA models can reproduce experimentally observed statistics and trends of stick-slip behavior is examined. Effects of particle properties and their interactions (i.e. particle size and shape, stiffness properties, interparticle rolling and sliding friction) and confining pressure are investigated.

A thermomicromechanical approach to multiscale modeling of granular media PO159

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A method for the development of thermomicromechanical constitutive laws, expressed solely in terms of particle scale properties, is presented. The focus of this study is on dense, cohesionless granular media under quasi-static loading. Micromechanical relations for the internal variables, tied to nonaffine deformation, and their evolution laws are derived from a structural mechanical analysis of a particular mesoscopic event: confined, elastic-plastic buckling of a force chain. The resulting constitutive law engenders physical transparency across micro-meso-macro scales, and can reproduce the defining behavior of strain-softening under dilatation on both the mesoscopic and macroscopic scales. The thickness and angle of, and the distributions of particle rotation and the emergent normal contact force anisotropy inside the shear band are consistent with those found in discrete element simulations and physical experiments.

Granular chains PO160

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In polymer chemistry, macromolecules can be modeled by freely jointed chains. The time averaged mean square end-to-end distance $<r^2>$ of a granular polymer in good solvent scales with the number of links N-1 connecting monomers $<r^2> \sim N^{2\nu}$. ν is the universal exponent and found to be around 0.59 in many polymer solutions, which is in agreement with the computational results of 3D self-avoiding random walk. In 2D self-avoiding random walk, ν is reported to be 0.75. Here, we investigate the dynamical behavior of different collections of granular chains in a 2D rotating cylinder at different rotation speeds. Both granular polymer and solvent molecules are represented by granular chains. In particular, we vary the solvent and the size of polymer chain by adjusting the number of links on the granular chain, and discover a cross over transition from 2D self-avoiding random walk to 2D random walk behavior. We also investigated the flow regime, chain conformation and packing porosity during the flow.

Rheological properties of a granular impurity in the Couette flow 💿 PO161

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Transport properties of an impurity immersed in a granular gas under the stationary nonlinear Couette flow are studied. The starting point is a kinetic model for low-density granular mixtures recently proposed by the authors [Phys. Rev. E **75**, 061306 (2007)]. Two routes have been considered. First, an exact hydrodynamic or normal solution is found by exploiting a formal mapping between the kinetic equations for the gas particles and for the impurity. This solution is valid in the bulk domain and applies to general values of the shear rate and of the parameters of the system. Second, in order to assess the reliability of this solution when realistic boundary conditions are present, the kinetic equations are numerically solved by means of a direct simulation Monte Carlo method. The state of the impurity is characterized by the ratio between the temperatures of the impurity and gas particles and by five generalized transport coefficients: three related to the momentum flux (a nonlinear shear viscosity and two normal stress differences) and two related to the heat flux (a nonlinear thermal conductivity and a cross coefficient measuring a component of the heat flux orthogonal to the thermal gradient). Comparison between theoretical predictions and computer simulations shows a good agreement, even for large shear rates and strong inelasticity. This shows again the validity of a hydrodynamic description for granular flows, even under extreme conditions, beyond the Navier-Stokes domain

Colloidal Gels and Glasses

Flow-assisted assembly of multilayer colloidal crystal arrays through spin coating PO163

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Spin coating colloidal suspensions is a robust, efficient method for creating colloidal crystal arrays with good long-range order for applications (Jiang et al., 2004, Journal of the American Chemical Society 126(42) 13778) including optical materials. To evaluate the potential for broad application of this method, we used direct visualization with confocal microscopy to investigate the effects of strain, and reduced stress on local crystallinity of 3D arrays assembled by spin coating. Specifically, our method uses charge stabilized, refractive index matched poly (12-hydroxystearic acid) stabilized poly(methyl methacrylate) colloids of size about one micron suspended in the viscous solvent dioctyl phthalate. To quench assembled structures for interrogation by 3D confocal microscopy, the suspensions (colloid volume fraction ~ 0.35) are spin coated on glass substrates with a small fraction of photopolymer that is subsequently gelled by UV exposure. Upon initiating spin coating, we find that excess suspension is expelled to the outside edge of the substrate by centrifugal forces, resulting in a thin, microscopically level film with complex, spatially varying crystallinity. The full thickness of the colloidal crystal array is imaged at a number of radial positions using confocal microscopy and particle centroids are located in 3D by means of quantitative image processing. Local crystallinity is quantified by application of local bond order parameter criteria developed by ten Wolde et al. (ten Wolde et al., 1996, Journal of Chemical Physics 104 9932). We found local ordering produced by spin coating to be a function of both local reduced critical stress and macroscopic strain. Crystalline structures form when the local reduced stress is of magnitude O(1) or higher and macroscopic strain is >=2. Peclet number was manipulated by varying radial position, spin speed and particle size.

Microstructure and mechanics of concentrated suspensions during in situ coagulation of particles directly observed by confocal microscopy PO164

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Using the internal gelation method Direct Coagulation Casting (DCC [1]) allows controlling the microstructure of densely packed gels with solids contents up to 60 vol%. As it uses an in situ coagulation, the development of the gel microstructure is uniform and undisturbed throughout the entire sample. The dynamics of the coagulation process strongly affects the microstructure and the mechanical behavior of the resulting gels. The dynamics has been extensively investigated using static light scattering and diffusing wave spectroscopy [2]. However, detailed information on the cluster structure and particle rearrangement within clusters during coagulation cannot be assessed with these methods. In order to shed more light into the dynamics of particle coagulation, we investigated the coagulation of fluorescent particles in concentrated suspensions by direct observation of the suspension in a confocal laser scanning microscope. Using this approach, the microstructure of the gel during coagulation could be directly obtained and compared with its rheological behavior. The internal gelation of particles is triggered via the enzyme-catalyzed hydrolysis of urea in water. The ions generated though this reaction can induce coagulation by either shifting the suspension pH towards the isoelectric point of the particles (?pH-coagulation) or by increasing the medium ionic strength at a given pH (?I-coagulation). Different amounts of urea and the enzyme urease were added to the suspension to deliberately change the dynamics of the coagulation process. Software extracted the particle positions from the images. The microstructural changes were examined and visualized with the radial distribution function, bond-angle distribution and common neighbor distribution. Results have shown that in the ?pH-coagulation the microstructure changes abruptly after some characteristic delay time, whereas continuous microstructural changes were observed during ?I-coagulation. The latter is attributed to the formation of a shallow secondary minimum in the interparticle potential energy curve, resulting in clusters of weakly bonded particles. The weak bonds allow for particle rearrangement, leading to dense clusters that remarkably increase the gel stiffness. On the other hand, ?pH-destabilized samples exhibited a more homogenous microstructure due to the rapid formation of a deep primary minimum in the potential energy curves after a certain delay time. The lower density of clusters obtained in this case reduced the stiffness of the final gel tenfold as compared to the ?I-coagulated samples. The interpretation of these results and the impact of such findings on the fabrication of advanced materials will be discussed in this poster.

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Avalanches of concentrated granular suspensions down an inclined plane PO165

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To address the problem of geophysical flow dynamics, we carry out experiments with granular suspensions. We focus our attention to the simple case of spherical non-buoyant particles in a Newtonian fluid flowing down an inclined channel. The refraction index of the fluid matches the particles' refraction index so that the suspension is transparent. A fraction of the particles are tagged with fluorescent dye and activated with a laser sheet. Particles are tracked using a high speed camera. This makes it possible to measure the flow characteristics inside the bulk (e.g., density and velocity profiles) far from the sidewalls. Dimensions of our flume are 3.5 m long and 10 cm width, the released volume is 10 l.

A meta-stable van der Waals gel: Transitioning from weak to strong interaction energies in the same system PO166

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Here we describe a method to create gels where the gel point is decoupled from gel elastic properties. Working with charge stabilized polystyrene latex particles with diameters, D, of 210-625nm at ionic strengths of 0.1-1M, the gel volume fraction is varied from 0.10-0.35 through the addition of less than submonolayer coverage of hexaethylene glycol monododecyl ether (C_6E_{12}). At each surfactant concentration, the gel volume fraction depends on the background ionic strength. The changes in gel point with surfactant concentration suggest the strength of interparticle attraction decreases with increasing surfactant concentration. These changes are not reflected in the gel moduli which are independent of surfactant concentration and ionic strength. We propose a model to describe this behavior based on gelation due to localization in a shallow truncated van der Waals minimum produced by the surfactant acting as a steric stabilizing layer. The surfactant remains mobile on the surface. Below the gel volume fraction the time particles spend in the truncated well are not sufficient for the surfactant to be displaced such that the particles can only sample the shallow well. Above the gel volume fraction, particles are localized in the truncated van der Waals minima for sufficient periods of time to displace the surfactant layers with the result being that the particles fall into a primary van der Waals minimum. The result is gel points sensitive to surfactant concentration but moduli that are independent of the gel volume fraction.

Time-dependent viscoelastic shear modulus during gravitational collapse of colloidal gels PO167

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We present a study of the time evolution of the elastic properties of colloidal depletion gels. Both the colloid volume fraction and the interaction strength (polymer concentration) were varied on the approach to gelation. We study the time evolution of the mechanical properties of the suspensions with a bulk rheometer in a double-wall Couette cell throughout the gel lifetime. The early lifetime is characterized by an elastic shear modulus that increases logarithmically with time, following which the gels experience catastrophic failure and the elastic modulus drops dramatically. As the gel collapses, various complex behaviors are seen, including a temporary stabilization against collapse, and reformation of a new gel with its own elastic properties which then follows its own trajectory to collapse. Time-lapsed images taken of identical samples in a separate transparent cell used to calibrate the measured shear modulus values allows us to see the sample-spanning collective rearrangement involved in the collapse.

A phenomenological classification of colloidal glasses based on their yielding PO168

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Metastable glassy states exhibit complex rheological behavior with solid like responce at low stresses and a complicated flow above the yield stress, usually accompanied by thixotropy and ageing. The mechanism of yielding is still far from understood, despite recent advances in both the theoretical and experimental fronts. We have been interested in exploring the influence of pair interaction potential on the vitrification-yielding behavior of colloids. To this end, we performed different experiments with three model systems of different, well-defined interactions: (i) high volume fractions of sterically stabilized hard spheres (ii) dense ultrasoft multiarm colloidal stars in an athermal solvent and (iii) soft thermosensitive migrogel particles. Using a wide range of rheological measurements, we detect the yield stress and yield strain and their volume fraction dependence, which we discuss in view of current theories. We also look at large amplitude oscillatory shear and identify details in the nonlinear response in the higher harmonics. More importantly, we focus on the creep and recovery analysis. We observe distinct yielding performance for the three classes of systems, which we are trying to rationalize in view of the softness and particular relaxation mechanisms (involving the cage picture). Last, we propose a possible crude, phenomenological classification of colloidal glasses based on their stress-dependent nonlinear recovered strain.

Solid rheology: Comparisons of molecular glasses and colloidal glasses PO169

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There is considerable interest in the analogies between molecular and colloidal glass-forming substances. Here we take the approach of comparing the phenomenological responses of both polymeric and colloidal systems in solid rheology-type experiments. Hence, we examine the response to torsional stress relaxation measurements and compare the isochronal responses between polymers and concentrated suspensions either of carboxylated polystyrene-polybutadiene co-polymer dispersions or an attractive dispersion of alumina nanoparticles. The torsional experiments are either in a cone and plate geometry or a parallel plate geometry. In addition to examining the behaviors up to and beyond yield, we also investigate the aging responses in experiments in which small strains are superimposed on large deformations. We will show that, while there are many points of commonality between the colloidal and molecular/polymeric glasses (such as the ability to go to large deformations, apparent softening followed by aging after the imposition of the large deformation) we also find that there are distinct differences. For one, the molecular glasses show classic viscoelastic behavior in that sequence effects in loading are not widely observed, while the colloidal systems show distinct sequence effects. Furthermore, the transient normal force responses in the torsional experiments are different in the two types of materials. The similarities and differences will be elaborated upon.

Microfluidics

A comparative analysis of the mixing efficiency of different types of passive micro-mixers PO171

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In terms of the efficiency of a passive micro mixer, two main characteristics need to be considered. First, besides an average degree of mixing, the homogeneity of the resulting fluid is often very important. For example, chaotic flows may induce an extremely fast mixing in certain regions of the flow domain while others may be hardly affected by the chaotic flow and unmixed islands may persist for long times. Secondly, the pressure drop has to be taken into account. In this regard, mixers relying on successive splitting and recombination or chaotic transversal advection are most favorable, since a logarithmic dependence of the mixing length on Pe is achieved, while typical pressure drops are similar to those of corresponding straight pipe flows, i.e. showing a linearly increase with the length of the mixing channel. The main objective of this work is to perform a comparative analysis of the mixing efficiency of different types of passive micro mixers, whose channel geometries are based on those of the screw(s) of single and twin-screw extruders, for inelastic and viscoelastic fluids. In order to achieve this objective we resort to micro-Particle Image Velocimetry techniques in addition to the more usual flow visualization, so that a full mapping of the velocity profiles in the channels can be made.

Diffusive and convective mass transfer in two-phase microchannel flow: Non-equilibrium interfacial tension PO172

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The kinetics of mass transfer from one phase to another is monitored in flow. The time-dependent interfacial tension between water and oil (determined from drop deformation dynamics in situ) serves as a measure of the butanol concentration within the drop. This concentration begins high and decreases, as the butanol diffuses into the surrounding oil. This diffusive process is effectively two dimensional, i.e. only transverse to the flow.

Electrokinetic microflows in curved rectangular channel under Newtonian slip boundary conditions PO173

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Understanding the physics of either microfluids or nanofluids involving electrokinetic phenomena is significant for the flow control in microelectro mechanical system (MEMS) devices, manipulation of small particles, and optimum design of micro-chips. The long-range nature of viscous flows and the small dimension inherent in confined spaces imply that the influence of boundaries is quite significant. Among the boundary effects, we should focus on the hydrodynamic slip at a solid-liquid interface and the electrokinetic phenomena [1-3]. The flow enhancement will benefit during the transport, since friction increases with the surface-to-volume ratio.

We first provide the explicit model for rectangular microchannels with solvophobic smooth surfaces. Hydrophobic materials have become attractive for use in MEMS fabrications, and the surface of channel wall frequently has inhomogeneous properties. The external body force originated from between the Poisson-Boltzmann field and the flow-induced electric field was employed in the Navier-Stokes equation taking into account the Nernst-Planck principle [4]. We obtained numerical results of the slip flow in highly charged (i.e., surface potential above $kT/e = 25.69$ mV) rectangular microchannels, allowing experimental verifications. In subsequent, the flow in 3-D curved rectangular channels that constitutes another source of the Aris-Taylor dispersion has been examined. Applying the finite difference scheme based on the successive iteration method, the resultant velocity profiles are computed with variations of geometry curvature, electric surface potential, and slip length [5]. The fluid slip induces a higher flow velocity, while the presence of electric double layer retards the flow rate. When the fluid slip is absent, a higher friction factor would be predicted in view of the electroviscous effect. In the case of curved channel, since a shear is created with the fluid flowing faster on the inside edge of the channel turn, fluid particles near the inner edge traverse a shorter distance at this higher speed than particles at the outer edge.

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Generation of non-Newtonian droplets using microfluidic flow focusing device PO174

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The generation of micron-sized droplets using microfluidic device has been of great interest in the fields of biosciences and pharmaceuticals. Until now most of the studies have been done with Newtonian fluids. In this research we investigated the generation of droplets from non-Newtonian fluids and compared the generation characteristics with that of Newtonian fluids. The microfluidic flow focusing device was made by bonding the PDMS-coated slide glass and PDMS replica bearing the flow pattern, and hence the wetting characteristics of the entire inner surfaces were the same. The microfluidic flow focusing device has three inlet channels. The aqueous solution flows through the inner channel and the oil flows through two outer channels. The three streams become focused at the neck and the inner fluid stream becomes a thread. The droplets were generated by the necking of the thread. Silicon oil (Dow corning, 10cs) was used for the outer flow. As the fluid for the inner flow, water or aqueous solution of xanthan gum (1000ppm) was used. SDS was added as the surfactant and the concentration of SDS was set at 0.3wt%. The flow rate ratio of inner and outer flows varied from 1/10 to 1/5000. The flow characteristics were observed using a high resolution

(1600x1200 pixels) and high speed (1/20000 sec. shutter speed) CCD camera. The size of droplets was measured using an image-processing system. The experimental result shows that, in the case of Newtonian fluid, the generation of droplets was sensitive to the length of the neck: as the length of the neck increases the spraying of droplets of approximately 5 μm was observed together with 10 μm or larger droplets. In the case of non-Newtonian fluids, however, the length of the neck does not strongly affect the drop generation and a stable and thin liquid thread was extended to the outside of the neck and uniform sized droplets of 3 – 5 μm were generated.

The behavior of non-Newtonian drops in microfluidic channels: Shear thinning, yield stress and elastic effects PO175

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Emulsions are an integral part of our daily life, with many processed foods, pharmaceutical and cosmetic formulations relying on the presence of a dispersed phase within a continuous matrix for structuring and delivery of actives. The majority of food, pharmaceutical and cosmetic formulations are not Newtonian/Newtonian systems, but more commonly one or both phases display non-Newtonian traits, especially at the rapid, high deformations normally imposed during conventional emulsification processes, such as high pressure emulsification. In this study, we have investigated the dynamics of droplet deformation and breakup within a microfluidic 4:1 contraction - expansion geometry. The geometric ratios of these devices not only mimic geometries currently utilized within high pressure homogenisers, but, due to microfabrication technologies, the relevant dimensions of the flow path are also now similar. The fluids utilized in this study have been chosen to display a wide range of properties and include Newtonian (viscosity matched) reference fluids, shear thinning fluids, yield stress fluids and low constant viscosity elastic fluids. Importantly, these fluids have been selected to show these traits alone, or in a combination (i.e. elastic or elastic and shear thinning). These thoroughly characterized (in shear and extension) fluids include PEO solutions at constant c/c* ratios but varying molecular weight and solvent viscosities (varying relaxation times), biopolymer solutions (alginate, carboxy methyl cellulose), and poly acrylic acid (PAA)/Carbopol solutions of varying pH and concentration. The drop deformation and breakup behavior of these model set of viscoelastic polymeric drops have been compared to Newtonian references of similar viscosity and interfacial tensions, over a wide range of continuous phase flowrates and disperse phase drop sizes. Definitive differences have been observed in both drop deformation dynamics and breakup modes, depending on the particular non-Newtonian trait displayed by the fluid during the movement of the droplet through the regions of variable shear and extensional deformation. The experiments have allowed us to determine when and where these characteristic non-Newtonian properties are relevant and deterministic of the observed droplet dynamics and breakup, or prevention thereof, as the case may be. Elastic drops did not deform as much as a Newtonian analogue and breakup was not observed over the ranges of Re and We explored, although elasticity does produce a new phenomena involving substantial interface deformation and folding. In all cases, numerical VOF codes have been co-developed and validated by these experiments. The insight gained from the numerical predictions allow greater detailed understanding of how, in particular, stress fields are varying during flow of the drop through the contraction, both within and external to the drop. Such data is difficult to obtain from experiments in microdevices, especially over the expanded Re-We/Ca space that we have investigated.

Electrohydrodynamic generation and transport of a single or multiple droplets of aqueous two-phase system in microfluidic device PO176

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As tiny vessels of liquids, droplets can be versatile tools for discrete process in microfluidic systems, being carriers and reactors of fluids in them. We report the electrohydrodynamic generation and transport of droplets in an aqueous two-phase system that consists of tetrabutylammonium bromide (TBAB) and ammonium sulfate (AS). This aqueous two-phase system is advantageous in that it can be applied in the analysis and separation of hydrophilic particles and molecules such as biomolecules without swelling problem in the widely used polymer materials of microfluidic devices. A single droplet and multiple droplets were generated by the application of d. c. electric field as a millisecond pulse across the liquid-liquid interface of two aqueous phase laminar flows. Shear force of the continuous phase, electrophoretic attraction of the dispersed phase to an electrode and interfacial tension of the dispersed phase stream were combined to generate droplets. The number of droplets produced at one pulse application was controlled by the change in the voltage and the duration of d. c. electric pulse. We were able to manipulate the movement of droplets in the microfluidic channels, separating and directing the droplets of specific number into desired part of the device from the sequential flow of droplets, by applying the programmed d. c. electric field which was synchronized with the droplet frequency.

Shear migration of suspensions in simple and chaotic microchannel flows PO177

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At relatively moderate to high volume fraction of solids, hydrodynamic interactions result in normal forces that induce migration of particles toward regions of low shear. This self-organization occurs despite dispersion via diffusion in simple shear flows. Alternatively, it is well known that mixing in many systems can be enhanced by inducing chaotic advection by breaking symmetries of the flow. Chaotic mixing has been demonstrated at various length scales, most recently in microchannels for lab-on-a-chip applications. What is unclear is how does shear migration interplay with chaotic advection. This interplay results in complicated concentration gradients that are dictated both by the underlying flow topology and the fluid rheology. Using high speed confocal laser scanning microscopy, particles in suspensions of index-matched silica and cells in whole blood are tracked in microfabricated channels having various flow topologies to determine their 3D positions and generate 2D concentration and velocity profiles, giving us details of the resulting particle migration.

Microfluidic emulsification and foods: Probing micro to macro lengthscales PO178

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Methods of manufacturing monodisperse emulsions are highly sought-after in industries requiring well-structured multiphase systems, such as food, pharmaceutical and cosmetic industries. Modern dispersing techniques achieve a polydispersity of the order of 10% (e.g. membrane emulsification), yet more recent outcomes of microfluidic technologies have achieved polydispersities of less than 1%, offering significant advantages to industrial producers, if only they could be utilised with 'real' fluids and scaled up without loss of control. In microfluidic devices, the resultant droplet size is a discrete function of the device length scales, device geometry and fluid properties. Much work has been performed investigating Newtonian/Newtonian multiphase systems, however, the majority of food systems, for example, are not Newtonian in their behaviour, but instead display complex non-Newtonian characteristics, especially at the high deformation rates imposed in conventional and newer generation emulsification processes. These fluid characteristics introduce anomalous behaviour and polydisperse drops are a common outcome. In order to produce uniform droplets from these 'real' systems using microfluidic devices, it is important to understand the influence of all relevant physical parameters and time scales and to control them appropriately. In this talk I will review recent investigations by our group into the effects of lengthscale changes, geometric variations and fluid properties on the creation of emulsions of controlled drop size and drop size distribution. I will provide pertinent examples of how, over a range of surfactant and biopolymer (alone or in combination) concentrations and disperse:continuous phase viscosity ratios, the resultant drop formation event can be explicitly controlled. Due to the range of lengthscales and fluids properties investigated in this work, a Re-Ca parameter space spanning 14 orders of magnitude has been explored. Monodisperse droplet formation within microfluidic devices at industrially applicable production rates is possible once applicable fluid properties and microdevice design guidelines are considered, contributing substantially to the final uptake of emulsion-based microfluidic technologies by industry and academe alike.

A novel microfluidic mixing element for viscoelastic fluids PO179

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The flow visualizations of viscoelastic flows in the mixing-separating geometry of Cochrane et al (1981) showed provocative flow features that inspired the current numerical research using the Upper-Convected Maxwell (UCM) model. The effects of Deborah and Reynolds numbers and gap size were analyzed in depth in this two-dimensional flow investigation. The normalized gap size was varied between 0 and 5, *Re* varied between 0 and 10 and *De* varied between 0 and the maximum attainable value.

The creeping flow of Newtonian fluids is always anti-symmetric, due to the anti-symmetry of the inlet conditions and the symmetry of the flow geometry. The increase in the gap size leads to an increase in the reversed flow rate ratio (r_r), here defined as the ratio between the reversed and total flow rates, an effect enhanced only for Reynolds numbers in excess of 1, which also introduces asymmetry in the flow.

The creeping flow of UCM fluids however, showed two distinct flow patterns. For normalized gap sizes below a critical value the reversed flow is slightly enhanced by viscoelasticity, followed by a strong decrease in r_r towards zero as *De* further increase, whereas for a supercritical gap size viscoelasticity is responsible for a continuous increase in r_r. For near-critical flow geometries it was possible to observe the sudden jump between the two flow conditions at slightly different Deborah numbers, thus suggesting the possibility to use such geometry as a micro-mixer for viscoelastic fluids if the imposed flow rates are made time periodic to enhance an oscillation between flow patterns.

At low Reynolds numbers the dependence of flow pattern on gap size and Deborah number still exhibits the described double behavior, but inertia naturally enhances the straight flow case and at $Re = 10$ r_r always decreases with Deborah number for the investigated gap sizes, i.e., for Newtonian fluids inertia increased the reversed flow, whereas for *De* at around 0.2 it reduced r_r.

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Micro-Rheology

Response function of a sphere in the two-fluid model with sliding boundary conditions PO181

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The technique of microrheology allows one to deduce macroscopic rheological parameters as well as information about local structure from the behavior of microscopic probe particles under thermal or active forcing. For microrheology, one must know the relation between macroscopic parameters and the force felt by a sphere in response to displacements. We investigate this response function using the two fluid model, in which the gel is represented by a polymer network coupled to a surrounding fluid solvent via a drag force. We obtain an analytic solution for the response function in the limit of small volume fraction of the polymer network, and neglecting inertial effects. We use no-slip boundary conditions between the sphere and solvent. For the boundary conditions between the sphere and the polymer network, the tangential stress is determined by the relative velocity; this encompasses both no-slip and frictionless boundary conditions as limits. Due to the coupling, in the far-field, the network and solvent act as a single incompressible material. The far-field solution takes the character of motion driven by no-slip boundary conditions at high frequencies, and the character of motion driven by freely slipping boundary conditions at low frequencies. In addition, at low frequencies compression of the network affects the force on the sphere. We find the crossover frequencies at which the effects of compression of the gel and slip between the sphere and polymer network become important. The effects of compression alone can lead to an underestimation of moduli by up to 20%, while slip and compression can lead to underestimation of moduli by up to 43%.

New Experimental Methods

Fourier transformation analysis in capillary flow: A new option to detect flow instabilities (shark skin) PO183

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Flow instabilities cause various problems in extrusion, coating, calandering and blow- or flat film processes. Especially shark skin is affected by the molecular structure and additives. This phenomenon is analyzed in various scientific works using apparatus that are complex or difficult in operation. A new set-up, now commercially available is being presented as an option for new and existing capillary rheometers and extruders, consisting of a special designed die and up to three fast responsive transducers systems. The work shows that the transducers are able to detect flow instabilities before they are visible. The transducers are arranged over the flow length of a slit die to also detect the dependency of flow instabilities from flow length. The software allows the evaluation of diverse pressure frequency regimes causing flow instabilities. Measurement examples are given for different shear rates and polymers. The measured frequency regimes are related to molecular parameters.

From sample changer to the robotic rheometer: Automation and high throughput screening in rotational rheometry PO184

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Reduced time for product development cycles is leading to an ever-increasing request for rheological measurements. One way for reducing the time the user needs to be present for preparing and running a test is to employ a sophisticated control of the rheometer and an intuitive user interface for the software. With such an approach the test itself can be pre configured and is running fully automatically including the analyzing of the data. However, still the sample loading before and the cleaning of the fixtures after the test is needed, which often takes the longest time and during which the rheometer sits idle. In addition loading and cleaning requires frequent interaction by the user when multiple samples are to be run. An automatic sample changer introduced in 1997 incorporates a sample magazine and a cleaning station for the geometry. The cleaning station for the measuring bob is adaptable to different applications like for example chocolate, washing detergents, or different types of coatings. An air bearing supported motor head allows all kinds of rheological measurements including oscillatory testing. The system is able to run up to 32 samples without further user interaction. However, in spite of the advantages of this system concerning the sample throughput it is limited to concentric cylinder geometries, a small temperature range and to liquid like samples. These limitations of the automatic sample changer system led to the idea of developing a fully automated, robotically operated rotational rheometer. The full functionality, modularity and accuracy of the rotational rheometer are available, which means the modern principles of high-throughput screening are brought to full function on the rheometer. The basic rheometer setup remains as modular as before including the ability to run all test modes the rheometer offers with the difference that the high-throughput rheometer now performs all measuring steps automatically. In addition, the standard and proven environmental chambers of the rheometer like Peltier temperature control, electrical heating or convection oven are available. The rheometer itself runs by the standard rheometer software and the measurement data and analysis results can be transferred to a monitoring database. The sample loading and the cleaning of the geometries is assisted by a sample preparation unit and a cleaning station, respectively. Both the sample loading and geometry cleaning can be flexibly configured to the needs of the specific type of samples being tested. The sample throughput is further maximized by the use of multiple geometries allowing the simultaneous rheological measurement by the rheometer and the cleaning of the geometries at the cleaning station by the robot. The high-throughput rheometer and its special adaptation to various applications as different as for example suspension or polymer melts are described and discussed.

Using rheo-optical methods to analyse the waxing of crude oil PO185

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The production and transportation of crude oil is a complex process. In every step of the process links to the rheological properties of the crude oil itself and the rheological properties of other materials used in the process, like drilling fluids etc., can be found. Whereas the rheology in the oil well is special due to the salinity, temperature and high pressure, which must and can be copied from the underground oilfield and then need to be simulated in the measuring cell of the rheometer, the rheology of the oil transportation is a completely different challenge.

One of the mayor issues simply is the huge volume of the oil flowing through a pipeline for example. Crude oil always contains certain waxes, which will precipitate when the oil cools down after being pumped to the surface. The precipitated wax may cause partial blockage of the pipeline which can lead to a significant pressure drop. Trying to encounter this so called “waxing” by insulating or even heating the pipeline requires huge financial efforts. Thus several projects focus on understanding and controlling the waxing by different means.

This paper outlines a rheo-optical method for analysing the waxing of crude oil using a rheometer equipped with a microscope module. While the changing rheological properties are monitored, the forming of wax crystals can be observed. The general method and data evaluation are presented.

Innovations in rheometer controlled-rate control loop design: Ultra low angular speed control and new applications PO186

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The design and implementation of an angular speed control loop for a universal rheometer is not a trivial task. The combination of a highly dynamic, very low inertia (drag cup) motor (motor inertia is 10^{-5} kg m^2) with samples which can range in viscosity from 10^{-3} Pas to 10^{+8} Pas, which can be between purely viscous and higly viscoelastic, which can exhibit yield-stresses, etc. asks for a highly adaptive digital control loop.

For the HAAKE MARS rotational rheometer a new adaptive control loop was developed which allows the control of angular speeds as low $5x10^{-9}$ rad/s and response times a short as 10 ms. The adaptation of the control loop to "difficult" samples is performed by analysing the response of the complete system to a short pre-test.

In this paper we will show that the (very) short response times at (very) low angular speeds are not only achieved with ideal samples, but due to the adaptable control loop, also with "difficult" samples. We will show measurement results on “difficult” samples like cosmetic creams and emulsions, certain food products, a laponite gel, etc. to proof that angular speeds down to 10^{-4} rad/s are reached within 10 ms to 20 ms and angular speeds down to 10^{-7} rad/s within 1 s to 2 s. The response times for reaching ultra low angular speeds down to 5×10^{-9} rad/s are in the order of 10 s to 30 s.

With this new control loop it is, for the first time, possible to measure yield stresses by applying a very low constant shear-rate to the sample and measuring the torque response as a function of time.

Extending the capabilities of the CaBER with highly sensitive force measurements PO187

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When trying to measure the extensional (elastic) properties of samples like cosmetic emulsions with the CaBER one quickly runs into the physical limitations of the capillary breakup technique on which this instrument is based. Due to the specific sample structure and the lack of a substantial surface tension a cylindrical fluid filament and therefore a capillary flow is not properly developed. As a consequence the interpretation of the measurement results is problematic. Since there is an industrial interest in measuring properties like strand formation, stickiness, spreadability etc. which are related to extensional properties a different measuring technique is needed. In this paper we present a solution which is based on measuring the normal force acting on the lower plate when the upper plate is quickly moved upwards thereby extending the sample. In order to be able to measure the small forces (in the order of milli Newtons) that arise in very short times (in the order of milli seconds) a state of the art Kistler force transducer was used in combination with modern data oversampling techniques to increase the sensitivity of the transducer. We will present details on the technical realization as well as first experimental results.

Effect of temperature modulation during time-sweeps PO188

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In quasi-isothermal dynamic mechanical time-sweep experiments, conducted at constant ?, temperature can be made to oscillate sinusoidally around its mean value according to: T=To + DT sin (2pifT t) where DT is less than 1oC, 2pifT is ~ 0.16. In the experiments analyzed in this work, a polymer melt is suddenly sheared dynamically with radial frequency w and strain g, T is modulated as described above, and G'(t), G"(t) measured at short time intervals until their value stabilize. Preliminary results on two polymer melts (PC and PETG), respectively studied at T=225° and 215° show that G'(t) and G"(t) assume the following forms: G'(t) = [Go1cosO1exp(-t /l1) + Go2 cosO2exp(-t /l2) + G'oo] . (1+A' sin (2pifT t + Y')) G"(t) = [Go1sinO1exp(-t /l1) + Go2sinO1exp(-t /l2) + G"oo] . (1+A" sin (2pifT t + Y")) The non-sinusoidal kernel (first term) implies for G(t) a split of the modulus into two relaxation terms and a steady state value: G(t) = [Go1exp(-t / l1) sin (w?t+O1)+ Go2 exp(- t / l2) sin(wt+ O2) + Goo] The accuracy in the determination of the fitted parameters is clearly amplified by the temperature modulation. In particular, in truly isothermal conditions, there is great uncertainty from the regression regarding the existence of a non-zero Goo term. The modulation of temperature allows to resolve the issue. The relaxation parameters l1 and l2 are function of temperature, the radial frequency w and the strain g? It is intriguing to note that A' and A" are different (A'~A"/2), as well as Y' and Y". This would imply a small phase shift, in steady state conditions, for the elastic and loss moduli as a result of the modulation of temperature.

Toward a carbon nanotube-based capillary rheometer PO189

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Nanofluidic devices featuring multi-walled carbon nanotubes (MWNTs) as fluid channels are fabricated for the purpose of measuring the flow of individual, submicron objects (e.g. polymers, nanoparticles) in solution. (Sun, Crooks J. Am. Chem. Soc. 122, 12340, 2000) The MWNTs serve as conduits between two electrolyte reservoirs and the passage of an analyte through the structure is detected by a decrease in the ionic conductance. Initial prototypes employ MWNTs with approximate inner diameters and lengths of 40 nm and 1 micron, respectively. However, because the devices are constructed using simple and generalizable processes, these geometric parameters can be easily varied. Such a device containing a single MWNT could be used to advance fundamental understanding of complex fluid rheology at the nanometer length scale and also function as a sensitive single-object characterization tool for nanoparticles and polymers.

Fully automated combinatorial exploration of rheological properties in multicomponent systems with a standard rotational rheometer PO190

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Inexpensive flow control units allow the construction of fully automated laboratory infrastructures for the investigation of complex fluid systems. By combination with intelligent process control techniques, combinatorial and evolutionary strategies can be employed to efficiently explore the enormous parameter spaces available in multi-component reactions and formulation. We have developed an apparatus based around an industry standard Malvern rotational rheometer (Bohlin C-VOR) for viscometry, oscillation and creep&recovery tests. Custom cup & bob geometries have been developed to allow for the automatic loading and unloading of samples, as well as the automatic cleaning of the rheometer between samples. The auto-loading system is capable of accurately mixing/reacting up to five separate components before loading into the rheometer. The system has been successfully tested and produces data that correlate well with data achieved using conventional measurements with manual sample loading. We will report results from initial studies of aqueous formulations with alkyl polyglycosides and non-ionic surfactants from renewable sources.

Development of a new opposed-nozzle fixture for measuring the extensional properties of low viscosity liquids PO191

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We describe the development of a new opposed jet device for measuring the apparent extensional viscosity of low-viscosity fluids at high deformation rates. The design builds upon the original opposing-jet device of Cathey & Fuller that was commercialized as the RFX instrument by Rheometrics (now TA Instruments). In contrast to the RFX stand-alone system, the new opposed-nozzle fixture can be mounted onto a controlled strain rheometer such as the ARES or ARES-G2. It consists of two opposed jets mounted on rigid arms and terminated with interchangeable disposable syringe needle tips. The first arm is directly connected to the force rebalance transducer (FRT) sensor of the ARES while the second one is attached to a three-axis translation stage for accurate positioning and alignment of the two opposing nozzles. The test fluid is forced out under pressure as two free jets through the opposed needle tips by the action of a twin syringe pump. The resulting stagnation flow generates an approximately uniform biaxial extension field and the resulting torque acting on the arm connected to the FRT is recorded as a function of time for each imposed volumetric flow rate. In this initial feasibility study, particular attention is paid to the coupling arrangement between the tubing from the twin syringe pump and the nozzle arm connected to the FRT so that a minimum residual torque resistance is guaranteed. Different size nozzles and moment arms are investigated to explore the operating envelope and stability boundaries of the FRT. Apparent extensional viscosity data are presented for different glycerol/water mixtures, dilute polymer and micellar solutions.

In-situ photorheology and electron spin resonance to assess polymer photoaging PO192

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It is known that polymers ages under UV irradiation. Thus, to predict polymer photo durability it is necessary to be able to characterize their evolution at a molecular level. FTIR spectroscopy gives the chemical evolution of the material by the analysis of their photoxydation products. UV coupled Melt Rheology and R.P.E techniques provide the evolution of the molecular structure as a result of chain scission and crosslinking. Due to the large frequency spectrum obtained by ESR, we were able to precise the chain scission/crosslinking/recombination reactions. Moreover, the local character of the ESR technique gives additional information on the heterogeneous character of these reactions. Till to now it was not so common to use ESR experiments to assess photo-oxidation of elastomers and even more for UV in situ irradiation. Our results proved the validity of this technique and will be the beginning of new further developments, for instance to reach to indentify the radicals species by a suitable choice of the nature and the functionality of the probe. Key words: photo oxidation - elastomers - photorheology - photo RPE

Ultrasound as a complementary tool to internal mixers for investigation of thermal mechanical degradation of PET PO193

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Internal mixer is a standard laboratory tool for studying rheological behaviors of polymers under a variety of processing conditions. In this work, an ultrasonically instrumented internal mixer was used to study the thermal mechanical degradation of PET samples with different levels of water content and under different processing temperatures and roller speeds. For ultrasonic tests, ultrasonic diagnostic signals were generated by an ultrasound sensor flush-mounted on the mixing head, propagated into the polymer, and then reflected by the rotating roller blade back to the same ultrasound sensor. Measurement results have shown a clear correlation between the torque value provided by the internal mixer and ultrasound velocity in the polymer melt. The fluctuation of the reflection coefficient of ultrasound signals at the ultrasound sensor/polymer interface also provided a good indication of the melting status of the polymer at different stages into the test. Furthermore, the strength of ultrasound signals reflected from the roller blade appeared to be more sensitive to PET degradation than the torque, suggesting that ultrasound could provide additional information on material property changes. A main advantage of ultrasonic degradation monitoring over torque measurement is that it could be implemented on extruders to obtain localized melt degradation information. An upscale application of this technology to extruders will be discussed.

A real-time ultrasonic technique for viscosity measurement during polymer processing PO194

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In this work, a real-time ultrasonic diagnostic technique was developed for in-process viscosity measurement during polymer processing. The establishment of the technique was based on combined uses of a slit rheometer whereby rheological behaviors of a variety of polymers were investigated under different temperatures and shear rates, and of two ultrasound sensors flush-mounted on the slit die of the rheometer whereby ultrasonic properties of a melt were measured simultaneously during rheological tests. It has been found that, for the polymers studied, there exists an empirical relation between ultrasound velocity (V) in the melt, the melt viscosity (η), the melt pressure (P), and melt temperature (T): $V=a*\ln(\eta+b)+c*P+d*T+e$, where a, b, c, d, and e are constants related with the properties of individual polymer melt. Therefore by measuring melt pressure, melt temperature, and ultrasound velocity in the melt, the above relationship enables convenient in-process measurement of melt viscosity during polymer extrusion as well as polymer injection molding processes.

Food Rheology

Comparison of methods for analyzing fruit-filled yogurt rheology PO196

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Helipath testing is a traditional method for analyzing heterogeneous materials, such as yogurt. A Brookfield HBDV-II+PRO viscometer, with Helipath stand and T-B spindle, was used to test fruit-filled yogurt at 9 °C. The spindle speed was 2 rpm, and data were acquired for six minutes, during each test. Blueberry had an average viscosity of 192,000 cP, Peach had an average of 199,000 cP and Strawberry's average was 250,000 cP. Helipath data had significant scatter, however. Yield tests were performed with a Brookfield HBYR-1, at 2 rpm. The V-73 vane spindle was used, immersed to its primary immersion mark. The average yield stresses were: Blueberry, 178 Pa, Peach, 230 Pa, and Strawberry, 470 Pa. The V-72 vane was also used, immersed to the secondary mark. The average yield stresses were: Blueberry, 196 Pa, Peach, 272 Pa, and Strawberry, 245 Pa. The same vanes and immersion levels were used with a Brookfield HBDV-II+PRO at 2 rpm, with a six-minute test time for each sample. The average viscosity maxima for the V-73 vane were: Blueberry, 567,000 cP, Peach, 704,000 cP, and Strawberry, 724,000 cP. The average viscosity minima measured at six minutes were: Blueberry, 121,000 cP, Peach, 156,000 cP, and Strawberry, 132,000 cP. The average viscosity maxima for the V-72 vane were: Blueberry, 601,000 cP, Peach, 622,000 cP, and Strawberry, 640,000 cP. The average viscosity minima at six minutes were: Blueberry, 122,000 cP, Peach, 142,000 cP, and Strawberry, 127,000 cP. The hardness of the yogurt was determined using the Brookfield LFRA-1500 Texture Analyzer. The compressive trigger load was 5.00 g_f, followed by a 10 mm/s testing speed through a 20 mm depth with a TA4/1000 probe that was 38 mm in diameter and 20 mm high. The average peak loads were: (1) Blueberry, 294 g_f, (2) Peach, 368 g_f, and (3) Strawberry, 338 g_f. Creep Relaxation tests were run with the Brookfield R/S-SST controlled-stress rotational rheometer for thirty seconds at 3% of full-range stress, followed by thirty seconds at zero stress, using the V40-20 vane spindle. The elastic indices were: Blueberry, 0.92, Peach, 0.89, and Strawberry, 0.90; that is, the yogurts appeared to elastically recoil, to some extent. Each individual test provided meaningful results. However, the combination of test methods gave a greater overall understanding of these heterogeneous materials' complex rheology.

Rheological behavior, granule size distribution and differential scanning calorimetry of cross-linked banana (*Musa paradisiaca*) starch 💿 PO197

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Starch is the main reserve carbohydrate synthesized by superior plants and represents an important component of a large number of agricultural products. In tropical fruits, like banana, which when green may contain up to 70% on a dry basis. Banana (Musa paradisiacal) starch has been isolated in pilot plant level, however the low stability to mechanical-thermal treatment during pasting limit its wide application and industrial use. To resolve this problem, the banana starch was cross-linked with adipic acid under diverse reaction conditions: adipic acid concentration, pH and temperature reaction effect. In this work, rheological, granule size distribution and Differential Scanning Calorimetry (DSC) tests were employed to study the effect of cross-linking of banana starch. Cross-linkage of starch was obtained in a glass reactor (300 mL) under pH and temperature controlled conditions. The rheological behavior of starch pastes with 6% (w/v) at 60 °C was examined on a AR1000N rheometer (TA Instruments) at 60 °C using cone/plate fixture (4°, 60 mm diameter, 110 micro m gap). Two consecutive up and down sweeps from 0 to 300 s-1 were chained to a final logarithmic ascendant from 0 to 300 s-1 in a total time of 12 min. Viscoelastic properties were examined under low amplitude oscillatory shear from 0.1 to 100 rad/s at 25 °C using the parallel plates fixture (40 mm diameter, 3 mm gap). The size of starch granules was determined by laser diffraction analysis (Malvern Master SizerS 2000). The thermal behavior was examined by DSC using a calorimeter (TA-Instruments, USA, model 2010). Rheological behavior from pastes of cross-linked starch at 60 °C did not show hysteresis, probably due the cross-linkage of starch that avoided disruption of granules, elsewhere native starch showed hysteresis in the two shear cycles. In the shear stress vs shear rate curve, all pastes showed the non-Newtonian shear thinning character. Frequency sweeps showed typical gel behavior with moduli independent of frequency from 0.1 to 100 rad/s, G´ greater than G´´ and Tan delta below 1.0. In general, the gels of cross-linked starches formed gels more rigid than those of native banana starch. Size distribution showed a decrease in the median diameter in cross-linked starches. This condition produces a decrease in swelling capacity of cross-linked starch. Finally an increase in gelatinization temperature was observed as an effect of cross-linkage of banana starch. The cross-linkage of banana starch produced granules more resistant during the pasting procedure.

Rheological study of batter dough for "Yorkshire pudding" production 💿 PO198

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Batter dough is widely used in food industry for many bakery products having different texture. Their liquid-like properties are used to control material flow during process and, as a consequence, final product texture and shape. "Yorkshire pudding" is a typical product based on a batter dough, its shape is mainly due to the shear flow induced by bubble growth during baking. Even though the typical recipe is quite simple being mainly based on water, flour and eggs, industrial evidence confirms that material properties and therefore process conditions, are strongly affected by slight changes in formulation. In this work we report a preliminary rheological study of a typical batter for Yorkshire pudding production aiming to evaluate the influence of some relevant ingredients (mainly eggs) on mechanical characteristics. Dynamic tests were carried out at different temperatures to evaluate how the change in recipe can affect different process steps; experimental data were analyzed by the weak gel model and computed parameters, interactions strength and network extension, were reported as temperature function, showing a significant dependence on recipe. Steady shear tests confirmed that viscosity, and therefore flow behavior during process, changes with adopted formulation. Rheological data were compared to industrial evidence aiming to find a relationship between process conditions and material parameters.

Olive oil based emulsions in frozen puff pastry production PO199

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Puff pastry is an interesting food product having different industrial applications. It is obtained by laminating layers of dough and fats, mainly shortenings or margarine, having specific properties which provides required spreading characteristic and are able to retain moisture into dough. The shortening is not mixed into the dough but is placed on top of it and folded to form several alternating thin layers of dough and fat. The fat keeps the layers of dough separate and flaky and the water turns to steam during the baking process yielding the layer expansion and the typical texture. Moreover when frozen pastry is produced a low temperature stable fat has to be used to avoid undesired crystals formation during storage. To obtain these characteristics, pastry shortenings are usually produced by hydrogenation and interesterification of different fats. However it seems that hydrogenated fats can negatively affect human health and in many products they are being replaced by more healthy products. However in puff pastry their role is strictly related to the high melting point and their consistency, mainly depending on the saturation degree and it is not easy to replace them by unsaturated fats, because of their low melting point and a prevalent liquid-like behavior at process conditions. It is well known the healthy character of olive oil but, due to its physical properties, it gives poor quality in puff pastry. To solve this problem, in the present work, a new product, based on olive oil, was studied as shortening replacer in puff pastry production. To ensure the desired consistency, for the rheological matching between fat and dough, a water-in-oil emulsion was produced based on olive oil, mono and diglycerides of fatty acids and a hydrophilic thickener agent able to increase material structure. Different oil/water ratio and thickener agents, mainly based on wheat flour, were adopted for sample preparation; obtained materials were characterised by rheological dynamic tests in linear viscoelastic conditions aiming to setup process and material consistency and rheological data were analysed by using the weak gel model. Time cure tests were carried out to evaluate material stability both at low and high temperatures. Results obtained for tested emulsions were compared to theological properties of a commercial margarine, adopted as reference value for texture and stability. Finally a lubricated squeeze test was used to evaluate material properties in kinematic conditions close to process applications. Obtained emulsions are characterized by interesting rheological properties strongly dependent on emulsifier characteristics and water phase composition. However a change in process temperature during fat extrusion and dough lamination seems to be necessary to match properly typical dough rheological properties.

Influence of fat content on chocolate rheology PO200

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Molten chocolate is a suspension made by particles of sugar, cocoa and /or milk solids dispersed in a continuous fat phase. Chocolate properties are strongly affected by particle size distribution including not only the dispersed particles but also the fat crystals formed during chocolate cooling and solidification. Cocoa butter is characterized by the presence of six different crystalline forms, having different dimensions and stability, that can be formed during chocolate cooling. Kinetics and physical properties of crystals are mainly determined by the adopted thermal history (i.e. temperature and time) therefore a controlled cooling, followed, often, by controlled heating under shear, is necessary to have the right crystalline forms. Even though chocolate rheology is extensively studied, mainly flow properties (i.e. viscosity) at high temperature (above 50°C) were determined; therefore no information on amount and type of fat crystals can be detected in these conditions. However chocolate texture and stability is strongly affected by the presence of specific crystals, therefore a link between fundamental rheological properties and microstructure seems to be relevant for a complete material characterization. In this work a different approach, based on creep test, was proposed to characterize chocolate samples at typical process temperatures (approximately 30°C). The analysis of compliance, as time function, at short times enable to evaluate a material "elasticity" related to the solid-like behavior of the material and given by the differential area between the Newtonian and the experimental compliance. Moreover a specific time dependent elasticity was defined as the ratio between the differential area in time range and total area. Chocolate samples having a different fat content were prepared starting by a typical commercial formulation based on cocoa liquor, cocoa butter, sugar, lecithin. Samples were conditioned directly on rheometer plate by applying a controlled cooling at two different temperature ramp, 5°C/min and 1°C/min, simulating, respectively, a typical process condition and a slow cooling. Then samples were analysed by creep at 30°C applying a low stress to test material in linear viscoelastic conditions. Experimental data were analysed by the proposed method ad total hysteresis area was found to be dependent on fat crystals amount whilst the specific elasticity was related to single crystal properties. It was that fat crystal amount and properties depend in different way on fat amount and cooling rate; moreover creep proved to be able to detect even small differences among tested samples. Finally, data obtained by rheological tests were compared to results yielded by X Ray Diffraction (XRD) analysis confirming the presence of specific crystal forms having well defined characteristics.

Mechanical modeling of foods including fracture and simulation of food compression PO201

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The purposes of this research are to simulate the solid food swallowing, and to investigate the relationship between the rheological properties of foods and swallowing. Swallowing of the solid foods is influenced by how the characteristics of foods are changed by mastication. Therefore, here we investigated the mechanical modeling of foods that could be applied to the mastication, and numerically simulated the food compression test using a finite element method. We used an elasto-plastic model as the rheological model of the foods, and used two types of elements. Lagrange elements were applied with a fracture control program Tiebreak, which decided the fracture between the elements based on the critical stresses. Euler elements were applied to simulate the large deformation. These food models were applied to simulate the compression test with a wedged plunger. The experimental results for tofus, bananas, and biscuits were compared with the simulations. In order to analyze the complex characteristics of the foods, non-homogeneous food models were introduced by combining the models with different model constants: a two-layer model, a three-layer model, and a roll model. These models were applied to simulate the test of a compression rate 40 %. Reasonable agreements were obtained on the fracture and the reaction forces between the simulations and the experiments.

Rheology of film-forming solutions prepared with modified banana starch and plasticizer PO202

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The potential application of edible film barriers for preservation of foods, has recently been recognized because of various factors such as, the use of environment friendly materials, consumer expectation for fresh foods and need for shelf life extension of foods. The physical properties of edible films depend to a great extent on those of their components, namely, the biopolymer and the plasticizer, which define its physical changes during heat processing and handling. The aim of this work was to determine the rheological profile of film forming solutions (FFS) composed of native and modified (oxidized) banana (Musa paradisíaca L) starch and the plasticizer glycerol. Lots of samples of FFS, containing 4%(w/w) of previously gelatinized banana starch (native and oxidized using sodium hypoclorite (1% v/v)) and glycerol 4%(w/w) were prepared. Two types of rheological tests were undertaken using a strain controlled Rheometer TA Instruments, model AR1000, with a cone and plate system, 60 mm of diameter and angle of 2°: a) isothermal oscillatory tests at 25°C, 90°C and once cooled down, at 25°C. This involved amplitude sweeps run in the strain range from 0.001 to 0.15 at 1 Hz, and frequency sweeps tested from 0.1 to 10 Hz, at a strain of 0.1. b) temperature sweeps with constant values of strain (0.1) and frequency (1Hz), run as the samples were heated up from 25°C to 90°C and also when cooling down to 25°C. Amplitude strain profiles showed linear viscoelastic behavior within the range tested with no indication of sample structure disruption. The isothermal tests showed that all pastes produced, behaved as weak viscoelastic gel-like materials, with the elastic modulus (G') > the viscous modulus (G") over the frequency range involved. The temperature sweeps also showed that all viscoelastic FFS, behaved as mainly elastic materials over the temperature ranges. The results suggested that all samples of FFS weakened its structure when heated up to 90°C, but when cooling down to 25°C, some structure strengthening was observed, probably because of retrogradation start. Overall, FFS from native starch yielded gels with higher moduli (G', G") values than those of the oxidized ones.

Effect of frozen storage on the gel-forming ability of surimi treated by acid and alkaline solubilization PO203

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Acid and alkali processing are new alternatives to manufacturing surimi; its traditional aim has been to recover a functional collagen-free protein with low levels of membrane lipids. The recovery proteins retain their functionality, including their ability to form a gel; however, it is well known that frozen storage reduces the gel-forming ability of surimi as a result of denaturation and aggregation of myofibrillar proteins. The inclusion of cryoprotectants (4% sorbitol + 4% sucrose) is required to ensure long-term stability. The present study was conducted to evaluate the rheological changes of horse mackerel (Trachurus trachurus) surimi elaborated by acid and alkali solubilization during five months of frozen storage, and their ability to form gels. Samples of this study were the following: surimi A and gel GA, made by acid solubilization, and surimi B and gel GB by alkali solubilization, both A and B with 4% sorbitol + 4% sucrose and neutralized with calcium hydroxide. Rheological properties were obtained using Bohlin CVO and RS600 Haake rheometers. In general, from oscillatory tests it can be seen that five months of frozen storage provoked slightly changes in the viscoelastic properties in two kinds of surimi. On one hand, samples A showed a weak increase of the consistency and little rigidity decrease, and on the other hand surimi B, undergone a significantly increase in rigidity and firmness, likely due to a loss of water holding capacity and the growth of hydrate crystals during the storage period which reflect the characteristic effect of frozen storage (more fibrous and dry structures), according with the common behaviour of surimi from other fish muscles. However, the effect of frozen storage was different in the ability to form gels. While GA gels undergone a significantly decrease of gel strength (creep and recovery test), toughness and deformability (stress and frequency sweep) after five months of storage, likely due to the greater lipid content in myofibrillar protein which is typical of acid treatment. However, gels from method B presented a remarkable increase of viscoelastic moduli, maximum stress and gel strength, showing a better gel structure after five months of frozen storage than gels formed by method A.

Rheological modification of reduced fat chocolate induced by the addition of limonene PO204

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In response to consumers' growing desire for healthy lifestyles, decreasing the fat content of food products has become of interest to food manufacturers. In terms of microstructure, chocolate is a suspension of particles (sugar, cocoa solids and milk solids) dispersed in a cocoa butter continuous phase. Decreasing the fat content of chocolate, usually around 30%wt, leads to an increase in the molten chocolate viscosity, due to more particle interactions. This makes chocolate manufacture more difficult. *Beckett (1)* claims that the addition of small amounts of limonene, a hydrophobic low molecular weight compound usually utilised as a flavour, leads to a significant decrease in the chocolate viscosity, facilitating the production of reduced fat chocolates. The goal of this study is to understand the functionality of limonene in decreasing the viscosity of reduced fat chocolate.

Our study shows that replacing a fraction of the cocoa butter by limonene in a 25%wt fat chocolate indeed leads to a significant decrease in the chocolate viscosity. After checking that limonene does not significantly affect the fat phase volume fraction, we show that limonene decreases the viscosity of chocolate by decreasing the viscosity of the continuous phase. It appears that adding a small quantity of limonene in cocoa butter leads to a great decrease in the liquid fat viscosity. This observation may simply be a result of increasing the amount of a lower viscous component in a simple mixture, or there may be specific interactions between limonene and cocoa butter, as also indicated by a complex mixture viscosity-limonene concentration relationship.

The results of this study demonstrates the potential for controlling the viscosity of fat or fat based dispersions by adding a hydrophobic low molecular weight compound such as limonene.

(1) Beckett, S.T., Preparation of chocolate with limonene to reduce fat content, U.S. Patent 6200625 (1999).

Utility of squeeze flow in food industry 💿 PO205

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The principle of squeezing flow for obtaining sheare viscosity on Newtonian and non-Newtonian liquids has long been established in the literature. RMS-800 from Rheometrics Inc. was employed to conduct the squeezing flow under a constant speed on a set of parallel plates. The calculated viscosity vs. shear rate for Polydimethyl Siloxane (PDMS) exhibit close agreement with that obtained from small amplitude dynamic oscillatory test using Cox Merz Rule. The technique was applied to food gel materials such as mayonnaise at room temperature. Viscosity data over a broad range in shear rates is compared between Hellmann's real (HRM) and light mayonnaise (HLM). HRM exhibits a more pronounced shear-thinning compared to HLM suggesting that HRM is more spread able. Sensory evaluation by trained expert panel ranked that the mouth feel in adhesiveness and cohesiveness of HLM is significantly higher relative to HRM. The method offers a unique advantage to develop shear viscosity over a broad shear rates which are otherwise not obtainable on rotational shear flow that causes flow instability or slippage or fracture as frequently reported in the literature. The method is proven to be fast, rugged, simple, and reliable. It can be developed as a QC tool. Possible errors involved in determining the viscosity from un-parallelism will also be discussed.

Rheology of Solids and Glasses

Vicsoelastic characterization of soft and rigid solids immersed in liquids PO207

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Dynamic Mechanical Analysis is one of the most effective and practical methods of studying the relationship of structure to performance in tissue engineered solid materials. Especially important is to understand their viscoelastic behavior in vivo conditions in order to maintain the same atmosphere under which these materials would be used. TA Instruments have therefore developed an immersion system for these types of viscoelastic measurements. Examples of Compression, Uniaxial Extension, and Three Point Bend Flexural modes have been treated on soft solid samples and discussed.

Rheological properties of carbon nanotube fiber networks in ionic liquids PO208

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The dispersion of nano-fibers (nm-thick and µm-long fibers) in matrices, without bundling or aggregation, is of crucial importance for the beneficial combination of fiber properties with those of matrix fluids in fuel cell and battery applications. For multi-walled carbon nanotubes (MWCNT) from different producers dispersed in an Ionic Liquid (Butylmethyl-imidazoliumtetrafluoroborate), we dealt with characterization of the dispersion properties using rheological and morphological techniques. We found that, regardless of the chemical nature of the fibers, the rheological properties of the tightly entangled fiber networks possess some unique characteristics. Measuring the dynamic moduli of different dispersions in dependence of temperature and concentration we identified the regions in which network formation (gel like state of suspension) is dominant for these systems. It turned out that different module-concentration curves can be superimposed to master curves. The shift factors are related to morphological properties of the different fibers such as persistence length and aspect ratio which were determined by TEM, centrifugation.

The effect of water on the modification of bitumen with MDI-PEG prepolymer 💿 PO209

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Asphalt, roofing and sealing markets strongly demand new materials for being used, for instance, as bituminous coating membranes. In that sense, the benefits to these bitumen-based composites of the addition of MDI-PEG reactive polymer, synthesized by the reaction of 4,4'-diphenylmethane diisocyanate with a low molecular weight polyethylene glycol, is assessed. A short-term modification, taking place during mixing, and a long-term bitumen modification, which develops for a long period of curing (up to several months), have been identified. Both of them result from chemical reactions between -NCO groups in the MDI-PEG and, mainly, the resin fraction. However, long-term bitumen modification seems to be related both to the reaction between reactive polymer and bitumen compounds and to the environmental conditions (probably due to air moisture). This fact may be used to improve the manufacture of new materials with suitable properties according to their final application.

Thermodynamic scaling of the dynamics in fragile glass-formers: Insight from computer simulations PO210

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The origin of the thermodynamic scaling of dynamic properties in supercooled liquids, experimentally observed for a wide range of materials, is investigated by means of molecular dynamics simulations. We present results for several models of fragile glass-forming liquids, for which we show that diffusion coefficients and structural relaxation times can be expressed as a unique function of T/ρ^{γ}, where T is the temperature, ρ is the density, and γ is a material-specific constant. We demonstrate a direct connection between the scaling exponent γ and the steepness of the repulsive part of the interaction potential u(r). Around the distance of closest approach between particles, estimated by inspection of the radial distribution functions, the potential u(r) can be well approximated by an inverse power law with exponent 3γ, thus providing a rationale for the observed thermodynamic scaling. On the basis of our results, we also discuss the relation between the magnitude of the scaling exponent and the Angell's fragility of glass-forming liquids.

Rheological properties of gels from pyrene based low molecular weight gelators 💿 PO211

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Pyrene derived low molecular weight organogelators and gels thereof in primary alcohols were characterized rheologically. Flow curves, temperature and stress sweeps were determined for gels from 1-decylpyrene (DP), 1-octadecylpyrene (ODP), 12-(pyren-1-yl)dodecanoic acid (PDOA), 1,1'-(dodecane-1,12-diyl)dipyrene (DDDP) and mixtures thereof with a rheometer using cone-plate configuration. The total gelator concentration was varied from 0.5 to 2.7 % w/w depending on the solvent and gelator, including equimolar amounts of gelator and 2,4,7-trinitrofluorenone (TNF) coupling agent which is needed for the gel network formation.

The thermal stability of the gels was determined by sweeping the temperature from 10 to 80 ^{o}C within one hour in oscillation mode using a frequency of 1 Hz and stress of 1 Pa. Mechanical stability of DP/TNF gel in octanol was determined at 0.5 and 1 % w/w gelator concentration by centrifuging at 1000 g acceleration for 1 hour. Relatively sharp melting points between 50 and 75 ^{o}C were observed and the room temperature elastic moduli were between 10 and 100 kPa. All the gels are thermally reversible and the gelation/decomposition is completed in a few minutes due to the non-covalent nature of the gel network bonding. The effect of the solvent on gel properties was investigated with 1-pentanol, 1-octanol and 1-dodecanol.

In addition to the gelator concentration, the strength of the gels was found to depend on the solvent and on the length of the side chain in the pyrene nucleus. Over 7 carbons long chain was found necessary for gel formation, but as the chain length increases over 10 carbons the gel stability decreases and the gels become weaker. Functional groups were observed to disturb gel formation and reduced the strength and the thermal stability of the gels. The adverse effects of the gelator functionality can be prevented by mixing nonfunctionalized and functionalized gelators or pyrene to keep the functional groups apart from each other. All gels were strongly shear thinning and showed a yield point between 20 and 1000 Pa depending on the solvent and gelator. The yield point and the elastic modulus of DP/TNF gel increased, when a small percentage of the DP was substituted by DDDP resulting to a supramolecular level crosslinking in the gel.

Experimental and numerical studies on mudstone's creep behavior during water injection and its effect on casing damage 💿 PO213

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During the process of water injection production in oilfield, when water cuts into the mudstone, as a result, large numbers of casings are damaged because of mudstone's creep characteristic. In order to analyze this phenomenon, the uniaxial compression experiments and creep experiments of mudstone from Daqing Oil Field under different saturation conditions were done, it was studied that how the mudstone's mechanical parameters and creep characteristic would change with the increment of water contents. The results indicate that the rock strength and elastic modulus are decreased rapidly with the increment of water contents, on the other hand, the creep strain and steady state creep strain rate are increased with the increment of water contents, and also the steady state creep strain rate is enhanced with the increment of deviatoric stress. Through the creep characteristic curves, a nonlinear creeping constitutive equation of mudstone considering the changes of water contents was established. In the deep stratum of the oilfield, the calculation model of casing-cement sheath-mudstone was built, based on the experiment results of mudstone and its creep constitutive equation, mudstone's creep pressure with time under different water contents was simulated. The simulation results show that the increasing water content accelerates the incremental rate of the creep pressure of mudstone, so the time of reaching yield state of casing will descend greatly, which means service time of casing becomes much shorter. Key words: casing damage; mudstone's creep behavior; uniaxial compression experiments; creep experiments; water content; numerical simulation

Influence of hydrated lime on mechanical properties of bitumen binders PO214

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Hydrated lime has been added to hot mix asphalt pavements for over 25 years, improving the mixtures in many ways and increasing the life of highways. Lime contributes to both the mechanical and rheological properties of asphalt mixtures, improving moisture sensitivity resistance and fracture toughness along with reducing the rate of oxidative aging of many bitumens. Hydrated lime (HL) reacts with acid components of bitumen to produce beneficial changes that contribute to the creation of high performance asphalt mixes. HL is active filler, but only in some bitumens. It was found that HL interacts with certain bitumens to develop an adsorbed (interactive) layer around the HL particles. The level of interaction between HL and bitumen is bitumen dependent. This interaction causes HL to strongly affect high-temperature rheology in certain bitumens, but it has less of an effect in others. The low-temperature stiffening effects of HL are less prominent, and a significant level of fracture toughening (at low temperatures) occurs through the addition of HL. In this work, the influence of HL on the mechanical properties of bitumen and bituminous mortar (mixture of filler and bitumen) was examined for two bitumen types: unmodified road bitumen B50/70 and polymer modified PmB II. These bitumens are the most frequently used in Slovenian asphalt mixtures production for wearing courses and wearing - close courses. The experimental work was carried out by using standard test methods (R&B softening point, penetration, Fraas breakig point, ductility) and rheological characterization. In bituminous mortars a part of filler was replaced with HL, the amount of HL varied from 0 to 20 wt.%. All the samples were examined before and after forced temperature ageing and after bituminous binder extraction (by trichloro-ethylene). The most evident effect of HL in bituminous mortars was found to be on the shear viscosity and on the parameter $G^*/\sin\delta$ which has been adopted by SHRP. Presence of HL in filler stiffen the mixture, the level of mixture hardening depend on the amount of HL and on bitumen type, higher increase in viscosity was found for unmodified road bitumen B50/70. The variation in low temperature properties of bituminous mortars was less prominent until to certain amount of HL, at high amounts they got worse. HL in bituminous mortar inhibited the process of oxidation. This effect was more pronounced for polymer modified bitumen. The mechanical properties of both types of bitumen, extracted from the different bituminous-filler mixtures didn't differ noticeable between each others.

UV curing analysis using AR rheometer

PO215

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UV-curable materials are widely used in coatings, adhesives and inks. When these systems are exposed under ultraviolet radiation, a fast crosslinking reaction occurs within a few seconds to a few minutes. To study this fast curing reaction, we are introducing a new UV curing system on TA Instruments AR series rheometer, which equipped with two types of UV light sources, the external light source system and the light emitting diode (LED) system. The external light source uses a high-pressure mercury lamp with a light guide. It provides a broad range of spectrum from 250 nm to 600 nm. The maximum output intensity using the external light source is 300 mW/cm^2. The LED system provides a unique single band wavelength at 365 nm with a maximum output intensity of 150 mW/cm^2. In order to better catch a rapid curing reaction and also get good reproducibility, a fast data acquisition and a temperature control accessory are also equipped together with the UV curing system.

Extended creep recovery via oscillatory shear and bending beam rheometers

PO216

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Relaxation and retardation spectra are often used to describe the linear viscoelastic properties of polymer melts, asphalts, and other viscoelastic materials, since the spectra contain sufficient information from which other linear material functions can be easily calculated. The applicability of these functions strongly depends on the range of frequencies or relaxation times over which the experimental data were obtained. Various techniques can be emloyed to expand the range of relaxation times, which involves using different types of tests, such as oscillatory shear or creep recovery. The overall range of relaxation times can be expanded by means of the time-temperature superposition. In the case of bituminous materials studied, creep experiments at lower temperatures involve different testing geometry, e.g. a bending beam rheometer (BBR). The challenge is to combine the spectra obtained from the oscillatory and creep/recovery in shear deformation with the spectra obtained from the extended flexural deformation. We demostrate a technique of combining the spectra obtained for two conventional bitumes (asphalts) of different origin, with a practical application to modelling a multiple creep and recovery test.

Large scale dynamics in a driven simple glass

PO217

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Diffusion in melts undergoing strong shear is investigated via large scale molecular dynamics simulations of a well established glass forming model system, namely the 80:20 binary Lennard-Jones system first introduced by Kob and Andersen [W. Kob and H.C. Andersen, PRL **73**, 1376 (1994)]. In previous works [F. Varnik JCP **125**, 164514 (2006) and F. Varnik and O. Henrich PRB **73**, 174209 (2006)], the interplay between the dynamics of structural relaxation on the length scale of the average interparticle distance and the stress response of the model was studied. Here we focus on the large scale dynamics under homogeneous shear by evaluating the time dependence of the mean square displacements for temperatures ranging from the supercooled state to far below the mode coupling critical temperature of the model. Particularly long simulations are performed allowing an accurate determination of the diffusion constant. For low temperatures and at not too high shear rates, the mean square displacements exhibit the well known two step relaxation behavior with a long time diffusive motion along the spatial directions perpendicular to the flow. In the flow direction, on the other hand, a third regime follows the diffusive motion, where Taylor dispersion with the typical t^3 time dependence clearly dominates the long time behavior of the particle displacements. At the lowest studied temperatures, the cross over from the diffusive regime to the regime where the contribution of Taylor dispersion becomes significant, occurs at length scales of the order of a particle diameter but is shifted towards progressively larger displacements as temperature increases. Moreover, once the contribution of Taylor dispersion is subtracted from particle displacements, diffusive motion is recovered also along the flow direction. Interestingly, a comparison of diffusive motion along the flow, the shear gradient and the vorticity directions shows small but systematic anisotropic effects.

Non-affine deformations of inherent structure as signature of cooperativity in supercooled liquids

PO218

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Approaching the glass transition, experimental and theoretical investigations as well as simulation results on dynamical heterogeneities strongly support the presence of cooperatively rearranging regions of growing size. However, it is still debated whether and how the onset of such cooperative dynamics can take place without any apparent or straightforward connection to structural changes.

We search for a signature of the onset of cooperative dynamics in the structural features of supercooled liquids from a novel perspective [1]. We unveil the existence of non-affinely rearranging regions in the inherent structures (IS) of supercooled liquids by numerical simulations of model glass formers subject to static affine deformations combined with local energy minimizations [2].

In the liquid state IS, we find a broad distribution of rather large, non-affine displacements which are correlated only over small distances. At low temperatures, the onset of the cooperative dynamics corresponds to much smaller non-affine displacements correlated over larger distances. This indicates the presence of non-affinely rearranging domains of relevant size in the IS, which can be seen as the IS counterpart of the cooperatively rearranging regions in the dynamics. This idea suggests a new insight into possible structural signatures of slow cooperative dynamics of supercooled liquids and supports the connections with elastic heterogeneities found in amorphous solids.

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Kinetic toy model for crystal plasticity

PO219

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We propose a kinetic toy model to describe the dynamics of sliding layers as it occurs in the plastic deformation of single crystals, be it of polymeric, colloidal, or metallic nature. As its basic ingredient, the distribution function of relative strains between adjacent crystal layers is introduced with time evolution described by a diffusion equation with periodic boundary conditions. The model highlights the conceptual difference in the dynamics of the elastic and plastic strains, the latter being related to an average hopping rate that captures the evolving reference state. We illustrate the model by calculation of the stress response for both stationary and transient conditions. In order to discuss the physics behind the parameter that drives the plastic flow in the kinetic model, we use nonequilibrium thermodynamics to unify this model with a nonisothermal hydrodynamic description, which renders the set of evolution equations closed. Finally, we examine the relation of the kinetic toy model to macroscopic theories of elasto-viscoplasticity that employ the macroscopic deformation gradient as a fundamental variable.

The research on rheology mechanism of coal-rock containing gas PO220

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Rheology mechanism is studied for the whole rheology process of coal-rock containing gas using rock servo system and rock shear rheology apparatus in triaxial compression. Experiment show that there are 3 typical creeping stages including instantaneous creeping I stage, stable development of deform II stage and acceleration deform to destroy stage III. According to the result of experiment and one-dimensional creeping constitutive equation, three-dimensional rheology constitutive equation is built by analogy and assumption method. And using rheology mechanism of coal-rock containing gas illustrates reasons of coal and gas outburst in mining work face.

General Rheology

Experimental research on pyromagnetic effect of PVC sheet PO222

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Experimental Research on PVC sheet with defects was conducted under tensile load. In the region of viscoplastic damage a heat was given out and the temperature was increased and measured by instrument named HX8600. Using the surveying system exploited by ourselves, a heat-force coupling pyromagnetic effect in the process zone of rheologically damaged fracture was measured. The system includes integrated circuit sensor, data collecting and analysis software, etc. Keywords: PVC sheet with defects, pyromagnetic effect, sensor, data collecting, surveying system Notes: The project supported by the National Natural Science Foundation of China (10672191), the Provincial Natural Science Foundation of Hunan (06A0110), the Key Laboratory of Low Dimensional Materials & Application Technology (Xiangtan University), Ministry of Education (KF0607).

Slump flows inside pipes: Numerical results and comparison with experiments PO223

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In this work an analysis of the buoyancy-driven slumping flow inside a pipe is presented. This flow usually occurs when an oil well is sealed by a plug cementing process, where a cement plug is placed inside the pipe filled with a lower density fluid, displacing it towards the upper cylinder wall. Both the cement and the surrounding fluids have a non Newtonian behavior. The cement is viscoplastic and the surrounding fluid presents a shear thinning behavior. A numerical analysis was performed to evaluate the effects of some governing parameters on the slump length development. The conservation equations of mass and momentum were solved via a finite volume technique, using Fluent software (Ansys Inc.). The Volume of Fluid surface-tracking method was used to obtain the interface between the fluids and the slump length as a function of time. The results were obtained for different values of fluids densities differences, fluids rheology and pipe inclinations. The effects of these parameters on the interface shape and on the slump length versus time curve were analyzed. Moreover, the numerical results were compared to experimental ones, but some differences are observed, possibly due to chemical effects at the interface.

Mechanical and optical measurement of planar elongation viscosity in two-dimensional opposing flow PO224

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Elongational flow can be classified into uniaxial, biaxial and planar elongational flow. In each elongational flow, uniaxial, biaxial and planar elongational viscosity are defined as the ratio between elongational stress and elongational rate. If a material has high viscosity, an elongational rheometer can grip both ends of the material and stretch it, allowing for elongational viscosities to be estimated from stretching force and speed. However, elongational flow fields cannot be generated easily for mobile fluids which cannot be gripped. Fiber-spinning, filament stretching and opposing jet nozzle devices can treat such fluids. Specifically, an opposing jet nozzle device is best technique to characterize uniaxial and biaxial elongational behavior of low viscosity fluids. In contrast, a technique using flow birefringence is the only method to characterize planar elongational flow behavior of low viscosity fluids. In this method, a 4-roll mill flow cell, a squeeze flow cell and a converging flow channel are used to apply planar elongational deformation to sample fluids. However, in order to apply this technique, fluids must have enough transparency to transmit light, show measurable birefringence and obey the stress-optic rule. Therefore, there are still many kinds of low viscosity fluids for which planar elongational viscosity cannot be measured.

In this study, a new technique for measuring planar elongational viscosity of low viscosity fluids is considered. Two dimensional opposing flow is used to generate planar elongational deformation. Two types of apparatus, namely, two dimensional opposing flow cell and two dimensional opposing jet nozzle device are designed. Two dimensional opposing flow cell consists of a flow path which is held between two optical glass plates. A laser beam can transmit through the stagnation line at the center of the flow cell and the flow birefringence induced by planar elongational flow can be measured. On the other hand, a two dimensional opposing jet nozzle device uses the same fundamental technique as an opposing jet nozzle device for measurement of uniaxial and biaxial elongational flow behavior. The apparatus consists of opposing nozzles with square cross section through which the liquid either exits or enters. One of the nozzles is fixed and the other one, which can rotate about a pivot, is linked to a load cell. This load cell measures the reaction force acting on the nozzle. Elongational stress is calculated as the reaction force divided by the cross sectional area of nozzle. The planar elongation viscosity for CTAB/NaSal aqueous solution, which is known as a Maxwell fluid, is measured by each apparatus. Planar elongational viscosity measured by optical technique show good agreement with the Maxwell model. Planar elongation viscosity measured by mechanical technique shows qualitatively agreement to the result of optical technique, but quantitatively is 10 times larger than the result measured by the optical technique.

Contrasting behavior of sheared thermotropic polymers: Wholly aromatic versus segmented architecture PO225

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We have contrasted the shear flow response at molecular and textural scales of wholly aromatic versus segmented thermotropic liquid crystalline polymers and attributed the finding to differences in molecular flexibility and conformation. The polymers include, for comparison, a wholly aromatic copolyester and a semiflexible polyether with a 10 methylene unit spacer alternating with mesogens in the backbone. The copolyester has restricted conformational mobility due to its aromatic units while the polyether is conformationally flexible. While both polymers display a polydomain texture in the quiescent nematic phase, shear orients and coarsens this texture dramatically only for the semiflexible LCP. Indeed, increasing the strain and rate of deformation reduces the defect texture to a size below the optical limit of resolution, therefore producing a defect-free texture with nearly planar alignment. In contrast, texture of the molecularly rigid LCP is largely unaffected by imposed shear. Comparison of molecular orientation states caused by drawing fibers from the respective nematic melts are surprisingly uncorrelated with the textural findings, revealing high orientation in the texture-ridden rigid LCP but modest orientation in the texture-free semiflexible LCP.

In-situ Rheo-SAXS study on shear induced alignment of liquid crystal (8CB) in the smectic phase under LAOS PO226

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In order to investigate shear induced alignment of lamellar layer of liquid crystal 4-n-octyl-4'-cyanobiphenyl (8CB), a new in-situ Rheo-SAXS, combination of commercial Rheometer (MARS, ThermoFischer scientific) and time-resolved synchrotron small-angle x-ray scattering, was established. For this, specific designed parallel-plate geometry made of transparent Polycarbonate for the upper plate to check the sample loading condition and Vespel for the lower plate was used. A unique special x-ray reflector [diamond, (004)] with d-space 3.51Å reflect x-ray by 90° along the shear gradient direction. Therefore this set-up is unique worldwide in order to measure in-situ 2D-SAXS with normal parallel plate geometry. Large amplitude oscillatory shear (LAOS) at a frequency 10 Hz and a strain amplitude of unity on 8CB with smectic-A at 24? was applied. After 1 hour of LAOS, the samples were rested during 40 min without shearing. Simultaneously 2D-SAXS pattern were measured. From the experimental results, rheological property and 2D-SAXS pattern, we investigated the mechanism from random lamellar structure towards a shear aligned lamellar structure of 8CB under LAOS. Typically time-resolved synchrotron SAXS could be measured at every 2s.

Molecular dynamics simulation of backflow generation in nematic liquid crystal between parallel plates PO227

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It has been known that velocity field changes the orientation of liquid crystalline molecules. Reversely, when the orientation is changed by application of an electric or magnetic field, a flow field known as backflow is induced. The backflow can be used to control motion of an object, and thus potential for development of micro actuator or micro manipulator [1, 2]. The generation of backflow has been investigated intensively using continuum approach, and it has been suggested that local velocity gradient induced by molecular rotation should play an important role in the backflow generation. However, for understanding of detailed mechanism in molecular level, further investigation is required. In this work, we investigate the mechanism using molecular dynamics simulation. We consider the dynamics of nematic liquid crystal confined between parallel plates. The liquid crystal molecules are considered as ellipsoids, which interact each other through a Gay-Berne potential. The effect of electric field is accounted by introducing a molecular torque that depends on the angle between molecular long axis and electric field direction. Layers of molecules with fixed position and orientation (pre-tilt angle) are introduced to account for the anchoring effect of the wall. Simulation results show that the electric field induced molecular rotation induces a transient S shaped velocity profile. The magnitude of velocity increases until maximum value is reached, and then decreases with the increase in time. These results confirm the results of calculation using continuum approach as reported in [1]. Furthermore, it is shown that the values of maximum velocity depend on initial order parameter and molecular aspect ratio.

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Phase behavior of varying spacer lengths of side-group liquid crystal polymers PO228

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A novel series of end-on side group liquid crystal polymers (SGLCPs) with varying spacer lengths was synthesized by first separately synthesizing the mesogenic side groups, followed by polymer analogous chemistry to attach these side groups to 1,2 polybutadiene backbones with controlled molecular weights. This series of SGLCP homopolymers readily swells in small molecule liquid crystal to form nematic gels and viscoelastic fluids. The dilute nature of these gels couples the fast re-orientation dynamics of the small molecule liquid crystal with stability, electro-optic and mechano-optic properties imparted by the polymer. Microstructure characterization of these materials is essential for potential tunablility of their propertiies. Small angle neutron scattering (SANS) studies in polar solvent have shown that as the spacer length decreases, the polymers' radii of gyration increase, while at the same time their structure factor becomes more Gaussian and less extended. In addition, as the polarity of the solvent increases, the polymers' radii of gyration all increase. Quantitative FTIR measurements are also being carried out in order determine the differences in the static and dynamic phase behavior of these polymers in small molecule liquid crystal solvent. Detailed knowledge of the microstructure and the resulting phase behavior of SGLCPs with differing spacer lengths will help the rational design of gels exhibiting higher-order liquid crystalline phases, such as ferroelectric gels.

Back-flow of nematic liquid crystals and its application to liquid crystalline microactuators PO229

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With the aim of the development of liquid crystalline microactuators, the numerical and experimental studies of the back-flow effect of nematic liquid crystals have been performed. The Leslie-Ericksen continuum theory is used to simulate the back-flow of a nematic liquid crystal, 4-n-pentyl-4-cyanobiphenyl (5CB), between parallel plates. The lower plate is fixed, and the upper plate can move freely. From the results, it is found that the translational movement of the upper plate occurs owing to the shear stress arisen from the back-flow, when an electric field is imposed between the upper and lower plates. By applying the pulsed voltage, continuous movement of the upper plate is able to be achieved. The effects of the applied voltage, frequency of the pulse, gap width, and the surface molecular anchoring condition on the driving efficiency of the actuators are thoroughly investigated to obtain the optimal condition for the actuators. For example, the averaged driven speed of the upper plate increases with increase of the frequency of the pulse and decrease of the gap width. These results are ascertained in the experiment, in which the translational movement of the upper glass plate is observed under a microscope when pulsed voltage is applied between the glass plates. Finally, we propose several types of liquid crystalline actuators, such as sliders and motors.

Experimental results on electrorheology of liquid crystalline polymer solutions PO230

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The electrorheological (ER) effect is known as the enhancement of the apparent viscosity upon application of an external electric field [1]. The external electric field lies perpendicular to the flow direction, originating a competition between both fields, electric and shear. Suspensions of polarizable particles in non-conducting solvents are the most studied electrorheological fluids, however, liquid crystalline materials may also present ER effect as long as their dielectric anisotropy is positive [2,3]. In the liquid crystalline state of a positive dielectric anisotropy, the application of the electric field makes the director align perpendicular to the flow direction, thus increasing the apparent viscosity. In this work results of two liquid crystalline polymer solutions, acetoxypropylcellulose (APC) in dimethylacetamide (DMAc) and poly-?-benzyl-L-glutamate (PBLG) in 1,4-dioxane, presenting opposite behavior upon application of the electric field, will be presented. APC/DMAc (negative dielectric anisotropy) presents a decrease of the apparent viscosity upon application of the electric field, as expected, while PBLG/1,4-dioxane (positive dielectric anisotropy) presents the opposite behavior. For this last solution we will present the shear flow curves for different electric fields in function of polymer molecular weight and solution concentration.

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Spatiotemporal orientational order dynamics in wormlike micelles en route to rheochaos PO231

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The nonlinear flow behaviour of wormlike micellar gels of surfactant cetyltrimethylammonium tosylate in the presence of salt sodium chloride show the route to rheochaos: for a suitable range of salt concentrations and for shear rate/stress fixed in the plateau region of the flow curve, we see the Type-II intermittency route to chaos in stress relaxation measurements and the Type-III intermittency route to chaos in shear rate relaxation measurements.

In the present study, we have carried out scattering dichroism experiments to probe the dynamics of the spatiotemporal nematic order en route to rheochaos. For shear rates past the plateau onset, we observe the presence of alternating bright and dark birefringent stripes stacked along the vorticity direction. The orientational order corresponding to these structures are predominantly oriented at +45° and -45° to the ?ow in the (flow, vorticity) plane. Our observations are in line with recent predictions of 2D Taylor-like vorticity rolls in a gradient banding fluid [S. M. Fielding, Phys. Rev. E. 76, 016311 (2007)]. The bands show spatial motion along the vorticity and the orientation dynamics of the interface delineating adjacent bands completely correlates with the temporal dynamics of the stress. Furthermore, the observed spatial dynamics of the rolls/interface crucially depends on the gap width of the Couette cell.

Modelling of ER squeeze films: An experimental investigation PO232

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The dynamics of an ER squeeze film are examined for small displacement amplitudes using the Micro Fourier Rheometer. Broad band random techniques are employed to gain an initial insight into the system behaviour using non-linear spectral analysis. This is followed with sine wave tests where a new parameter termed the piecewise stiffness is introduced to gain an insight into the film dynamics. The response of the system is dependent on the boundary conditions at the surface of the plates where a complex regime of partial slip occurs. As well as variable boundary conditions the ER fluid is shown to exhibit elastic behaviour beyond the yield stress which is considered in terms of the deformation of the particle chains.

Teaching rheology using product design PO233

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Over the past several years each of us has taught rheology to seniors and first year graduate students using complex materials available on the shelves of Wal-Mart (US) or Carrefour (EU). We have found that measuring the rheology of face cream, shampoo, paint, chewing gum or plastic bags provides great motivation for students to learn rheology fundamentals. Students are particularly eager to understand the microstructural bases for different rheological responses in anticipation of having to solve a real problem by the end of the course. They also seem to be able to differentiate between the usage of rheology as an 'analytical method' and as a valuable engineering tool for finding parameters relevant for processing conditions or for designing end-use properties. Student response has been overwhelmingly positive and we have enjoyed teaching it and exchanging our experiences. The poster will present our class schedules and will illustrate specific commercial products in five material categories: polymeric, suspension, emulsion, surfactant and gel. It will show how we use rheological measurements to assist reverse engineering of these products.

Reverse Poiseuille flow: The numerical viscometer PO234

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Simulations using the Dissipative Particle Dynamics method (DPD) were carried out on fluid systems composed of chains having N = 2, 5, 10, 25 beads connected by FENE springs, and without any solvent particles. Steady-state rheological properties (non-Newtonian viscosity and normal stresses) were derived from simulations of plane reverse-Poiseuille flow (RPF), where a body force drives the flow in opposite directions in the upper and lower halves of a box.

Periodic boundary conditions ensure the macro velocity to be zero on the walls without density fluctuations. Properties at several temperatures were found to satisfy the superposition principle. Where strain rate overlap was feasible, the same properties calculated in Couette flow (Lees-Edwards) were found to be in excellent agreement.

The RPF simulations are numerically more efficient and span a greater range of shear rates than their Couette counterparts.

Fluid-solid transition approach using continuum damage mechanics PO235

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A lot of materials have a solid or a liquid behaviour, depending on the value of the stress level. These materials are typically observed in alimentary industry, but also in geotechnical or civil engineering. This paper is devoted to the proposition of a fundamental constitutive model, for the understanding of such transition. A lot of studies were aimed at developing a theory to explain the material behavior for low or medium level stresses. The well established framework of linear viscoelasticity is generally used, in order to predict creep evolutions. For higher stresses, the creep phenomenon is strongly nonlinear, and may lead to the liquid transition phenomenon. Continuum Damage Mechanics models seem to be well adapted to describe the time-dependent microcracking phenomena during the shear flow. Thermodynamic basis and experimental background of Continuum Damage Mechanics (CDM) theory have been well established, since the pioneer works of Kachanov. However, very few CDM have focused on the specific creep failure phenomenon, associated to a stress threshold. In previous studies, we have developed a simple model for the prediction of creep failure of geomaterials such as concrete or rock materials. For these solid materials typically encountered in civil engineering, the delayed microcracking phenomena may lead to the structural collapse. Moreover, it has been proven that creep failure can be understood as a bifurcation phenomenon. We show in this paper that some similar constitutive behaviour can be applied to pastes or gels materials. The present model is written in the framework of irreversible thermodynamics. We present an extension of the model of Challamel et al (2005) for solid-fluid transition modelling. The rate equation is a slight modification of Kachanov's original proposal which was meant for creep conditions, and not coupled with any deformation stress relationship, but was used for analysis along with creep equation. The present model depends only on three parameters. The differences between this model and the reference Kachanov's model, can be highlighted for the damage rate equation, for sustained shear stress. The long-term behaviour of the initially solid material, is checked for different values of sustained stresses. For sufficiently high stress level, typically creep failure curves are obtained, associated to realistic times to failure. Under a shear stress smaller than a critical stress, the solid evolves more or less rapidly towards complete stoppage, while under a slightly larger stress, the solid evolves towards rapid flow and fluid state, and failure is reached. It is then theoretically and numerically shown that such an elementary damage model may accurately describe the solid-fluid transition of various time-dependent materials.

Nanoplasmonic particle tracking method PO236

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Conventionally, florescent particles have been used for particle tracking methods, which have the limitations of photo-bleaching and requiring high-sensitivity cameras. Here we explore the method of tracking nanoplasmonic particles, which overcomes those limitations and is simple to implement. For the initial demonstration, we tracked the Brownian motion of 80nm silver nanoparticles in Dextran solution (M.W. =70,000, concentration from 0 to 20% dissolved in water). The particles are clearly observed by Rayleigh scattering under simple dark-field microscope. On the basis of the mean square displacement (MSD) of particles and Einstein equation, the viscosity (0%: 1.2cp, 20%, 3.8 cp) is calculated and are consistent with known value. As the nanoplasmonic particles are bio-inert and have unique optical properties, this nanoplasmonic particle tracking method is expected as a new rheology tool for biomedical and biological researches of both in vitro and cellular types.

Correlation between organic matter degradation and the rheological performance of waste activated sludge during anaerobic digestion PO237

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Anaerobic digestion has demonstrated to be a good possibility to reduce the organic matter contents in waste activated sludge resulting in the effluents treatment. An anaerobic digestion was carried out in a 2 L reactor at 35 °C for a period of 20 days. An electronic thermostat controlled the temperature. The reactor was agitated at a rate of 200 rpm. The study of the rheological behavior of the waste activated sludge was done with an Anton Paar TM rheometer model MCR301 with a peltier plate for temperature control. Four-blade vane geometry was used with samples of 37 mL for determining rheological properties. Sampling (two samples) was taken every four days of anaerobic digestion through a peristaltic pump. The samples behavior was characterized by the Herschel-Bulkley model, with $R^2 > 0.99$ for most cases. In all samples were found an apparent viscosity (η_{app})and yield stress (τ_0) decrement when organic matter content diminishes. This demonstrates a relationship between rheological properties and organic matter concentration (% volatile solids). Also the flow activation energy (*Ea*) was calculated using the Ahrrenius correlation and samples of waste activated sludge before anaerobic digestion. In this case, samples were run in the rheometer at 200 rpm and a temperature range of 25 to 75 °C with an increment rate of 2 °C per minute. The yield stress observed was in a range of 0.93 – 0.18 Pa, the apparent viscosity was in a range of 0.0358 - 0.0010 Pa·s, the reduction of organic matter was in a range of 62.57 – 58.43% volatile solids and the average flow activation energy was 1.71 cal·g-mol^{-1}·K^{-1}.

Effect of humidity on a material's mechanical properties PO238

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To fully understand the mechanical properties of a material, dynamic mechanical testing needs to be performed over a wide range of experimental conditions. While typical variables include temperature and frequency, varying humidity is not as common. In this poster, a newly designed humidity control chamber on the TA Instruments Q800 Dynamic Mechanical Analyzer is used to characterize a variety of materials as a consequence of the relative humidity.

The generalized power-law: A new viscosity model PO239

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For non-Newtonian inelastic fluids, several models have been proposed to describe the relation between shear viscosity and shear rate. In this work, the simple power-law model is generalized in order to include both shear-thinning and shear-thickening behaviors simultaneously. The model is based on using shear rate dependent consistency index (m) and power-law exponent (n). As a first approximation, the consistency index is approximated by a generalized Carreau-Yasuda type of equation while the power-law index is assumed to follow a generalized normal distribution. The resulting model has a total of 9 parameters to adjust for the viscosity level, slope of changes and critical shear rates between zero and infinite shear rates values of the viscosity. For the purpose of comparison, the proposed model is fitted to experimental data taken from the literature. Very high level of prediction is obtained over a wide range of shear rates and different rheological behaviors showing the usefulness of this generalized model.

Numerical simulation of heat transfer enhancement in laminar flow of viscoelastic fluids through a rectangular channel PO240

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Laminar duct flows of some non-Newtonian fluids are characterized by enhanced levels of heat transfer relative to the corresponding Newtonian flows, even though the pressure drop is not significantly different, as was demonstrated experimentally by Hartnett and Kostic [1]. This phenomenon has only been observed in ducts of non-circular cross-section and is associated with the existence of secondary flows. The objective of this work is to quantify and understand the extent of this effect by a systematic numerical investigation.

A finite-volume method is used to simulate the laminar flow and heat transfer of viscoelastic fluids in a duct of rectangular cross-section under hydrodynamically fully-developed and thermally developing conditions (large Prandtl numbers). Here, the rectangular duct has an aspect ratio of 2 and constant heat fluxes are imposed at the walls. The viscoelastic fluids are represented by the Phan-Thien-Tanner (PTT) rheological constitutive equation with zero and non-zero second normal-stress differences.

Validation is performed initially against analytical solutions for fully-developed [2] and thermally developing [3] pipe flows of simplified PTT fluids for which the data collapse. Then, the heat transfer in the rectangular duct flow is investigated as a function of fluid rheology to show the enhanced heat transfer levels as a function of secondary flow intensity. This is quantified both in terms of local and mean Nusselt numbers. The discrepancies between the predictions and the experimental data of Hartnett and Kostic [1] are related to the selection of rheological constitutive equation (only steady shear viscosity data are available for fitting the rheological model), but especially to the free convection effects when a constant heat flux is imposed at the bottom wall of the duct, since free convection was not accounted for in the calculations.

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Abnormal viscosity behaviour of ionic liquid 1-n-butyl-3-methylimidazolium chloride PO241

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Ionic liquid are a molten salt at low temperature, normally room temperature or lower than 100oC. It is attracted by many researchers because it is a new category of solvent with unique characters and can dissolve some materials which can not be dissolved in conventional solvents. In this paper, effect of adding an inorganic salt, lithium chloride, and water on viscosity of an ionic liquid, 1-n-butyl-3-methylimidazolium chloride (BmimCl), was investigated by shear stress measurements with a rheometer. Shear rate dependence of viscosity showed shear thinning behaviour, which implies that some structure should exist in the liquid and the structure should change at high shear rates. The logarithmic value of zero shear viscosity of BmimCl increases linearly and largely with increasing the added salt contents. The rate of the viscosity increment was about ten times larger than the rate when BmimCl is added to water. When water is added into BmimCl, viscosity decreased. Even when water is added to BmimCl, the rate of the viscosity increment with adding LiCl into BmimCl was almost constant in the content range measured in this study.

The use of rheological and thermal measurements to characterize PVC formulations in which the variables include base resin, plasticizer, and their respective concentrations PO242

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Several PVC formulations were prepared with various types of base resins, plasticizers, and relative concentrations of each component. These formulations were analyzed by dynamic rheological means that included rotational rheometry on molten material and dynamic mechanical analysis in the linear mode on self-supporting specimens. Rheological testing was complemented by differential scanning calorimetry and thermogravimetric analysis. Correlations between formulation variables and rheological and thermal properties will be presented. For melt rheology, methods where recently developed accessories were used will be presented, which optimize the chances of successful rheological characterization.

Rheological properties of vegetable oil-diesel fuel blends PO243

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Environmental issues such as emissions of pollutants and possible future petroleum shortages has led to intensified research efforts into sustainable alternatives for the use of diesel fuel in ignition engines. Straight vegetable oils provide cleaner burning and renewable alternatives, however their comparatively high viscosities may contribute to increased engine wear. Lowering the viscosity can be achieved by both increasing the temperature of the oil and mixing it with diesel fuel. The aim of this study is to investigate the rheology of diesel fuel and vegetable oil mixtures at differing compositions with respect to temperature to determine a viscosity-temperature-composition relationship, which can be used for the design and optimisation of heating and fuel injection systems. A rotational rheometer with concentric cylinder geometry was employed to determine the rheological properties of blends based on soybean, olive, canola and peanut oils with a commercial diesel fuel at temperature ranging from 20 to 80°C. All samples tested exhibited time-independent Newtonian behaviour over concentration and the temperature ranges studied. A modified Arrhenius relationship was developed to predict the viscosity (dynamic and kinematic) of the mixtures as functions of temperature and composition. The activation energy terms were found to be dependent on the oil concentration but relatively insensitive to the type of vegetable oil used.

Thermal and rheological behavior of CYPHOS® IL phosphonium liquids PO244

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Ionic liquids are salts with weak crystal lattice energies, which results in them being liquids below 100 °C or even at room temperature (Room Temperature Ionic Liquids, RTIL). Ionic liquids have unique and interesting physical and chemical properties such as very low vapor pressure, inflammability below decomposition temperature, high electric conductivity, thermal and electrochemical stability, and wide liquid ranges. As a result, they have been used in applications such as separation technology, electrolytes in fuel cells, organic and inorganic synthesis and catalysis, heat transport and storage, functional fluids (surfactants, lubricants etc.). Phosphonium based ionic liquids have better chemical and thermal stability than the corresponding ammonium based ionic liquids and do not have "reactive" acidic protons which are associated with imidazolium salts. This presentation discusses the effect of impurities, anion types and various phosphonium cations have on the thermal and rheological properties (oscillatory, flow, viscosity vs. temperature). With a judicious selection of anions and wide variety of available phosphonium cations, one can optimize the thermal and rheological properties of these fluids. The ionic liquids studied were Newtonian in most cases and viscosities obeyed Arrhenius equation. The magnitude of viscosity, Arrhenius constants and thermal properties depended strongly on the anion.

High shear-rate viscometry of low-viscosity lubricating oils PO245

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This poster concerns the measurement of the viscosity of low viscosity multi-grade lubricating oils. The oils of interest have High-Temperature High-Shear (HTHS) viscosities of the order of 26 – 30 mPa.s at standard temperature, shear rate and pressure (i.e. 150 °C, 10^6 1/s, 10^5 Pa). The fluids are likely to possess a significant but low relaxation time of the order of 10^{-5} to 10^{-7} s. Non-Newtonian effects will manifest themselves in flows where strain rates are of the order of 10^5 to 10^7 1/s. Using standard techniques in such extreme conditions is dificult and so, we adopt a pragmatic approach. A Cross model is employed, modified to satisfy the principle of time/temperature superposition. Thus, the temperature dependence is built into a 'shift factor' for the time-scale and the 'shape' of the viscosity function is the same for all temperatures. Then the temperature dependence may be determined at low shear rates where the fluid viscosity is Newtonian and the non-Newtonian character may be determined at a convenient fixed temperature. The study has two principal phases. In the first, the oils are characterised (T A Instruments AR2000 Controlled Stress Rheometer) at low shear rates and at temperatures from 0 to 140 °C. This data provides the temperature dependent shift factor and the zero-shear viscosity. The second phase involves characterising the fluids, at a single temperature (25 °C), at shear rates up to a few million 1/s (Rosand RH10 Capillary Rheometer, Malvern Instruments Ltd). This then provides the remaining parameters required to completely specify the viscosity model. In order to reach the high shear rates required, capillaries with smaller than standard diameters were constructed from steel tubing of two different nominal diameters, 0.25 mm and 0.125 mm. Precise diameters were inferred by calibrating against standard fluids. Different length capillaries were made for each diameter. The lengths were chosen to be sufficiently long to ensure that entry and exit effects are negligible and also to ensure that viscous heating in the longer capillaries WAS significant. Since the heating effect cannot be reliably eliminated, we choose to enhance the effect in order to build it into the model describing the process. The resulting data show very clearly that viscous heating leads to anomalously low viscosity values at the higher shear rates (> 10^5 1/s) and the effect increases measurably with the aspect ratio of the capillary. Values of the capillary aspect ratios ranged from 40 to 220. The Cross model was modified to reflect the effect of viscous heating. Assuming that the heating effect is not too severe we may treat it as being a perturbation about the no-heating model. This approach then allows us to extract the true viscosity function as a function of shear rate. The final results compare very favourably with (very limited) independent data. Approximate analytical results and numerical simulation are also employed to corroborate the validity of the data.

Development of EHD motor of water solution utilizing electrohydrodynamics PO246

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Dielectric fluids are characterized by very low values of the conductivity ($< 10^{-8}$ Sm^{-1}) and commonly regarded as insulating oils in industries. When a dielectric fluid is subjected to a high electric field (> 1 $kVmm^{-1}$), electric body forces are generated due to the nonuniformity of electric conductivity and dielectric constant. Under some conditions, macroscopic motions such as convection, turbulence, and chaos are induced in the systems. The secondary motions of fluid, which are produced in high electric fields, are known as electrohydrodynamic (EHD) effects. According to the numerical simulation and EHD experiments in direct current (DC) fields, the velocity of the flow has been reported to be of the order of $10^{-2}ms^{-1}$ in electric fields of several $kVmm^{-1}$. However, on the application of high DC electric fields to some insulating oils, a fluid jet with a velocity of about 1 ms^{-1} is created from the positive electrode as a bulk flow. In the EHD jet flow, the electric energy is effectively converted to kinetic energy of fluid. Therefore, the EHD jet is very attractive in application to new fluid devices. In previous work, we developed fluid motors, ink jet nozzles, and electrorheological elements by the use of insulating fluids.

In this work, our attention is focused to the prototype of EHD motor by the use of conductive fluids including pure water and aqueous solutions of ethanol and glycerin as working fluids. The aqueous solutions are environmentally friendly and easy to use. We have succeeded in generating high-speed jet for aqueous solutions and designing the water motors. The motors consist of a vane wheel with eight blades, a cup, two sets of wire electrodes, and working fluid. The typical motor has a vane wheel radius of 10mm and immersion length of 30 mm. The electrodes are so arranged symmetrically that the angle of two lines connecting the electrodes with the same sign is 45°. In actual operation, the negative electrodes are connected to the ground (= 0 V). The rotational direction is regulated by the polarity because the secondary flow of water is induced in the direction from the negative to positive electrodes. The rotation speed is of the order of 100 rpm at 5 kV. The motor performance is discussed in relation to viscosity and conductivity of working fluids.

Motion control of disc electrode by electrorheological fluids PO247

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A reversible and rapid change in viscosity of fluids on the application or removal of electric fields is commonly referred to as the electrorheological(ER) effect. Typical ER fluids are suspensions of polarizable particles dispersed in insulating oils. In electric fields, each particle acquires an induced dipole. When aligned along the field direction, the particles attract one another, whereas the particles plane perpendicular to the field direction repel one another. The dipole-dipole interactions cause the particles to form chain structures in direction parallel to the field vector. When subjected to very slow deformation, the chains spanning the electrode gap rupture in the center and immediately swing back to reform with the nearest chain on the opposite electrode. The equilibrium conformations of chains are always aligned with the electric field. In inclined chains, the forces can be generated in direction perpendicular to the field vector. If the chain configuration is arranged in movable electrodes at a constant gap, the parallel motion of electrodes can be actively regulated. Usually the fundamental evaluation of ER effects is carried out in the uniform electric fields that are produced between two plate electrodes with flat surfaces. In electrified suspensions, the particles form columns consisting of a collection of many chains due to long-range lateral attractions. However, the thickness and distribution of columns cannot be controlled in the uniform electric fields. In the suspensions electrified in electrodes with a striped pattern of line and space, the particles construct striped aggregates along the electrodes and no particles remain in the insulating region. This implies that the configuration of columns developed between electrodes can be controlled by the electrode design. If the application procedure of electric fields is programmed to move the columns between striped electrodes, the ER fluids can be utilized as working fluids for a new type of actuators. In this work, the ER suspensions are sandwiched between two flat disc electrodes with the radial line patterns. The electrodes are formed on the parallel plate geometry on a stress-controlled rheometer which was modified for the ER experiments. The motion of disk electrodes with striped patterns is analyzed to obtain the basic data. The feasibility of ER motors will be discussed in relation to ER mechanism of suspensions.

Application of a variable order operator to constitutive modeling of linear viscoelastic behavior PO248

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A brief overview of some of the fractional calculus operators and proposed variable order operators is presented, along with the formulation of a simple constitutive equation for linear viscoelastic materials strained at constant strain rates. The model consists of a derivative of varying order that is a function of the independent variable (time), rather than a constant of arbitrary order. We generalize previous works that used fractional derivatives for the stress and strain relationship by allowing a continuous spectrum of non-integer dynamics to describe the physical problem. We develop a statistical mechanical model that is in agreement with experimental results for strain rates varying more than eight orders of magnitude in value. Using experimental data for a carbon/epoxy composite and an epoxy resin undergoing constant rate compression in the linear range, we derive a semi-empirical functional relationship with the normalized time that is used in a VO constitutive equation to model the viscoelastic deformation in time. The resulting dimensionless constitutive equation agrees well with all the normalized data while using a much smaller number of empirical coefficients when compared to available models in the literature.

Transient shear flow of model lithium lubricating greases PO249

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This work deals with the analysis of the transient shear flow behaviour of lithium lubricating greases differing in soap concentration and base oil viscosity. The shear-induced evolution of grease microstructure has been studied by means of stress-growth experiments. With this aim, different lubricating grease formulations were manufactured by modifying the concentration of lithium 12-hydroxystearate and the viscosity of the base oil, according to a RSM statistical design. Moreover, atomic force microscopy (AFM) observations were carried out. The transient stress response can be successfully described by the generalized Leider-Bird model based on two exponential terms. Different rheological parameters, related to both the elastic response and the structural breakdown of greases, have been analysed. In this sense, it has been found that the elastic properties of lithium lubricating greases were highly influenced by soap concentration and oil viscosity. The stress overshoot depends linearly on both variables in the whole shear rate range studied, although the effect of base oil viscosity on this parameter is opposite at low and high shear rates. Special attention has been given to the first part of the stress-growth curve. In this sense, it can be deduced that the "storage" energy density not only depends on grease composition, but also on shear rate. Moreover, an interesting asymptotic tendency has been found for both the "storage" energy density and the stress overshoot by increasing shear rate. The asymptotic values of these parameters have been correlated to the friction coefficient obtained in a ball-disc tribometer.

Geometric interpretation of linear viscoelasticity and time-temperature superposition PO250

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Dynamic moduli data are considered as a curve on the plane of loss tangent and storage modulus. The curve can be parameterized by the material frequency which is defined as the arc length of the curve. The relationship between real frequency and the material frequency determines the horizontal and vertical shift factors. Scaling analysis by the material frequency will be given for several kinds of linear viscoelastic functions.

Determination of discrete relaxation time spectrum by use of continuous wavelet transform PO251

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We have developed a simple method for determination of discrete relaxation time spectrum from loss modulus data. The method is based on wavelet transform, which is superior to other method such as SA(simulated annealing) and PL (Padé-Laplace method). Our method determines the number of relaxation times (the number of Maxwell modes) automatically in a single step of numerical operation, because the wavelet transfor of loss modulus is a series of peaks whose positions indicate the logarithm of relaxation times. The principle and results of the method can be understood as directly as those of spectroscopic analysis such as IR and NMR.

Numerical simulation in steady flow of Newtonian and shear thickening fluids in pipes with circular cross-section PO252

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Process engineering deals with the processing of large quantities of materials and they must be transported from one unit operation to another within the processing environment. This is commonly made through pipelines, where occurs a dissipation of energy due essentially to frictional losses against the inside wall of the pipe and changes in the internal energy. Additional energy dissipations are introduced as the fluid passes through the fittings, like contractions, expansions, elbows, tee connectors, etc. Then it is needed an energy source to keep the fluid moving, commonly a pump. Due to differences in the internal structure, dissipations of energy must be different from Newtonian fluids to shear thickening fluids. The term shear-thickening is typically used to refer to a non-Newtonian flow behaviour observed in which there is an increase in apparent viscosity when the applied shear rate is increased. Various studies have suggested an explanation of this phenomenon based on "hydrodynamic clustering". These clusters are composed of compact groups of particles formed as shear forces drive them to contact. A range of parameters control this behaviour, among the most important being particle size distribution, particle content, particle shape, particle-particle interactions, and the viscosity of the suspending phase. The accumulative effect of these factors determines the extent its characteristics. Moreover, because of the inherent structure that is exhibited by shear thickening fluids, laminar motion of these fluids is encountered far more commonly than with Newtonian fluids. Therefore, it is interesting to examine the simple case of laminar flow in a pipe with circular cross-section theoretically and numerically for Newtonian and shear thickening fluids. By means of rheological experiments it has been determined that Polypropylene glycol (PPG) of low molecular weights (400 and 2000 g/mol) exhibit Newtonian behaviour at room conditions. However, the addition of Aerosil®R816 at 5%v/v generates suspensions which show reversible shear thickening behaviour. Results confirm that Cross model fits properly the dependence of apparent viscosity with shear rate in the region of shear thickening behaviour. All steady rheological experiments have been carried out in a RheoStress 600 (Haake) in order to obtain the viscosity curve of Aerosil®R816 suspensions in PPG. The volume fraction and temperature have been kept unaltered, 5%v/v and 25.0±0.1ºC, respectively. Finally, steady flow within a circular cross-section pipeline has been analysed theoretically and numerically for PPG and Aerosil®R816 suspensions in PPG. The formers exhibit a parabolic velocity profile completely different from the latter ones.

Emptying time of a tank filled up with explosive paste: Comparison between experimental measurements and predictions based on rheological characterization of the paste PO253

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One industrial process used to manufacture pyrotechnical materials consists in preparing an emulsion of wax in TNT (2,4,6-trinitrotoluene) and adding Aluminium and ONTA (3-nitro-1,2,4-triazole-5-one) particles. When the suspension is homogeneous, it is allowed to flow by gravity through a pipe located at the bottom of the tank and to fill up a shell body.

The suspension is characterized by a solid volume fraction of 53,4%, which leads to high viscosities. In some circumstances, the emptying time is prohibitively long and the economic profitability is reduced. This study has been performed to make the emptying time lower with the constraint of unchanged volume fractions and grains mean diameter.

So, we investigated the influence of the grain size distribution on the suspension viscosity. Different samples of Aluminium and ONTA have been used, with rather small differences in grain size distributions. The suspensions have been prepared in the industrial tank and the flow cast times measured. It has been observed that they differ by one order of magnitude.

To avoid situations with too high emptying times, a procedure has been implemented to make prior characterization of the suspension rheology. Because of particles sedimentation and emulsion destabilisation, the classical Couette rheometer is not adapted. So, we designed and built a small size tank (113 cm3), where the suspension is continuously stirred and kept homogeneous. The measurement of the torque and rotational speed together with the use of the Couette analogy (Cf. Bousmina et al.) allowed us to observe an Ostwald fluid behaviour (flow consistency index k, flow behaviour index n).

To gain in prediction, we established a correlation between the measured (k,n) values and the grain size distributions. We characterized each suspension by the ratio of phi to phimax, where phi is the solid volume fraction (imposed by the commercial specifications) and phimax is the maximum packing fraction. Because of the strong analogy between concrete and energetic paste, we chose the widely used De Larrard model to compute phimax. A linear dependance between the ratio phi/phimax and the indices k and n was observed.

The second step was to provide an analytical expression for the flow cast time of a power-law suspension from a tank with a given geometry. Considering the large difference between the industrial inner tank diameter and the evacuation pipe diameter, we assumed that all the pressure drop was located in the evacuation pipe. Then, extending the Hagen-Poiseuille equation to Ostwald fluid, we were able to predict the emptying time with the knowledge of k and n.

Experimental and predicted emptying time are in very good agreement. This work helped the industrial manufacturer to divide the emptying time by a factor 12.

Author Index

Paper Index