παντα
ῥει

THE SOCIETY OF RHEOLOGY

84TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Pasadena Convention Center
Pasadena, California
February 10 - 14, 2013

Program Committee:

Shelley Anna (Co-chair)
Carnegie Mellon University
Carlos Rinaldi (Co-chair)
University of Florida
Surita Bhatia
Stony Brook University
Xue (Ida) Chen
The Dow Chemical Company
Ubaldo M. Córdova-Figueroa
University of Puerto Rico–Mayagüez
Suraj S. Deshmukh
The Dow Chemical Company
Kendra Erk
Purdue University
Randy Ewoldt
University of Illinois at Urbana-Champaign
Savvas G. Hatzikiriakos
University of British Columbia
Aditya Khair
Carnegie Mellon University
Anson Ma
University of Connecticut
Craig Maloney
Carnegie Mellon University
Florian Nettesheim
DuPont CR&D - Experimental Station
Chinedum Osuji
Yale University
Yuriko Renardy
Virginia Tech
Charles M. Schroeder
University of Illinois at Urbana-Champaign
Sachin Velankar
University of Pittsburgh
Petia Vlahovska
Brown University
Isidro (Dan) E. Zarraga
Genentech, Inc.
Roseanna Zia
Cornell University

Local Arrangements:

John F. Brady (Chair)
California Institute of Technology
Julie Kornfield
California Institute of Technology
Andy Kraynik
California Institute of Technology
Maryam Sepehr
Chevron

Abstract Book Editor and Webmaster:

Albert Co, *University of Maine*

Meeting Schedule

Monday, February 11, 2013

	C106	*C107*	*C101*	*C105*
8:30	C. F. Zukoski (PL1) - *C102*			
9:20	Coffee Break			
10:00	SC1	PS1	BC1	EF1
10:25	SC2	PS2	BC2	EF2
10:50	SC3	PS3	BC3	EF3
11:15	SC4	PS4	BC4	EF4
11:40	SC5	PS5	BC5	EF5
12:05	Lunch Break			
1:30	SC6	PS6	BC6	EF6
1:55	SC7	PS7	BC7	EF7
2:20	SC8	PS8	BC8	EF8
2:45	SC9	PS9	BC9	EF9
3:10	Coffee Break			
3:35	SC10	EM1	BC10	EF10
4:00	SC11	EM2	BC11	EF11
4:25	SC12	EM3	BC12	EF12
4:50	SC13	EM4	BC13	EF13
5:15	SC14	EM5	BC14	EF14
5:40	End			

Tuesday, February 12, 2013

	C106	*C107*	*C101*	*C105*
8:30	R. H. Colby (PL2) - *C102*			
9:20	Coffee Break			
10:00	SC15	EM6	SA1	EF15
10:25	SC16	EM7	SA2	EF16
10:50	SC17	EM8	SA3	EF17
11:15	SC18	EM9	SA4	EF18
11:40	SC19	EM10	SA5	EF19
12:05	Lunch Break / Society Business Meeting			
1:30	SC20	PS10	SA6	SG1
1:55	SC21	PS11	SA7	SG2
2:20	SC22	PS12	SA8	SG3
2:45	SC23	PS13	SA9	SG4
3:10	Coffee Break			
3:35	SC24	PS14	SA10	SG5
4:00	SC25	PS15	SA11	SG6
4:25	SC26	PS16	SA12	SG7
4:50	SC27	PS17	SA13	SG8
5:15	SC28	PS18	SA14	SG9
5:40	End			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, February 13, 2013

	C106	*C107*	*C101*	*C105*
8:30	M. D. Graham (PL3) - *C102*			
9:20	Coffee Break			
10:00	SC29	PS19	SA15	BS1
10:25	SC30	PS20	SA16	BS2
10:50	SC31	PS21	SA17	BS3
11:15	SC32	PS22	SA18	BS4
11:40	SC33	PS23	SA19	BS5
12:05	Lunch Break			
1:30	SC34	PS24	SA20	BS6
1:55	SC35	PS25	SA21	BS7
2:20	SC36	PS26	SA22	BS8
2:45	SC37	PS27	SA23	BS9
3:10	Coffee Break			
3:35	SC38	PS28	SA24	BS10
4:00	SC39	PS29	SA25	BS11
4:25	SC40	PS30	SA26	BS12
4:50	SC41	PS31	SA27	BS13
5:15	End			
5:30	Poster Session & Reception			

Thursday, February 14, 2013

	C106	*C107*	*C101*	*C105*
8:00	C. M. Schroeder (AP1) - *C106*			
8:40	SC42	PS32	SA28	BS14
9:05	SC43	PS33	SA29	BS15
9:30	SC44	PS34	SA30	BS16
9:55	Coffee Break			
10:25	SC45	PS35	SA31	BS17
10:50	SC46	PS36	SA32	BS18
11:15	SC47	PS37	SA33	BS19
11:40	SC48	PS38	SA34	BS20
12:05	SC49	PS39	SA35	BS21
12:30	End			

Session and Room Codes

AP = Award Presentations
BC = Blends and Composites
BS = Rheology in Biological Systems
EF = Emulsions, Foams and Interfacial Rheology
EM = Electric and Magnetic Field Effects in Rheology
PL = Plenary Lectures
PS = Polymer Solutions and Melts

SA = Self-Assembling, Associating and Gel-Like Systems
SC = Suspensions and Colloids
SG = Solids and Glasses

C101 = Room C101
C102 = Rooms C102-C104
C105 = Room C105
C106 = Room C106
C107 = Room C107
CCLL = Conference Center Lower Level

Contents

This publication was generated with macros developed by Albert Co. The contents of this publication were extracted from the database of The Society of Rheology abstract submission web site at http://www.rheology.org/sorabst/. Online version is available at http://www.rheology.org/sor132/.

Monday Morning

Symposium PL

Plenary Lectures

Monday 8:30 C102-C104 PL1

Rheological consequences of localization

Charles F. Zukoski
Department of Chemical and Biological Engineering, University at Buffalo, Buffalo, NY 14260-1601, United States

A long standing challenge in the field of colloid science and suspension mechanics has been to understand the origin of gelation. Of particular interest is understanding how to link particle pair potentials to the onset of gelation and the magnitude of the rheological properties of the resulting gels. Many models have been developed to understand the volume fraction scaling of elastic modulus based on the gel's fractal dimension. While predicting volume fraction scaling, these theories cannot predict absolute magnitude of the modulus and the volume fraction where gelation occurs. More recently mode coupling theory and dynamic localization theory have been proposed which correlate gel and glass formation with the onset of sluggish long range diffusion. Rather surprisingly these theories predict magnitudes and volume fraction scaling of mechanical properties on the basis of integrals over structure factors with a heavy emphasis on short range particle density fluctuations (i.e., the integrals heavily weight high wave vector components of the structure factor). The dynamical properties of gels and glasses are predicted in terms of single particle diffusion where attributes such as the gel's fractal dimension are not relevant. Experimental evidence supporting these models are discussed with a particular emphasis on understanding why the flow properties of diverse ranges of suspensions have very similar flow properties.

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Monday 10:00 C106 SC1

Shear-induced aggregation and orientation of particles in a polymer solution: Formation and evolution of microstructure

Emily C. Peterson and Victor Breedveld
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, United States

Suspensions with a viscoelastic continuous phase can exhibit interesting microstructural features, one of which is the formation of small, vorticity-aligned particle clusters. While this behavior has been occasionally observed in the past [e.g., DeGroot et al., J. Coll. Interf. Sci. (1994) and Pasquino et al., Rheol. Acta (2010)], the underlying mechanism is not entirely understood. In this study, we used shear-SALS to probe the dynamics of this effect for a suspension of colloidal silica particles in an entangled polymer solution. Shear rates in the solution's shear-thinning regime resulted in particle aggregation and orientation along the vorticity axis. In contrast, when the equivalent amount of strain was applied at a shear rate in the Newtonian regime, no vorticity orientation occurred. When a sample already containing vorticity-oriented aggregates was subsequently subjected to shear rates below the onset of shear-thinning, shear forces restored a uniform particle distribution through a two-step process in which aggregates first rotated 90 degrees towards a flow-oriented microstructure before eventually being broken up and redistributed isotropically. The presence of the aggregated structures was found to reduce the low-shear viscosity of the suspension, relative to the value measured before structure formation. During redistribution of the aggregates at low shear rates, the viscosity gradually returned to its initial value. Comparing the measured viscosity with changes in the scattering intensity along the flow and vorticity directions provided interesting insight regarding the structural evolution during this recovery. Viscosity growth closely tracked the changes in intensity along the flow direction. Changes in intensity along the vorticity direction, however, occurred on a faster time scale that was not detected by the sample viscosity, indicating that changes in particle-particle aggregation status are more important for the viscosity than the vorticity-to-flow orientation transition.

Monday 10:25 C106 SC2

Non-linear structure response of liquid state colloidal suspensions under oscillatory shear

Neil Y. Lin[1], Sushmit Goyal[2], Xiang Cheng[1], Roseanna Zia[2], Fernando Escobedo[2], and Itai Cohen[1]
[1]Physics Department, Cornell University, Ithaca, NY 14853, United States; [2]Department of Chemical and Biomolecular Engineering,, Cornell University, Ithaca, NY 14853, United States

When driven out of equilibrium many thermodynamic systems exhibit fascinating nonlinear responses ranging from nonlinear elasticity to non-Newtonian fluid flows. Colloids have been a valuable system for studying the underlying mechanisms responsible for many non-linear behaviors since it is possible to conduct experiments on time scales comparable to the system relaxation time. The response of hard sphere colloidal liquids to large amplitude oscillatory shear is particularly interesting, since it is highly non-linear and important for many industrial processes. Although colloids have been studied extensively using conventional rheological techniques, the mechanisms underlying such nonlinear behaviors are still poorly understood due to the lack of measurements that report on the microscopic suspension structure. Here we use fast confocal imaging to investigate the structural response of sheared colloidal suspensions over a wide range of oscillation amplitudes. By tracking distortions in the pair correlation function, we show that the structural response amplitude exhibits two saturations: the first at large imposed-strain amplitudes, and a second at high oscillatory-strain frequencies — both of which are related to the non-linear rheology of colloidal dispersions. Based on a scaling analysis, we demonstrate a collapse of flow curves across these cases onto a single master curve.

Monday 10:50 C106 SC3

Structure and rheology of vorticity-aligned string phase in sheared colloidal suspensions

Xiang Cheng, Neil Y. Lin, and Itai Cohen
Physics Department, Cornell University, Ithaca, NY 14853, United States

When driven out of equilibrium, sheared colloidal suspensions exhibit many fascinating phases under the influence of hydrodynamic, inter-particle and thermal interactions. However, mechanisms underlying out-of-equilibrium colloidal assembly are still poorly understood, though such processes are clearly relevant in many natural and industrial systems. Even in the simple case of hard-sphere colloidal particles under shear, there are still conflicting predictions about whether particles link up into string-like structures along the shear flow direction. Here, using a newly-designed multi-dimensional confocal rheometer, we study the shear-induced non-equilibrium suspension structure and its corresponding rheological responses in 3D. We find that, rather than flow-aligned strings, particles form log-rolling strings normal to the plane of shear. We systematically investigate how the string phase depends on the shear rates, the confinement of shear plates, and the volume fractions of samples. Surprisingly, we find that such a strongly anisotropic structure exhibits uniform shear viscosities along the shear flow and vorticity directions. Finally, we propose a simple mechanism for the formation of this novel phase.

Monday 11:15 C106 SC4

Suspension structure visualization in simple and complex flows

James F. Gilchrist, Tharanga Perera, and Bu Xu
Lehigh University, Bethlehem, PA 18015, United States

We will present experimental results of structure in shear flows and in micropost arrays that have mixed shear and extensional flows. From these measurements we will calculate local stresses and discuss the evolution of particle chaining along streamlines.

Monday 11:40 C106 SC5

Phase separating mixtures of colloidal rods and spheres in shear flow

Donald Guu and Pavlik Lettinga
Institute of Complex Systems, Forschungszentrum Juelich, Juelich, Nordrhein Westfalen 52428, Germany

We determined the phase behavior of an ideal rod-sphere mixture consisting of fd-virus, which are mono-disperse colloidal rods, and density matched mono-disperse polystyrene beads, using a combination of diffuse wave spectroscopy and optical microscopy. Equilibrium phase diagrams were mapped out for various σ/L ratios, where L is length of the rod and σ is the bead diameter. At low σ/L we observe droplets of a liquid phase of the beads, while at higher σ/L the droplets are crystalline. We studied the susceptibility of the droplets to shear flow, using a counter rotating cone-plate shear cell mounted on a fast confocal microscope. We observed a shear rate dependent melting of the structures, which is a function of the location in the equilibrium phase diagram of the sheared mixture. We show that the melting of liquid droplets takes place via another mechanism than for crystalline droplets.

Symposium PS

Polymer Solutions and Melts

Organizers: Randy Ewoldt and Suraj S. Deshmukh

Monday 10:00 C107 PS1

Emerging signs calling for a different framework for nonlinear rheology of entangled polymers

Shi-Qing Wang[1], Yangyang Wang[1], Shiwang Cheng[1], Yuyuan Lu[1], Howard Wang[2], Zhen-Gang Wang[3], and Lijia An[4]
[1]Department of Polymer Science, University of Akron, Akron, OH 44325, United States; [2]Department of mechanical engineering, Binghamton University State University of New York, Vestal, NY, United States; [3]California Institute of Technology, Pasadena, CA, United States; [4]Changchun Institute of Applied Chemistry, Changchun, China

We design various experiments to obtain clues about how to improve the current theoretical description of nonlinear rheology of entangled polymers. First, a slowly imposed step strain is found to result in non-monotonic evolution of the state of chain entanglement during quiescent relaxation, consistent with the concept of elastic yielding after step shear. Second, the stress relaxation upon a sizable step strain is found to be identical to that for small step strain, indicating that a strained entangled melt has an entropic barrier to resist chain retraction. Third, the ability of a step-strained polymer to undergo elastic recovery is found to be the same up to strain amplitude of unity, and a sample sheared for a period much longer than the Rouse time is shown to still undergo nearly full elastic recovery. Fourth, an entangled melt, stretched at a rate significantly lower than the Rouse relaxation rate, undergoes full elastic recovery until the point of tensile force maximum. Fifth, SANS measurements of a slowly stretched PS melt reveal an unexpected degree of chain stretching. Sixth, molecular-dynamics computer experiments of startup shear show similar level of chain stretching despite the fact that the imposed rate is much lower than the Rouse relaxation rate. These results suggest that the standard model in polymer rheology, i.e., the tube theory, may have oversimplified the physics governing the nonlinear responses of entangled polymers and a realistic theory needs to be built on the basis of molecular force balance and imbalance between multiple chains.

Monday 10:25 C107 PS2

Assumptions in entanglement models and their effect on non-linear rheology predictions

Marat Andreev[1], Jay D. Schieber[2], and Rudi Steenbakkers[2]
[1]Department of Physics, Illinois Institute of Technology, Chicago, IL 60616, United States; [2]Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL, United States

The two most common non-linear rheology experiments are shear flow and elongational flow. For shear flow, as the strain rate increases, the transient viscosity shows strain softening before reaching a steady state, which at high rates is preceded by an undershoot in viscosity. Elongational flow, on the other hand, is believed to produce qualitatively different behavior, it features transient strain hardening, which is not seen in shear flow. Entanglement the- ories have succesfully predicted shear data but failed in elongation. GLaMM "tube" model is able to predict transient shear viscosity, but it shows un- realistic infinite viscosity in case of elongational flow. Multichain primitive chain network (PCN) simulations qualitatively capture transient shear flow viscosity, but PCN shows higher steady state viscosity in elongation. The single-chain mean-field discrete slip-link model (DSM) predictions for shear flow agree very well with experimental results. The DSM is able to capture the transient response as well as the steady state viscosity. However, for elongational flow, agreement is unsatisfactory at large strains. The DSM captures onset of strain hardening, but after hencky strain of approximately 2, it predicts strain softening. We explore a number of assumptions of the model and their effect on flow predictions. Only after careful examination of all approximations and assumptions can we conclude with certainty whether the standard view of entanglement dynamics is incomplete.

Monday 10:50 C107 PS3

From non-Gaussian chain stretching to real “shear hardening” in simple shear of branched polystyrene solutions

Gengxin Liu[1], Hyojoon Lee[2], Shiwang Cheng[1], Hongwei Ma[1], Roderic Quirk[1], Taihyun Chang[2], and Shi-Qing Wang[1]
[1]Department of Polymer Science, University of Akron, Akron, OH 44325, United States; [2]Department of Chemistry, Pohang University of Science and Technology, Pohang 790784, Republic of Korea

Entangled polymers with long chain branching (LCB) exhibit a higher apparent viscosity than the zero-rate viscosity upon startup uniaxial extension whereas polymers either with LCB or of linear chains usually only show a lower transient viscosity than the zero-rate viscosity envelope. We show for the first time that simple shear of well-entangled polystyrene solutions with LCB produces a higher transient viscosity than the envelope. Apparently, in presence of sufficient LCB, non-Gaussian stretching can even show up in simple shear, which was previously only observed to occur in uniaxial extension. Moreover, the LCB resists against a structural breakdown of the entanglement network, postponing the stress overshoot to a shear strain of 30 when the backbone of the PS would be nearly straightened and disentangled. In melt state, this PS with LCB shows "strain hardening" in uniaxial extension because the delayed yielding of the entanglement network allows the geometric condensation to show up in the evaluation of the transient viscosity.

Monday 11:15 C107 PS4

Tube models for branched polymers: Revisiting the “simple” case of star/linear blends

Priyanka S. Desai[1] and Ronald G. Larson[2]
[1]Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, United States; [2]Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI, United States

Computational models based on the tube theory, including the Hierarchical (Larson, 2001; Park *et al.*, 2005; Wang *et al.*, 2010) and Branch-on-branch (BOB) (Das *et al.*, 2006) models, have been fairly successful in predicting linear rheology of general mixtures of polydisperse branched polymers. However, for the simple case of a binary blend of a monodisperse star and a monodisperse linear, the model fails to reliably correctly predict rheology without case-by-case adjustment of parameters such as the dilution exponent, α, and the fluctuation potential, ν. Primitive path statistics calculations using the Bond fluctuation model by Shanbhag and Larson (*Phys. Rev. Lett.* **94**, 076001 (2005)) suggest that the fluctuation potential exponent ν is a decreasing function of the molecular weight. The relaxation of stars depends exponentially on the value of the potential and thus is extremely sensitive to the value of ν. In present work, we study the impact of changing the strength of the fluctuation potential, ν, on the predictions of the Hierarchical model for the case of star-linear blends. We also propose a unified parameter-set and test it thoroughly against experimental data for linear, stars, star-linear blends, H shaped polymers and other architectures. We point out inconsistencies between available data sets from experiments that suggest the need to have new well-characterized polymer samples, which will help us better test and exploit the new parameters chosen.

Monday 11:40 C107 PS5

Particle tracking velocimetry of polybutadiene mixtures under nonlinear viscoelastic shear flows

Yanfei Li[1], Miao Hu[1], Gregory B. McKenna[1], Christopher J. Dimitriou[2], Rebecca M. Mick[3], David C. Venerus[3], H. Wang[4], and Lynden Archer[4]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; [3]Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States; [4]School of Chemical and Biological Engineering, Cornell University, Ithaca, NY 14853-5201, United States

The Doi-Edwards (D-E) tube model [1], which is based on de Gennes' reptation idea [2], has been accepted as the paradigm for the dynamics of entangled polymers for decades, and D-E theories as well as most of the rheological measurements in the literature are based on the assumption that the strain field is homogeneous. However, recently S.Q. Wang has reported evidence of shear banding [3, 4]. This controversial observation challenges both the reliability of conventional rheological tests [5] and the D-E theories. The ultimate goal of the present research is to examine if shear banding is inherently present, as suggested by S.Q. Wang [6], if it is a phenomenon caused by some edge instability and, consequently, non-universal. Using a self-designed particle tracking velocimeter, start up shear and step strain tests were conducted under a series of systematically varied rheological and the velocity profiles of different well-entangled polybutadiene/oligomer solutions were observed. In the regime of entanglement density and Weissenberg number reported by Wang and co-workers to show shear banding, we observe either wall slip and a linear velocity/strain profile or a linear profile with no wall slip unless edge fracture or instability has occurred in the sample. The results lead us to a conclusion that there is no compelling evidence of shear banding; rather, observed bandings probably are caused by edge effects, which are probably also present in the S.Q. Wang work.

1. M. Doi and S.F. Edwards, the Theory of Polymer Dynamics (Clarendon Press, Oxford, 1986).
2. P.G. de Gennes, J. Chem. Phys. 55, 572 (1971).
3. S. Ravindranath, S.Q. Wang, M. Olechnowicz and R. P. Quirk, Macromolecules. 41, 2663 (2008).
4. S.Q. Wang, S. Ravindranath, P. Boukany, M. Olechnowicz, R. P. Quirk, A. Halasa and J. Mays, Phys. Rev. Lett. 97, 187801 (2006).
5. E.V. Menezes and W. W. Graessley, J. Polym. Sci., Polym. Phys. Ed. 20, 1817 (1982).
6. P. Tapadia and S.Q. Wang, Phys. Rev. Lett. 96, 016001 (2006).

Symposium BC

Blends and Composites

Organizers: Anson Ma and Savvas G. Hatzikiriakos

Monday 10:00 C101 BC1

Effect of carbon nano-tubes on the rheological properties of polymer nano-composites: A comparison between different nano-particle shapes

Hojjat Mahi and Denis Rodrigue
Chemical Engineering, Université Laval, Quebec, Quebec G1V0A6, Canada

While several papers have been published on the effect of spherical and platelet nano-particles on polymer melt rheology, the focus of this work is on cylindrical or tubular shape geometry (needle-like). In particular, multi-wall carbon nano-tubes (MWCNT) were used to study the linear

and non-linear rheological properties of nano-composites based on ethylene vinyl acetate (EVA) for a concentration range between 0 and 10% wt. From the results obtained, comparisons are made with our previous works on other nano-particles based on talc, calcium carbonate and clays in the same polymer matrix. The structure of the nano-composites was studied by TEM and SEM analyses to relate with the rheological properties obtained via frequency sweeps, shear transients and uniaxial elongation. The results obtained showed that MWCNT has the highest impact on chain confinement compared to spherical and platelet particles. This was related to the very small diameter (10 nm) of the particles, as well as their hollow structure which enhance chain entanglement with the particles. Chain confinement combined with the formation of a continuous particle network resulted in a substantial increase of stress overshoot in shear transient experiments, while reduction in strain-hardening was observed for transient extensional tests.

Monday 10:25 C101 BC2

Wrinkling instabilities in polymer-supported nanotube films: Mitigating van der Waals attraction through excluded-volume interactions

John M. Harris[1], Matthew R. Semler[1], Erik K. Hobbie[1], Jeffrey A. Fagan[2], Ji Y. Huh[2], and Christopher M. Stafford[2]
[1]Department of Physics, North Dakota State University, Fargo, ND, United States; [2]National Institute of Standards and Technology, Gaithersburg, MD, United States

Strain-induced structural and electronic changes in polymer supported membranes of purified single-wall carbon nanotubes (SWCNTs) are evaluated through the wrinkling instabilities that develop under uniaxial and isotropic compression. Nanotubes that have been purified by electronic type through density-gradient ultracentrifugation are assembled as surfactant-free thin membranes on polydimethylsiloxane (PDMS) substrates, and the strain response of the layered nanocomposites is measured using a broad range of techniques. Measurements suggest a remarkable degree of strain softening that can strongly couple to the anisotropic sheet resistance of the films, where this softening arises from van der Waals attraction between contacted nanotubes and the parallel coarsening of SWCNT bundles in response to small external forces. By capping the elastomer-supported SWCNT films with a thin layer of a second glassy polymer, we demonstrate a dramatic improvement in the mechanical response, and we link this behavior to the stabilizing influence of excluded-volume interactions mediated by the vitrified polymer coating.

Monday 10:50 C101 BC3

Electrically percolating clusters in sheared carbon nanotube composites

Doyoung Moon, Jan Obrzut, Jack F. Douglas, Thomas Lam, Renu Sharma, James A. Liddle, and Kalman B. Migler
NIST, Gaithersburg, MD 20850, United States

The electrical conductivity of polymer nanotube composites can be dramatically modified by processing flows and subsequent annealing. The mechanism is widely believed to be nanotube structural rearrangements that occur during flow and alter the percolating pathways. We analyze the 3D percolating clusters via three-dimensional confocal microscopy and electron microscopy to extract the distributions of nanotube cluster size, orientation, and nanotube-nanotube distance. We correlate these network properties with electrical conductivity and find several regimes of structure and conductivity in a polystyrene MWCNT composite. Our results demonstrate the extreme sensitivity of structure to conductivity near the percolation transition.

Monday 11:15 C101 BC4

Shear and extensional flow-induced particle orientation in a polypropylene/clay nanocomposite

Wesley R. Burghardt and Erica M. McCready
Northwestern University, Evanston, IL, United States

Synchrotron-based in situ x-ray scattering is used to monitor the orientation of dispersed particles in molten polypropylene/clay nanocomposite melts during flow. Nanocomposite samples were prepared via twin screw extrusion processing, and the degree of clay exfoliation assessed in terms of the magnitude of the low frequency enhancement in viscoelasticity. In shear flow, an annular cone and plate flow cell is used which allows measurement of the degree and direction of particle orientation in the flow-gradient (1-2) plane. Samples were also studied in extensional flow, using an SER extensional flow fixture installed in a custom-built convection oven that provides x-ray access. In both shear and extensional flow, only a moderate degree of particle orientation is observed. Extensional flow studies are complicated by (i) the tendency of samples to fail at moderate Hency strain, and (ii) a heterogeneous initial distribution of particle orientation in the SER specimens, prepared by compression molding of extruded pellets of the nanocomposite.

Monday 11:40 C101 BC5

Rheology of the dispersed conductive filler, graphene nanowire, with poly vinylidene fluoride (PVDF) composite as a stress and strain sensing material

Brooke E. Berwald[1] and Leela Rakesh[2]
[1]Mechanical Engineering, Central Michigan University, Mt Pleasant, MI 48858, United States; [2]Science of Advanced Materials-Mathematics Department, Central Michigan University, Mt Pleasant, MI 48858, United States

Mechanical, electronic, high mobility, thermal conductivity and strength of nanofillers like graphene and carbon nanotubes in polymer matrix can be increased using various dispersion techniques and processing conditions. Interfacial interaction between nanofillers and the polymer that increase these conditions could be because of effective load transfer between the nanofiller and polymer, which depends on the shear stress. Present research involves melt blending nanocomposites of polyvinylidene fluoride(PVDF) with graphene nanowires(GNWs) using a minijet-minilab twin screw extruder (ThermoFisher Inc). Electrical resistance of the material can be related to the change in the stress and strain. Since PVDF has a potential to be piezo-resistive based on the crystalline phase, GNW can affect PVDF's crystallinity, crystalline phase, and quasi static. The dynamic mechanical properties are studied using the AR 2000 rheometer at a frequency of 1 Hz, a temperature of 280-340 degree C, and a strain of 0.1% to 50% to determine the linear viscoelastic region. Various time dependencies such as transient and quasi-static responses of the strain with time and viscoelastic behavior were examined for the PVDF and GNWs melt nanocomposites. Using the dynamic measurements, the peak temperature of the tan δ (damping), G' (storage modulus), and G"(loss modulus) it indicated how effectively the material lost or stored energy due to molecular rearrangements and internal friction. The α and β transition region of the PVDF and its composites were also determined using the dynamic measurements. We will discuss fractional crystallinity and glass transition temperature effects on mechanical performance. Such sensitive responses in the presence of GNW-PVDF composites could help us understand structural and environmental signals which could be used to introduce new ways to engineer its physical, mechanical, and chemical properties for further applications.

Symposium EF

Emulsions, Foams and Interfacial Rheology

Organizers: Sachin Velankar and Petia Vlahovska

Monday 10:00 C105 EF1

Equilibrium and dynamic surface properties of poly(ethylene oxide) based homopolymers and block copolymers

Zachary A. Zell, Gary Leal, and Todd M. Squires
Department of Chemical Engineering, Univeristy of California, Santa Barbara, Santa Barbara, CA 93106, United States

Poly(ethylene oxide) (PEO) is a water-soluble, yet surface active polymer, which allows it to be spread as a monolayer on the air-water surface. Measured surface pressure-density isotherms using both the Wilhelmy plate and our custom microtensiometer[1] allow us to quantify a critical concentration, at which entire PEO chains desorb from the interface, when the surface segment density of EO monomers becomes sufficiently high. Interestingly, we see that this critical concentration increases with the molecular weight of the PEO, indicating that larger molecular weight polymers are more insoluble, due to their higher adsorption energy. Unlike with the PEO homopolymer, compressed monolayers of block copolymer polystyrene-b-poly(ethylene oxide) (PS-PEO) at the air-water surface do not undergo a desorption transition as the PS block anchors the chain to the surface due to its low solubility in water. In fact, AFM images of deposited monolayers confirm the self assembly of the PS-PEO copolymer into nanosized, disk-like aggregates, with a PS-rich core. Using our active microrheometer[2], we also measure the surface shear properties. Strain-amplitude sweeps at a fixed oscillation frequency suggest that the monolayer behaves as a soft solid with a yield stress at low amplitude. At higher amplitudes, the microstucture 'melts' to become liquid-like and behaves as a shear thinning fluid. This observation of soft-solid behavior, which has been seen in both bulk and interfacial colloidal suspensions may suggest that the monolayers acts as a 2D suspension of nanoparticles.

[1] Zell, Z. A. ; Choi, S. Q. , Leal, L.G.; and Squires, T. M. Applied Physics Letters 97, 133505 (2010) [2] S.Q. Choi;, S. Steltenkamp; J.A. Zasadzinski, T.M. Squires; Nature Communications 2, Article number: 312

Monday 10:25 C105 EF2

Comprehensive analysis of surfactant-biofilm interactions

Cynthia F. Wu[1], Ji Youn Lim[2], Lynette Cegelski[2], and Gerald G. Fuller[1]
[1]Chemical Engineering, Stanford University, Stanford, CA 94305, United States; [2]Chemistry, Stanford University, Stanford, CA 94305, United States

Bacteria tend to aggregate on surfaces and form biofilms that are characterized by an extracellular polymeric matrix consisting of proteins and polysaccharides. The unique structure of biofilms prevents bacteria from harsh environmental conditions so they could survive in a broad range of conditions. Biofilms are implicated in most infectious diseases such as catheter infections, cystic fibrosis, endocarditis, and urinary tract infections. Successful treatments of these diseases require thorough understanding of the biochemical and physico-chemical properties of biofilms that relate to function. In this work, we combined conventional biofilm research methods with interfacial science techniques including interfacial rheometry and tensiometry to study air-liquid interface biofilm (pellicle) formation by uropathogenic E. coli and its interaction with a surfactant. We analyzed the bacteria cell growth, adhesion ability, and curli expression, and relate them to the interfacial viscoelasticity during biofilm formation. Our results showed that biofilm formation was very sensitive to surfactant concentration. Below the critical micelle concentration (CMC), the surface was dominated by bacteria-degradable proteins from the nutrient broth, and pellicle formation was observed with delayed inception at increasing surfactant concentration. Above the CMC, the surface was dominated by surfactants, and biofilm formation was inhibited. Our study demonstrated a physico-biological approach to comprehensively examine air-liquid interface biofilm formation and investigate the influence of curli content and surfactants on amyloid-integrated biofilm formation. The application of this approach is extensible to studies of amyloid-integrated biofilm formation among other microorganisms as well as interactions of surfactant-protein and surfactant-polymer at air-liquid and oil-liquid interfaces.

Monday 10:50 C105 EF3

Unusual surface mechanical properties of poly(α-methylstyrene): Surface softening and stiffening at different temperatures

Taskin B. Karim and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

In the present work, we have used the spontaneous particle embedment technique[1] with sub-micron and nanometer size particles to estimate the surface compliance of poly(α-methylstyrene) (PaMS) for the temperature range from room temperature to Tg+21°C (192 °C). The embedment of the particles was determined using atomic force microscopy (AFM) measurements and the embedment data was used in the Lee and Radok (LR)[2] model to estimate the surface shear compliances. The work of adhesion between submicron/nano particles and the polymer surface was considered as the driving force for particle embedment. Dynamic mechanical data was used to compare macroscopic to the surface compliance values. The major result is that surface softening was observed in the low temperature range of room temperature to Tg-21°C and there was a cross-over to a surface mechanical response that was stiffer (lower compliance) than the macroscopic material in the higher temperature range of Tg-18°C to Tg+21°C. These findings were observed for both 199 nm and 60 nm diameter silica particles and will be discussed in context with literature reports of surface dynamics obtained by other methods.

REFERENCES: 1. J. H. Teichroeb and J. A. Forrest, Physical Review Letter, 91, 016104 (2003); 2. E. H. Lee and J. R. M. Radok, Journal of Applied Mechanics, 27, Trans. ASME, 82, Series E, 438-44, (1960).

Monday 11:15 C105 EF4

Producing high melt strength long-chain branched polylactide (PLA) for foaming

Naqi Najafi[1], Marie-Claude Heuzey[2], Pierre Carreau[2], and Daniel Therriault[1]
[1]Mechanical Engineering, Ecole Polytechnique de Montreal, Montreal, Canada; [2]Chemical Engineering, Ecole Polytechnique de Montreal, Montreal, Canada

Polylactide (PLA) is a bio-sourced and biodegradable polymer, serving as an alternative to petrochemical-derived products. The manufacturing of PLA foams has recently drawn great attention, considering that foaming reduces the weight and cost of the final products. A major obstacle in stabilizing the foamed cell structure of PLA is its low melt strength. In this work, a multifunctional chain extender was used in order to generate a long-chain branched (LCB) structure PLA with high melt strength. Two PLA grades from NatureWorks LLC were used: 2003D and 3001D, which have different molecular weight and isomer D-content. The multifunctional chain extender used was Joncryl© ADR 4368F. The rheological and thermal properties of the PLA and Joncryl-treated PLA were investigated. The comparison between PLA with and without chain extender showed that the steady shear and complex viscosity of the Joncryl-treated PLA were markedly increased as a consequence of increased molecular weight and LCB structure. The LCB structure was also found to affect the transient viscosity in the startup of shear and elongational flow experiments. Contrary to the neat PLA, the Joncryl-treated PLA exhibited prominent overshoots in its transient shear response due to an increase of entanglement density and, consequently, more melt elasticity. The transient elongational viscosity of the Joncryl-treated sample also showed a pronounced strain hardening, compared to the neat PLA. Non-isothermal and isothermal DSC results revealed that the addition of Joncryl increased degree of crystallinity from 3 to 22% and 15 to 35% in PLA 2003 and PLA 3001, respectively. The incorporation of Joncryl into PLA3001, moreover, led to formation of bimodal melting endotherms.

Monday 11:40 C105 EF5

Development of an engineering model to describe polyurethane foam expansion and cure

Lisa A. Mondy, Rekha R. Rao, Mathias C. Celina, Jamie M. Kropka, Edward M. Russick, Nicholas B. Wyatt, and Bion Shelden
Sandia National Laboratories, Albuquerque, NM 87185-0346, United States

We are developing computational models to elucidate the dynamic filling of a mold with a polyurethane foam. The polyurethane of interest is chemically blown foam, where the carbon dioxide (CO_2) gas that is responsible for blowing the polymer into foam is produced from a reaction between polyisocyanate and water, forming carbamic acid, which then decomposes to form an amine group and CO_2. Polymerization occurs via a competing reaction of the polyisocyanate and polyol to form cross-linked polyurethane. The kinetics of the resin polymerization were evaluated using a IR Spectrophotometry on both wet and dry polyurethane precursor, as water is essential to the CO_2-formation reaction, in order to separate the curing and blowing reactions. The kinetics of the foaming reaction was measured by tracking volume evolution with time in the curing system, which gives an apparent measure of carbon dioxide formation as some of the material is lost due to bubble breakage at the surface of the foam and some of the gas formation is masked by bubble pressurization as the material cures and becomes more viscoelastic. Heat generation from the exothermic reactions was measured with Differential Scanning Calorimetry. Rheology was performed on the dry polyurethane system in order to quantify the effects of cure and temperature on the continuous phase viscosity. Rheology of the foam was carried out to understand the effect of gas fraction on the flow of polymer and verify whether or not the effects of the dispersed and continuous phases can be decoupled in the viscosity model. A finite element model was developed combining the equations of motion, an energy balance, and two rate equations for the polymerization and foaming reactions. This was combined with a level set method to track the location of the free surface as it evolves in time. The model predicts the evolution of the foam-gas interface and density of the foam. It is compared to experimental flow visualization data, temperature measurements, and x-ray images of density.

Monday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Monday 1:30 C106 SC6

Particle alignment in sheared vicoelastic fluids: Novel experimental results

Sylvie M. Van Loon, Jan Vermant, and Christian Clasen
CIT, KU Leuven, Heverlee 3001, Belgium

Alignment of spherical particles into strings in sheared viscoelastic fluids has first been observed now about 40 years ago. Many mechanisms have been proposed for this phenomenon but a conclusive explanation has never been given. In the present work, the importance of the nature of the fluid and of the geometrical conditions are investigated. By inducing alignment in strings in an essentialy inelastic but shear thinning fluid, the requirement for the presence of significant normal stress differences can be questioned. Moreover, detailed tracking of large non-Brownian particles which approach one other in a sheared wormlike micellar surfactant show that these are very similar to the Newtonian case. This suggests that the specific rheology of the fluid is not responsible for "pushing" the particles together, but merely for stabilizing the structures in the flow direction after they have been formed. When small particles are mixed into the suspending fluid in addition to the large ones, a depletion interaction between the large particles is induced, whose strength can be controlled by the concentration of small ones. When the strength is increased, the structures observed during shear flow differ greatly. Strings aligned in the flow direction no longer form, rather dumbells and triplets are observed which tumble on drifting Jeffery orbits. Under steady state condition they end up 'log-rolling', oriented along the vorticity direction similar to observations for ellipsoids. The suppression of the string formation upon increasing attraction suggests that enabling the rotation of the separate particles within the string is crucial for maintaining the structure aligned in the flow direction. This points to the importance of shear thinning in reconciling the zero torque condition with the formation of an aligned object. Moreover, from the calculation of the depletion effect, the force required to keep a string stable in the flow direction, can be quantified.

Monday 1:55 C106 SC7

Hydrocluster formation in colloidal suspensions: A mesoscale simulation study

Safa Jamali, Mikio Yamanoi, and Joao M. Maia
Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

Dissipative Particle Dynamics (DPD) has been used extensively the past few years to study different aspects of complex fluids. The method writes the equation of motion for the DPD particles based on the calculation of three different forces acting between each pair of particles. The conservative force gives the chemical identity of each particle, while dissipative and random forces control the thermal forces in the system by forming the canonical ensemble. In order to study colloidal suspensions and specifically their rheology core-modified DPD as an alternative method has been proposed. CMDPD in addition to those three forces utilizes two more forces to write the equation of motion: a short-range lubrication force based on the pair drag between particles, and also a semi-hard potential in order to avoid any overlap between the hard-spheres. Our work previously has shown semi-quantitative agreement between the simulation and the experimental results on a wide range of different systems, from monodispersed to bimodal suspensions with changing size ratio and compositions. We classified our forces into Brownian, Hydrodynamic and Inter-particle and studied each of these forces in different flow regimes. Using a criterion of having 6 or more particles in close vicinity for a period of time, hydro-clusters in the system were identified and studied over a wide range of Pe numbers for different systems. A direct correlation between the number of particles in the hydro-cluster structures and the shear-thickening behavior was observed. So in this work, using CMDPD we focus on the hydro-clusters, specifically to study if the clusters really undergo more stress during the shear-thickening regime. Furthermore, the performance of the method at the equilibrium regime is validated via calculation of zero shear viscosity for different systems.

Monday 2:20 C106 SC8

Shear-induced diffusion in suspensions of curved fibers

Jianghui Wang[1], Emilio J. Tozzi[2], Michael D. Graham[1], and Daniel J. Klingenberg[1]
[1]Chemical Engineering, University of Wisconsin Madison, Madison, WI 53706, United States; [2]Aspect Imaging, Davis, CA 95616, United States

Lignocellulosic biomass processing can be made more economical by reducing the water content of the biomass. However, increasing the solids concentration increases the apparent viscosity of the biomass, which makes mixing reactants and conveying the biomass challenging. In an effort to understand the factors that influence mass transfer in biomass, we have investigated shear-induced diffusion in suspensions of fibers using fiber-level simulation. We have found that suspensions of slightly curved fibers behave qualitatively differently than suspensions of straight fibers. The coupling of rotational and translational dynamics, and the combined effects of flipping, scooping, and spinning motions cause slightly curved fibers to drift in the gradient direction. Drift and random collisions cause large increases in the shear-induced diffusivity in the gradient direction in dilute and semidilute suspensions. At large concentrations, the formation of fiber networks decreases the mobility of individual fibers and decreases the diffusivity. Shear-induced diffusion is also intimately coupled with the rheological properties: in dilute and semidilute suspensions, we find that the shear-induced diffusivity is proportional to the derivative of normal stress with respect to concentration.

Monday 2:45 C106 SC9

Microstructure and rheology of suspensions at finite inertia

Hamed Haddadi[1] and Jeffrey Morris[2]
[1]Chemical Engineering, Benjamin Levich Institute of Physico-Chemical Hydrodynamics, New York, NY 10032, United States; [2]Chemical Engineering, The City College of New York, New York, NY, United States

The role of particle scale inertia on microstructure and rheology of suspensions of neutrally buoyant spherical particles has been studied. Inertia at particle scale is characterized by the Reynolds number defined as Re = ? ? a2 ? in which ? ? is the shear rate, a is the particle radius and ? is the kinematic viscosity; Re = O(1) for most of the work reported. The solid volume fraction which is denoted as f, and is studied up to f = 0.3. Trajectories and velocities of particles are extracted via numerical simulations using lattice-Boltzmann (LB). Trajectories and velocities of particles are extracted via numerical simulations using lattice-Boltzmann (LB) method simulation. To study the separate effects of shear flow and fluctuations on the microstructure as described by the the pair distribution function, g, the mean relative trajectories were determined from simulation and used in an advection equation describing the pair distribution. The results of this simplified calculation capture gross features of the structure, showing the dominant influence of advection. However, dispersion of the pair trajectories caused by interactions with the remaining 'bath' of particles was found to be necessary to incorporate, resulting in an advection-diffusion equation for g which has been solved numerically with good agreement to simulation results. The relationship between microstructure and stress system of suspensions has been examined by sampling the pair space and mapping the force moment (stresslet, here the dominant stress contribution) at various pair separations. In addition, the contribution of the Reynolds stress due to velocity fluctuations has been analyzed.

Monday 3:35 C106 SC10

Flow of biomass undergoing enzymatic hydrolysis

Emilio J. Tozzi[1], David M. Lavenson[2], Maria Cardona[2], Nardrapee Karuna[3], Tina Jeoh[3], Pernille A. Skovgaard[4], Henning Jorgensen[5], Robert L. Powell[2], and Michael J. McCarthy[6]
[1]Aspect Imaging, Davis, CA 95616, United States; [2]Chemical Engineering and Materials Science, University of California, Davis, Davis, CA, CA 95616, United States; [3]Department of Biological & Agricultural Engineering, University of California Davis, Davis, CA 95616, United States; [4]Forest & Landscape Denmark, Forestry and wood products, University of Copenhagen, Copenhagen, Denmark; [5]Forestry and wood products, University of Copenhagen, Copenhagen, Denmark; [6]Food Science and Tech., Biotechnology & Agricultural Eng., University of California Davis, Davis, CA 95616, United States

The rheological properties of cellulosic biomass suspensions undergoing hydrolysis are influenced by many factors including particle size, shape and concentration. We performed magnetic resonance flow imaging to characterize velocity profiles and rheograms for lignocellulosic and delignified fibers. Depending on the concentration and flow rate many flow phenomena are observed that include turbulence, laminar symmetric and asymmetric velocity profiles and settling. Symmetric, laminar velocity profiles that are well described by generalized Newtonian models only occur at certain ranges of concentration and flow rate. Rheograms obtained during hydrolysis of delignified fibers having different average fiber lengths suggest that crowding numbers computed using length-averaged lengths can be used to predict yield stresses of suspensions where particle aspect ratio undergo rapid changes. In experiments with wheat straw at 5% solids loading the velocity profiles changed as the hydrolysis progressed from an initially flat plug flow with apparent wall slip to a concentric flow that has a central plug surrounded by an annular region moving at a non-zero velocity, and finally to more conventional shear-thinning profiles for which rheograms can be obtained. The wheat straw slurries displayed significant rheological changes over time before any addition of enzymes which are attributed to hydration of the fibers.

Monday 4:00 C106 SC11

Comparing responses of different stiff particles using LAOS in combination with in situ time-resolved SANS

Pavlik Lettinga[1], Simon A. Rogers[2], and Joachim Kohlbrecher[3]
[1]Institute of Complex Systems, Forschungszentrum Juelich, Juelich, Nordrhein Westfalen 52428, Germany; [2]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [3]Paul Scherrer Insritut, Villigen, Switzerland

Dispersions of rod-like particles are known for their strong shear thinning behaviour and resulting hydrodynamic instabilities. The shear thinning is thought to be connected to the shear induced orientation of the stiff entities. The rheological and structural responses of the dispersions can be conveniently studied by large amplitude oscillatory shear in combination with in situ time-resolved small angle neutron scattering. We apply this technique to three different rod-like systems: block-copolymer worm-like micelles, surfactant worm-like micelles and filamentous viruses (fd virus). Although on first sight responses look very similar, there are subtle but important differences that elucidate the different physical origin of shear thinning. Responses are quantitatively and unambiguously decomposed into instantaneous elastic and viscous contributions that allow for interpretation in terms of sequences of processes. Using this approach we are able to attribute differences to the physical properties of real rods, stiff living polymers, and stiff poly-disperse worm-like structures.

Monday 4:25 C106 SC12

Response of an elastoviscoplastic material to oscillatory shear flow in the parallel plate and cylindrical Couette geometries

Jonathan J. Stickel[1], Jeffrey S. Knutsen[2], and Matthew W. Liberatore[2]
[1]National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO, United States; [2]Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO 80401, United States

Large-amplitude oscillatory shear (LAOS) rheology has been the subject of intense study during the last decade. It is commonly recognized that the nonlinear oscillatory response of a non-Newtonian material to an imposed sinusoidal oscillatory shear can provide substantial information about the constitutive behavior of the material. It is of particular interest to study highly structured materials, including suspensions and colloids, using LAOS with a rotational rheometer. These materials jam or slip near the tip of the cone with a cone-and-plate geometry, and hence parallel plate (PP) and cylindrical Couette (CC; cup-and-bob or cup-and-vane) are often used. However, many researchers use the linear form factors programmed in the rheometer's software for mapping torque and rotation to shear stress and strain, respectively, even though non-linear shear profiles may exist in the gap.

In this work, we employed an elastoviscoplastic (EVP) model to represent materials that undergo elastic deformation at small strains and exhibit yielding behavior and flow at large strains [Cheddadi *et al.*, (2012), *J. Rheol.* **56**, 213-239]. Using the EVP model, we simulated LAOS in PP and CC geometries for both imposed sinusoidal strain and torque. We present examples of the oscillatory signals that result from the imposed shear and the non-linear shear profiles that are present in the gaps for both geometries. We also illustrate cases where the linear form factors give reasonable results and cases where they should not be used. Alternative methods will be proposed for analyzing data from LAOS experiments in PP and CC geometries. Experimental data from a Carbopol suspension undergoing LAOS in PP and CC geometries were found to be in reasonable agreement with the model results.

Monday 4:50 C106 SC13

A quantitative instantaneous approach to analyzing data from LAOS: Theory and applications

Simon A. Rogers
Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

An entirely new way of analyzing linear and nonlinear oscillatory material responses is presented. Previously untreatable start-up oscillatory data as well as steady-state 'alternance' responses of a number of simple models are presented to accustom researchers to its function. Application of the method to data from colloidal and biopolymer suspensions illustrates the power and utility of the technique. The new quantitative method views oscillatory responses within the Frenet-Serret frame as sequences of planar 2D curves embedded in the 3D space defined by the strain, strain rate, and stress axes. Associated with the curve within each so-called "osculating" plane is a binormal vector that wholly determines the orientation of the plane. Physically meaningful information is obtained by calculating the angles between a modified form of the binormal vector and two reference vectors from local information at any point in a cycle. Information from a full period of oscillation is not a requirement of this technique, so that moduli can be calculated from partial or incomplete oscillations. Time-dependent phase and complex modulus information, or dynamic moduli information are obtainable throughout a period for arbitrary oscillatory responses.

Monday 5:15 C106 SC14

Structure and flow behavior of cubic nanoparticle suspensions

Rajesh K. Mallavajula, Donald L. Koch, and Lynden Archer
School of Chemical and Biological Engineering, Cornell University, Ithaca, NY 14853-5201, United States

The shape of particles plays an important role in their suspension flow behavior. Polyhedral particles have unique shape characteristics such as flat surfaces, corners, edges and yet no aspect ratio. Cubes are the simplest polyhedral shape that can be studied both theoretically and experimentally to understand the effect of these unique shape characteristics on rheology, flow dynamics, and structure. At very low volume fractions, we find that the sharp edges and corners of cubes affect the flow profile around the cube. We used finite element simulations and analytical solutions of the quasi-two-dimensional Stokes flow near edges to show how the intrinsic viscosity of cubes increases with increasing sharpness of cube edges and corners. At low to moderate cube volume fractions, Brownian dynamics simulations over a range of volume fractions and Pectlet numbers indicate that the suspension rheology of cube-shaped particles with volume fractions less than 0.25 is similar to that of a suspension of spheres circumscribed over the cubes. At higher volume fractions, the neighboring cubes restrict cube's orientational freedom. We have synthesized narrowly dispersed PbTe nanocubes (10 nm) as model hard cube particles to study these rheological behaviors. We also use Small Angle X-ray scattering (SAXS) to study the equilibrium suspension structure at high nanoparticle loadings and, consistent with theory, find that the suspensions exhibit ordering transitions at modest particle loadings. As an extreme example, we also characterize the structure and rheology of cubes densely grafted with molecular and oligomeric ligands to create a self-suspended suspension. These systems exhibit unusual low-angle scattering and pronounced caging dynamics.

Symposium PS

Polymer Solutions and Melts

Organizers: Randy Ewoldt and Suraj S. Deshmukh

Monday 1:30 C107 PS6

Modelling flow-induced crystallisation in polymer melts: Crossing length-scales and modelling approaches

Richard S. Graham
School of Mathematical Sciences, University of Nottingham, Nottingham NG7 2RD, United Kingdom

The recent GO model of flow-induced crystallisation (FIC) in polymers has been shown to be able to describe the crystal nucleation rate from a flowing iPP melt. However, there is still considerable work to be done to produce a model of flow-induced crystallisation that is suitable to model industrial processes. In particular, less coarse-grained models are required to elucidate the physical mechanisms at high flow rates and to derive methods to determine model parameters. Conversely, more coarse-grained models are necessary to allow computational studies of the complex flow geometries used in polymer process. I will present a method to semi-analytically predict the nucleation rate from the GO model, which allows a wider comparison with experimental data. This method can also be used to derive an FIC model based only on deterministic ODEs. I will also present preliminary results from the method that will allow much more detailed molecular simulation of FIC in polymer melts.

Monday 1:55 C107 PS7

Rheology during structure formation in polypropylene

Peter C. Roozemond, Zhe Ma, and Gerrit Peters
Materials Technology, Eindhoven University of Technology, Eindhoven, The Netherlands

Understanding and predicting structure development during flow is key in the processing of semi-crystalline polymers. Not only does the crystalline structure determine mechanical and optical properties of the solidified material, it also affects the rheology of the melt thus influencing the velocity field and pressure distribution during processing.

In this work we study the coupling between the formation of highly oriented crystallites and rheology during flows relevant to polymer processing. A commercial grade of isotactic polypropylene was subjected to a poiseuille flow in a modified multi-pass rheometer (MPR). By combining in-situ wide angle synchrotron x-ray diffraction with an unprecedented sample rate of 30 Hz and the pressure signal in the MPR we are able to simultaneously probe crystalline structure and viscosity. It is shown that even during very short flows (0.25s with an apparent wall shear rate of 480 s^{-1}) the viscosity strongly increases due to the formation of crystalline structures. The depth sectioning technique is applied to quantify structure formation for different positions in the slit.

Experimental results are compared with simulations of the flow field. We show that due to viscous heating and heat release due to crystallization, the crystal growth rate after flow is significantly affected. Both these effects are quantified and incorporated in the Schneider rate equations to capture the crystallization kinetics.

Monday 2:20 C107 PS8

Melt fracture and wall slip of metallocene-catalyzed bimodal polyethylenes in capillary flow

Yongwoo Inn
Bartlesville Reaserch and Technology Center, Chevron Phillips Chemical Company LP, Bartlesville, OK 74003-6670, United States

The melt fracture and wall slip behaviors of three metallocene-catalyzed bimodal polyethylene (PE) resins and one unimodal PE resin were investigated and critically compared. By comparing the flow curve observed by capillary rheology measurements with the linear viscoelastic (LVE) data, it was observed that the apparent slip increased with the content of low molecular weight (MW) component. The bimodal resins that had higher content of low MW component first showed a matte surface at lower stresses. The plateau modulus estimated from the LVE data decreased with the increase in low MW content. The onset stress of the sharkskin melt fracture was proportional to the plateau modulus. The matte surface remained until the extrudate converted to a wavy appearance before the stick-slip transition as shear rates were increased. One of the bimodal PE resins was also fabricated into pipe and size exclusion chromatography measurements done on the surface section of the pipe showed that the wall material had enriched low MW component relative to the core. It is proposed that the distinct separation of the two modes of the bimodal PE resin and the high content of small chains promotes the flow-induced fractionation leading to the small chains being more concentrated near the die walls, which in turn result in significant wall slip and the unusual melt fracture behaviors observed.

Monday 2:45 C107 PS9

Analysis of forcespinning method of producing nanofibers at high throughput

Seyed Mohammad Taghavi[1], Simon Padron[2], Karen Lozano[2], and Ronald G. Larson[1]
[1]Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI, United States; [2]Mechanical Engineering, The University of Texas-Pan American, Edinburg, TX, United States

We analyze a rotary jet spinning method called Forcespinning^{TM}, wherein a rapidly rotating spinneret expels polymer solution or melt by centrifugal force, leading to the formation of nanofibers at high rate. Nanofibers are of value in various applications such as tissue engineering scaffolds, filtration, drug delivery, solar cells, sensors, batteries and polymer transistors, and our motivation is determine the spinning conditions under which sub-micron diameter fibers can be produced at high rate. Through theoretical and experimental studies, we provide understanding of the mechanisms of the fiber formation and the limiting effects of various parameters involved. Our main focus is on the effect of Rossby number, which is the ratio between characteristic rotational and radial velocities. The other parameters studied are viscous and inertial effects as well as heat and mass transfer for solutions and melts respectively. Since a diameter as small as possible is desired at the highest throughput, determining what sets the fiber diameter is important both scientifically and commercially.

Symposium EM

Electric and Magnetic Field Effects in Rheology

Organizers: Aditya Khair and Yuriko Renardy

Monday 3:35 C107 EM1

The bulk electroviscous effect

Aditya S. Khair and Andrew G. Star
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Electroviscous stresses arise as hydrodynamic flows disturb the ionic (Debye) clouds that screen charged surfaces in electrolyte solutions. The contribution thereof to the effective bulk viscosity (also known as the second or volume viscosity) of two-phase suspensions is quantified in this talk. Specifically, the bulk viscosity of two model suspensions is calculated: (i) a dilute dispersion of rigid charged spherical particles immersed in a compressible electrolyte that undergoes uniform dilatation; and (ii) a dilute suspension of charged gas bubbles expanding uniformly in an incompressible electrolyte. In both cases, it is assumed that the fluid flow only slightly drives the Debye cloud out of equilibrium, which formally requires that the ratio of the ion diffusion to flow time scales (a Peclet number) is small. For a suspension of rigid particles, the electroviscous contribution to the effective bulk viscosity is proportional to the particle volume fraction and decreases monotonically as the ratio of the particle radius to the Debye length increases. Similar behavior is well known for the electroviscous contribution to the effective shear viscosity of a dilute hard-sphere suspension; a quantitative comparison between the bulk and shear viscosities is made. In contrast, the electroviscous contribution to the bulk viscosity of a dilute suspension of bubbles is independent of the bubble volume fraction and attains a finite value in the limit of vanishing Debye length.

Monday 4:00 C107 EM2

Electrohydrodynamic instabilities in thin viscoelastic films: AC and DC fields

Leonardo Espin, Andrew J. Corbett, and Satish Kumar
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Electrohydrodynamic instabilities in thin liquid films are a promising route for the self-assembly of well-defined topographical features on the surfaces of materials. Here, we study the effect of viscoelasticity on these instabilities under the influence of AC and DC electric fields. Viscoelasticity is incorporated via a Jeffreys model and both perfect and leaky dielectric materials are considered. In the case of DC fields, asymptotic methods are employed to shed light on the nature of a singularity that arises when solvent viscosity is neglected (i.e., the Maxwell-fluid limit). In the case of AC fields, we apply a numerical procedure based on Floquet theory to determine the maximum growth rate and corresponding wavenumber as a function of the oscillation amplitude and frequency. Elasticity is found to increase both the maximum growth rate and the corresponding wavenumber, with the effects being the most pronounced when the oscillation period is comparable to the fluid relaxation time.

Monday 4:25 C107 EM3

Rheology and structure of magnetic colloidal liquid crystal composites

Heberth Diestra-Cruz[1], Carlos Rinaldi[2], and Aldo Acevedo[1]
[1]Department of Chemical Engineering, University of Puerto Rico, Mayagüez Campus, Mayagüez PR 00681, Puerto Rico; [2]Dept. of Biomedical Eng. and Dept. of Chemical Eng., University of Florida, Gainesville, FL 32611-6131, United States

Magnetic colloidal liquid crystal composites (MCLCs) were obtained by the suspension of commercial magnetic microparticles in the low molecular weight liquid crystal (LC) 4'-pentyl-4-biphenylcarbonitrile (5CB). These tunable magnetic soft materials combine the phase transition

properties of LCs and the field response of magnetic colloids. The optical, thermal and rheological characterization demonstrated that the LC phase transition induced formation of a three-dimensional particle network, which in turn changes drastically the viscoelastic properties of the MCLCs. Microscopy reveals that in the absence of a magnetic field a space filling cellular structure is formed while an anisotropic particle network, elongated in the field direction, is obtained under the action of an external magnetic field. Magnetorheological measurements show viscoelastic moduli increments with magnetic field, reaching mechanical saturation at high fields (~0.64T). Saturation moduli increase with particle concentration following a linear relationship. In addition, the 3D distribution of the particle network evaluated at quiescent conditions by confocal microscopy showed single LC domains throughout the sample thickness. The structure can be controlled by formulation and processing parameters, which may allow for the design of free-standing LC sensors.

Monday 4:50 C107 EM4

Design of integrated electrorheological (ER) valves

Ahmed Helal[1], Maria Telleria[1], Julie Wang[1], Bian Qian[1], Marc Strauss[2], Mike Murphy[2], Anette Hosoi[1], and Gareth H. McKinley[1]
[1]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; [2]Boston Dynamics, Waltham, MA 02451-7507, United States

In integrated microfluidic circuits, valve elements play an important role in flow control. Electrorheological (ER) valves are a promising means to create integrated switch and/or variable resistor elements for integrated microfluidic circuits and potentially more complex microfluidic logic gates. Composed of a microchannel with two electrodes perpendicular to the direction of flow and an ER fluid (a Newtonian fluid that can develop a controllable yield stress within milliseconds of the application of an electric field), ER valves offer a low-power, inexpensive and rapidly actuatable alternative compared to traditional servo-valves. In addition, ER valves can be readily manufactured at various scales as in MEMS-based designs. We present experimental data highlighting the rheological behavior of the ER fluid, an analysis of a single-channel ER valve design and various preliminary design rules for integrated ER valves. To demonstrate the applicability of these rules, Boston Dynamics has fabricated individually addressable centimeter-scale ER "pixels" that form a multiplexed array to create a highly parallel and programmable manifold.

Monday 5:15 C107 EM5

Magnetic fluids and magnetization relaxation equations

Purna N. Kaloni
Maths. and Stats., University of Windsor, Windsor, Ontario N9B3P4, Canada

Magnetic fluids (ferrofluids) are stable colloidal suspensions of subdomain ferromagnetic nano particles in a liquid carrier.These fluids are not found in the nature but must be synthesized. The theory of the magnetic fluid when the magnetization field is collinear with the magnetic field,is well understood and has found enormous applications. Several complications,however,arise when the lagging of the magnetic particles.due to the change in the magnetic field is taken into consideration. Besides other things,this involves the development of a magnetization (relaxation) equation. In the recent years there has been a flurry of interest in developing different forms of magnetization equations with different approaches. Our purpose here is to elaborate on their developmens and to discuss the merits of these equations in describing the real behaviour.

Symposium BC

Blends and Composites

Organizers: Anson Ma and Savvas G. Hatzikiriakos

Monday 1:30 C101 BC6

Tethered nanoparticle–polymer composites: Structure, dynamics and rheology

Samanvaya Srivastava and Lynden Archer
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Polymer nanocomposites comprised of functional nanoparticles uniformly dispersed in a polymeric host are attractive for a growing list of technological applications in diverse fields. However, only limited control of the nanoparticle dispersion state is possible with current approaches. Here we explore the phase behavior and properties of nanoparticles densely grafted with short and medium-sized polymer chains in polymeric hosts. Small angle X-ray scattering (SAXS), X-ray correlation spectroscopy (XPCS), electron microscopy and mechanical rheology are used to study the structure and dynamics of these suspensions in order to assess their dispersion state. We show that SAXS provides important insight into the phase behavior of these nanocomposites, and on this basis present a comparison with contemporary studies as a first step towards defining the phase boundaries. Additionally, we report an anomalous structural transition in well-dispersed nanoparticle-unentangled polymer composites, wherein particle correlation decreases with increasing particle loading in the composites. This anomaly foreshadows a dynamic anomaly revealed by XPCS measurements, wherein the nanoparticle motion speeds-up with increasing particle loading in the host polymer. Possible origins of this unusual behavior are explored using models that combine hard-core and soft repulsive interactions.

Monday 1:55 C101 BC7

Effect on the drainage time of polymer-coated janus gold nanoparticles compatibilizing immiscible polymer blends

Carolina Vannozzi
Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA, United States

Polymer-coated Janus gold nanoparticles (PJGNPs) can be used as stabilizers in immiscible polymer blends. However, recent flow-induced head-on coalescence experiments [1] of two drops compatibilized by this type of nanoparticles showed a measured drainage time considerably shorter than that of the same system stabilized by block-copolymer surfactants, despite being highly surface active. This was attributed to the nanoparticle metallic core, which increases the magnitude of the attractive van der Waals interactions in the thin film between the drops, favoring coalescence. However, this finding can also be the consequence of other causes. To discern the importance of the different causes involved, we used boundary integral simulations of the coalescence process of two drops compatibilized by PJGNPs, treated as insoluble surfactants. A new expression [2] for the van der Waals interactions of films with PJGNPs, derived via a hybrid Hamaker-Lifshitz approach, was used to evaluate the effect on coalescence of the enhanced VDW interactions due to the nanoparticle gold cores as a function of the nanoparticle concentration and dimension. The effects of the surface diffusivity Ds, via the surface Peclet number, and surface elasticity, via the Marangoni number, on coalescence were also considered. Overall, the gold cores in PJGNP stabilized blends can reduce dramatically the drainage time, however, the soft corona, which keeps the gold cores apart, reducing the maximum interfacial concentration of the cores, can soften this effect considerably for particles whose ligand radius of gyration is comparable to the core dimension. Our simulations also suggest that the entropic attraction between two drop interfaces stabilized by PJGNPs, whose ligands are in a dry-brush regime, could be one of the main reasons, together with the enhanced VDW interactions and a Ds higher than the one estimated based on the Stokes-Einstein relation to explain the experimental data.

[1] Borrell, Leal, Langmuir, 23, 2007 [2] Vannozzi, Soft Matter, 8, 2012

Monday 2:20 C101 BC8

The effects of low level silanization on the rheology and microstructure of silica / PEG nanocomposite melts

Moulik Ranka and Charles Zukoski
Department of Chemical and Biomolecular Engineering, University of Illinois, Urbana-Champaign, Urbana, IL 61801, United States

The microstructure and flow properties of nanocomposites are coupled to the strength of interaction between polymer segments and particle surface. Methods to characterize these chemical interactions are limited. Here we explore the effects of increasing silanization on the microstructure and flow properties of nanocomposite melts composed of silica and PEG. In the low surface coverage limit, small angle x-ray scattering studies indicate increasing interparticle repulsion with increasing surface coverage of alkyl silanes. The rheological consequences of these repulsions will be discussed with a focus on the state of dispersion of the silica particles and the effect of increasing silanization on tan(d).

Monday 2:45 C101 BC9

Comparison of diffusion models for fiber-fiber interactions within fiber-filled thermoplastics using bulk mechanical stiffness results

Benjamin Lewis and David A. Jack
Mechanical Engineering, Baylor University, Waco, TX 76798, United States

The spatially varying fiber orientation within an injection molded composite can lead to variations in injection molded part's local and global mechanical properties. Thus the proper modeling of the injection molding process of a fiber orientation within a fiber-filled thermoplastic is essential. For concentrated suspensions there are three commonly used fiber diffusion models to represent fiber- fiber interactions during the mold filling: the Folgar-Tucker model (FT), the FT Model with the Reduced Strain Closure (FT-RSC) recently introduced by Wang et al. (2008), and the Anisotropic Rotary Diffusion Model (ARD) of Phelps and Tucker (2009). This work investigates the dependence of the processed part's mechanical properties as a function of these three fiber interaction models based on the predicted spatially varying fiber orientation distributions. This work also seeks to identify appropriate structural tests to allow a laboratory scale comparison of the fiber interaction diffusion models so that the proper diffusion model can be used to obtain the most accurate results in a real world part. As part of this work, the authors perform a finite element analysis (FEA) for the mold filling of the non-Newtonian fiber suspension for select industrially relevant flow domains, where the non-Newtonian viscosity profile employed is obtained from in-house rheological measurements of the fiber filled polymer. From the velocity gradient data we use an in-house MATLAB code to predict the fiber orientation, and map the spatially varying fiber orientation to the spatially varying stiffness using micromechanics techniques. From these spatially varying stiffness values we then import the results back into our FEA software and perform structural tests from the results obtained from the three different fiber interaction models to highlight the strength's and weakness of each of the three diffusion model approaches.

Monday 3:35 C101 BC10

Can only rheology be used to determine the phase separation mechanism in dynamically asymmetric polymer blends (PS/PVME)?

Jafar Khademzadeh Yeganeh[1], Fatemeh Goharpey[1], and Foudazi Reza[2]
[1]Department of Polymer Engineering, Amirkabir University of Technology, Tehran, Iran; [2]Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, United States

We investigated theoretically and experimentally the correlation between the time evolution of different phase-separating morphologies and corresponding linear and transient rheological behaviors for the dynamically asymmetric PS/PVME (polystyrene/polyvinyl methyl ether) blend in which there is a large difference between the glass transition temperatures of the pure components (about 125 ^{o}C). The sensitivity of different rheological analyses was examined to distinguish different phase separation mechanisms from each other, including nucleation and growth (NG), spinodal decomposition (SD), and viscoelastic phase separation (VPS). We found that a combination of experimental and theoretical studies of the linear and nonlinear rheology could provide satisfactory criteria to distinguish effectively samples phase separating by different mechanisms. Furthermore, the variation of fractal behavior by phase separation time was investigated for interconnected and percolated network structures induced by SD and VPS, respectively, which suggested that both network structures are controlled by a diffusion-limited cluster aggregation (DLCA) mechanism.

Monday 4:00 C101 BC11

Phase diagram of poly(ε-caprolactone) and polylactide biodegradable blend under oscillatory shear flow

Nazbanoo Noroozi[1], Laurel L. Schafer[2], and Savvas G. Hatzikiriakos[1]
[1]Chemical & Biological Engineering, University of British Columbia, Vancouver V6T 1Z3, Canada; [2]Chemistry, University of British Columbia, Vancouver, Canada

The phase separation boundary of the Poly(ε-caprolactone) and Polylactide blends has been determined using small amplitude oscillatory shear. According to the rheological analysis, this blend system exhibits a lower critical solution temperature (LCST). The effect of shear frequency and heating rate on the phase separation binodal and spinodal temperatures has been studied for the near-critical and off-critical blends. Results indicate that the shear frequency has a minor effect on the binodal boundary in contrast to a large effect of heating rate on the binodal temperature at the near-critical concentration. In the case of the off-critical concentration blends, the phase diagram shifts to higher temperatures at higher frequencies and higher heating rates. Calculating the spinodal temperature by using the Ajji-Choplin theoretical approach, demonstrates a weak influence of heating rate on the spinodal temperature of near-critical blend and a strong one for the off-critical blends.

Monday 4:25 C101 BC12

Study of negative intrinsic viscosity in polymer melts

Mansi Agarwal[1] and Charles Zukoski[2]
[1]Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, IL 61801, United States; [2]Department of Chemical and Biomolecular Engineering, University of Illinois, Urbana-Champaign, Urbana, IL 61801, United States

It is quite intuitive to think of increase in viscosity as a function of increasing concentration of solute in a solution. In the low volume fraction limit, the enhanced energy dissipation in a sheared Newtonian fluid due to the presence of spheres is captured by the relative viscosity increasing as 1+2.5?,where ? is the volume fraction of the added solute. The enhancement of viscosity by the presence of particles with sizes greater that a few tens of nanometers is also commonly observed in polymer melts. However, there have been recent reports that addition of nanoparticles to highly entangled polymer melts will reduce the melt viscosity. Conditions associated with this viscosity reduction are that the molecular weight of the polymer (Mw) is greater than the molecular weight of entanglement (Mw$_e$); the distance between the added particles (h) and also, the size of the added particles (a), both are less than the radius of gyration (R$_g$) of the melt polymer. It has been speculated that the addition of the nanoparticles alters the reptation dynamics of the polymer. In this study, we investigate the difference between flow properties and polymer segment dynamics of adding a low molecular weight polymer or a nanoparticle to high molecular weight polymer melts. We conclude that while the addition of both solutes can reduce melt viscosity, the particles and polymer alter polymer chain relaxation processes through different mechanisms.

Monday 4:50 C101 BC13

Influence of temperature on shear stress growth and modeling parameters for long glass fiber thermoplastic composites

Mark J. Cieslinski and Donald G. Baird
Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States

The ability to understand the flow behavior of long fiber reinforced composites in a well-defined geometry can be instrumental in predicting the fiber orientation in industrial processes. A sliding plate rheometer was used to investigate the stress growth and fiber orientation evolution during the startup of steady shear flow for composites of long glass fiber in polypropylene. Predictions of the fiber orientation evolution and subsequent stress growth have been modeled using a semi-flexible fiber orientation model and a semi-flexible stress model based on the bead-rod representation of flexible fibers and empirical modifications to the Lipscomb stress tensor. To further evaluate fitting parameters found in these models, experiments were performed at varying temperatures to assess the impact of matrix viscosity. Thermal trends in the shear stress growth for long glass fiber composites will be discussed, along with the ability of rheological measurements to quantify changes amongst model parameters.

Monday 5:15 C101 BC14

Study for extrusion of wood plastic composites

Krzysztof Wilczynski, Andrzej Nastaj, Zbigniew Szymaniak, Adrian Lewandowski, and Krzysztof J. Wilczynski
Polymer Processing Department, Warsaw University of Technology, Warsaw 02-524, Poland

Studies on the WPC rheological properties and extrusion characteristics are very limited. It is known that WPC are non-Newtonian materials, and their viscosity decreases with increasing shear rate and temperature. An increase of melt viscosity and a decrease of melt elasticity with increasing filler content has been reported. Yield stress and wall slip have been also detected. With increasing shear rate the slip velocity increases leading to plug flow. An increase in wood content promotes a plug flow behavior. An extrusion operation design requires a proper knowledge of the flow mechanism of these highly filled materials. This is fundamental for modeling of WPC extrusion. However, current extrusion theories do not predict the process behavior. Experimental studies have been carried out for single screw extrusion of PP/wood flour composite. "Screw Pulling-out Technique" was used for investigation of the material behavior, melting and filling of the screw channel.Pressure and temperature were measured. An effect of operating conditions, screw speed,flow rate,and starving level was studied.It is concluded that WPC single screw extrusion is totally different from thermoplastics extrusion. The contiguous solid melting mechanism CSM which is typical for thermoplastics is not valid for WPC extrusion. In this case, material is melted in the mass with a melt layer on outer surfaces. Melting is dependent on the screw speed,and it is not dependent on the starvation. Surface tearing has been seen.It increases with screw speed and starvation. Segregation of the two base materials of the composite has not been observed. Acc. to our observations the flow of WPC may be considered as a plug flow with a melt layer at the outer surfaces. At the point where melting finishes the plug flow is replaced by shear flow with slipping at the walls. An attempt of simulation of the WPC extrusion using the SSEM model developed at Warsaw University of Technology has been carried out.

Symposium EF

Emulsions, Foams and Interfacial Rheology

Organizers: Sachin Velankar and Petia Vlahovska

Monday 1:30 C105 EF6

Response of capillary suspensions to external deformations

Erin Koos, Wolfgang Kannowade, and Norbert Willenbacher
Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Baden-Württemberg 76131, Germany

When a small amount (less than 1%) of a second immiscible liquid is added to the continuous phase of a suspension, the rheological properties of the mixture are dramatically altered from a fluid-like to a gel-like state or from a weak to a strong gel and the strength can be tuned in a wide range covering orders of magnitude[1]. The response of a capillary state suspension to steady and oscillatory stresses is examined in this current work. This suspension, where the secondary fluid does not preferentially wet the particles, is particularly sensitive to magnitude of deformation and shows varying characteristics with the amount of secondary fluid. These admixtures also show significant time varying behavior at constant oscillatory strain amplitudes with an initial increase in the network strength and then a sudden decrease in the strength as the network is destroyed.

E. Koos and N. Willenbacher. Science, **331** (2011) 897

Monday 1:55 C105 EF7

Rheology and structure of ternary fluid/fluid/particle systems

Sachin S. Velankar and Shailesh P. Nagarkar
Dept. of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States

We will present the rheology and structure of Pickering emulsion type systems composed of two immiscible liquids (molten polymers) and a small quantity (< 1vol%) of a particulate species that adsorbs at the interface between the two liquids. Addition of particles causes profound and remarkable changes in the rheology of the emulsions. For example, at very low particle loadings, the viscosity first decreases and then increases with particle loading. At slightly higher particle loadings, the effects depend severely on the wettability of the particles towards the two immiscible fluids. Emulsions containing particles that are preferentially-wetted by the drop phase show rheological characteristics typical of reversibly-aggregating systems: yield stress-like behavior, severe shear thinning, and overshoots in viscosity during startup of steady shear. Emulsions containing particles that are equally-wetted by both phases do not show any of these features. The results can be interpreted in terms of the structural changes caused by particle addition. Although our experiments are conducted with immiscible polymers, they likely apply to oil/water systems as well and we will place these results in context of results on other ternary fluid/fluid/particle systems.

Monday 2:20 C105 EF8

Highly porous ceramic foams from magnesium oxide-stabilized Pickering emulsions

Christine C. Roberts, Lindsey G. Hughes, Lisa A. Mondy, Anne M. Grillet, Chris Diantonio, Tom Chavez, and David Ingersoll
Sandia National Laboratories, Albuquerque, NM, United States

Porous and permeable ceramic scaffolds are useful to many applications ranging from catalyst supports, filtering molten metal alloy, and high temperature insulation. Ceramic foams with porosities over 90% can be created by drying and sintering particle stabilized oil-water emulsions. This technique is optimized for the creation of magnesium oxide porous scaffolds. Processing parameters such as emulsion mixing speed, particle concentration, and drying time are related to final properties such as porosity, permeability, and mechanical strength. The impacts of the hydroxylation of magnesium oxide to brucite on the foam performance will also be discussed. Finally, the quality of the ceramic foams will be compared to porous ceramics produced by other methods: 1) blade coating of an MgO slip, which is then laser-drilled with a set array of holes, 2) blade coating of a slip with added pore formers, and 3) impregnation of a reticulated foam sponge with a slip in a replication process.

This research is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Monday 2:45 C105 EF9

Flow of concentrated emulsions: A cooperative process

Annie Colin
LOF, University Bordeaux 1, Pessac 33608, France

Emulsions display complex flow properties intermediate between a solid and a liquid. At rest they behave as a solid and respond elastically at the sollicitation and flow as a liquid under a sufficient sollicitation. In this work, we show that flow in emeulsions is a cooperative process. We report confocal microscopy experiments under shear and show that the local strain rate fluctuations that reflect the number of plastic events by unit time are inversely proportional to the inverse of the local viscosity coined the fluidity. Fluidity is shown to increase as a function of the local shear stress and to be spatially correlated. In the neighborhood of an active zone, the rate of plastic events is higher than close to a quiete one. We analyse our data in the framework of the fluidity model. We measure correlation lenght and discuss the role of the boundary conditions for the flow.

Monday 3:35 C105 EF10

Shear-induced migration of semi-dilute emulsion in a microchannel

Vincent Mansard[1], Florinda Schembri[2], Hugues Bodiguel[2], and Annie Colin[2]
[1]Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106-5080, United States; [2]LOF, University Bordeaux 1, Pessac 33608, France

When shearing particles suspension, one observes apparition of inhomogeneity of concentration with higher concentration where the shear rate is lower. This is called shear-induced migration. Migration has been an active research area for the past 20 years. From an industrial viewpoint, keeping a suspension as homogeneous as possible remains an important challenge.

The two phases model [1] has reached success to explain some experiments. It considers a suspension as a two phases system, the particles and the continuous phase, and separates the component of the stress due to each phases. Nevertheless there is no theoretical prediction on this separation and only few experiments have measured the different stress components. In the literature some basic hypotheses are done to solve the problem.

In this work we will focus on shear-induced migration of semi-dilute emulsion of silicon oil in water-glycerin, with droplet's diameter of 5um. The emulsion can be considered as a suspension of soft particles. We flow the emulsion in a microchannel of 50um to create a Poiseuille flow. This geometry is efficient to study steady state phenomena.

We get a transparent emulsion by controlling the ratio water glycerin to get the same refractive index in the two phases. By adding fluorescein in the water phase, we visualize directly the droplets with a confocal microscope. We measure the velocity profile in the channel and the local concentration. From these measurements, we will discuss the two phases model and show that we can extract information on the stress decomposition.

Furthermore, we have developed an original method to measure the difference of velocity between the particles and the continuous phase. This experiment, which has never been managed in the literature, gives a direct measurement of the shear stress component due to the particles. We will show that our measurements are in contradiction with the classical hypothesis.

[1] J.F. Brady and J.F. Morris. Journal of Fluid Mechanics, 348:103-139, 1997.

Monday 4:00 C105 EF11

Nonlinear electrohydrodynamics of a viscous droplet

Paul F. Salipante and Petia M. Vlahovska
Brown University, Providence, RI, United States

A classic result due to G.I. Taylor is that a drop placed in a uniform electric field adopts a prolate or oblate spheroidal shape, the flow and shape being axisymmetrically aligned with the applied field. We report an instability and transition to a nonaxisymmetric rotational flow in strong fields, similar to the rotation of solid dielectric spheres observed by Quincke in the 19th century. Our experiments reveal novel droplet behaviors such as tumbling, oscillations and chaotic dynamics even under creeping flow conditions. A phase diagram demonstrates the dependence of these behaviors on drop size, viscosity ratio and electric field strength. The theoretical model, which includes anisotropy in the polarization relaxation, elucidates the interplay of interface deformation and charging as the source of the rich nonlinear dynamics. Strong DC electric fields are also reported to lower the effective emulsion viscosity below that of the matrix fluid. We discuss the relation of emulsion electrorheology to drop-level dynamics.

Monday 4:25 C105 EF12

Fourier transform rheology as an innovative morphological characterization technique for the emulsion volume average radius and its distribution

Kathrin Reinheimer, Dimitri Merger, and Manfred Wilhelm
Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

This article extends previous works on emulsion characterization via Fourier Transform Rheology. The interest here is on the effects of (i) polydispersity and (ii) high volume fraction (often associated with commercial samples) on the nonlinear rheological behavior. To analyze the effects of polydispersity on the LAOS measurements, the investigated samples were characterized with respect to their volume average radius, R43, and the polydispersity index of the distribution. As the nonlinear mechanical emulsion value E0 introduced in the literature is a function of both nonlinear rheological parameters, such as I5/3, as well as emulsion properties including the volume average radius, interfacial tension and viscosities of the matrix and dispersed phase, it is, therefore, a useful tool for emulsion characterization. In addition, the analysis of the higher harmonic ratios, I7/5, has been demonstrated to provide information about the width of the distribution. With respect to the characterization of the high volume fraction samples, these first experiments on commercial w/o-emulsions were shown to relate nonlinear rheological properties to the droplet size and droplet size distribution of highly filled systems, demonstrating that LAOS experiments can give useful insights on the average droplet size and its distribution.

Monday 4:50 C105 EF13

Dynamic characterization of high internal phase emulsions during polymerization

Reza Foudazi[1], Polina Gokun[1], Donald L. Feke[2], Stuart J. Rowan[1], and Ica Manas-Zloczower[1]
[1]Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States; [2]Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

The close-packed polyhedral microstructure of high internal phase emulsions (HIPE) allows for the dispersed phase to occupy over 74% of the system volume, which is well beyond the packing limit of hard spheres. In the case of water-in-oil HIPE systems, polymerization of monomers present in the continuous phase yields open porous foams, known as polyHIPEs. In this work, the evolution of dynamic moduli and microstructure of HIPE systems containing 94.4% water in 2-ethylhexyl acrylate (EHA) and ethylene glycol dimethylacrylate (EGDMA) was studied. Isothermal, oscillatory time sweeps in the linear viscoelastic regime were used to follow the kinetics of polymerization. Due to the solid-like behavior of uncured HIPEs, methods reported in the literature for obtaining the gel-point during polymerization were not successful. However, the kinetics of different stages of polymerization including (i) initiation (ii) propagation (iii) molecular network formation and (iv) the final equilibrium state were quantified by rheological measurements of both the storage and loss moduli. The final equilibrium moduli can also be used to predict the poromechanical behavior and thus the reaction conversion of polymerized HIPEs.

Monday 5:15 C105 EF14

Flow of a viscoelastic fluid around a deformable droplet

Baltasar Mena
Institute of Engineering, National University of Mexico UNAM, Mexico, D.F., Mexico

The flow of a viscoelastic fluid around a deformable elastic droplet is examined experimentally. A droplet of a viscoelastic material (polyisobutilene in cetane and polybutene oil) is injected in a large bath of aqueous polyacrilamide solution and followed as it travels upward towards the surface. Measurements are taken of the velocity profile around the droplet using PIV and the flow pattern is observed with standard visualization techniques. The deformation of the droplet is closely recorded and the shape is the result of a balance between viscous, elastic and surface tension forces. The terminal velocity is determined for a large variation of droplet volumes and conditions are examined for a critical volume in which a velocity jump may be present. Results are then compared to the flow around rising bubbles and to the flow around solid spheres. The cases of two or more droplets rising in the same trajectory is also examined and compared to two spheres falling along the same pathline.

Tuesday Morning

Symposium PL

Plenary Lectures

Bingham Lecture

Tuesday 8:30 C102-C104 PL2

Linear viscoelasticity of associating ionomers

Ralph H. Colby
Materials Science and Engineering, Penn State University, University Park, PA 16802, United States

Polymers that associate by either hydrophobic interactions, hydrogen bonding or ionic interactions have been of interest since the pioneering 1946 work of Green and Tobolsky. Ionomers can have remarkable mechanical properties that stem from ion associations, with interesting melt rheology, studied more recently by ionomer experts such as Eisenberg, Register and Weiss. Such ionomers typically have very strong ionic interactions, since the surrounding media is hydrocarbon polymer of low dielectric constant, often with high glass transition temperature. In our quest to develop polymer membranes that transport specific ions for a variety of energy materials applications, we have developed a new class of ionomers based on higher dielectric constant polymers that solvate ions. These ionomers are liquids at room temperature, with rather short chains (M ~ 10000) yet they are strongly viscoelastic. Some even exhibit rubbery plateaus that span many decades of frequency despite their short chain lengths.

In this talk we show how simple ideas using a sticky Rouse model with three parameters can be applied to short chain ionomers. The first two parameters, glassy modulus and monomer relaxation time, are common to all molecular polymer models; they reflect the fact that we do not yet understand well the glass transition. The third parameter is the association lifetime and for ionomers this can be directly observed in dielectric spectroscopy, as a large relaxation where ions start to move. We show examples of how this model works for polyester sulfonate ionomers based on poly(ethylene oxide), polyester sulfonate ionomers based on poly(tetramethylene oxide), and polysiloxane ionomers with a random mixture of phosphonium and poly(ethylene oxide) side chains. In each case, knowledge of the molecular weight distribution and the association lifetime from dielectric measurements allows the full linear viscoelastic response to be understood.

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Tuesday 10:00 C106 SC15

Rheological and diffusion properties of charged particles dispersions: From big colloids to nanosized bioparticles and electrolyte ions

Gerhard Naegele[1], Claudio Contreras-Aburto[1], and Marco Heinen[2]
[1]Institute of Complex Systems, Soft Matter Division ICS-3, Research Centre Juelich, Juelich, Germany; [2]Institute of Theoretical Physics II, Heinrich-Heine-University Duesseldorf, Duesseldorf, Germany

We report on a comprehensive theoretical study of rheological and diffusion properties of dispersions of charged particles. The study encompasses a broad range of systems, including suspensions of micron-sized colloidal particles such as charged silica spheres and microgels, solutions of nano-sized globular proteins, and electrolyte solutions. The dispersed particles are modeled as charged rigid spheres, and their configurational evolution is described by the many-particle generalized Smoluchowski equation, with the solvent-mediated hydrodynamic interactions properly accounted for. Various analytic methods have been developed and tested, including a simplified mode coupling scheme with hydrodynamic forces included. These methods allow for a fast calculation of dynamic properties, including high-frequency and steady-state viscosities, hydrodynamic functions, collective and self-diffusion coefficients, and electrolyte conductivities and electrophoretic mobilities. The good performance of these methods has been assessed by an extensive comparison with elaborate Brownian dynamics simulation results and experimental data. Our theoretical and simulation methods were used to examine the application range of generalized Stokes-Einstein relations between viscosity and diffusion properties, in particular with regard to protein solutions, and concentrated suspensions of solvent-permeable colloidal particles. The flow inside permeable particles was described by the Brinkman fluid model, and dynamic properties of dense permeable particle systems were calculated to high precision using a hydrodynamic force multipole simulation method.

Tuesday 10:25 C106 SC16

Self-suspended nanoparticle fluids – structure, rheology and dynamics

Praveen Agarwal[1], Samanvaya Srivastava[2], Sung A. Kim[1], and Lynden Archer[2]
[1]Cornell University, Ithaca, NY, United States; [2]School of Chemical and Biological Engineering, Cornell University, Ithaca, NY 14853-5201, United States

This talk focuses on structure, relaxation dynamics, and rheology in a class of self-suspended nanoparticle fluids. Created by densely grafting short polymeric ligands to inorganic nanostructures, the materials exhibit liquid-like mobilities and soft-glassy rheology, yet are able to relax to an equilibrium state in the absence of an explicit solvent. Using mechanical rheometry, dielectric relaxation, and scattering we investigate how polymer- and particle-scale interactions influence rheology, structure, and transport properties of the materials.

Tuesday 10:50 C106 SC17

Brownian dynamics simulations of a local-fluid-volume preserving model of solvent-free nanoparticle fluids

Arijit Sarkar and Donald L. Koch
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Nanoparticle-organic materials (NOHMs) consist of inorganic cores with tethered oligomeric brushes which provide fluidity to the system even in the absence of unattached solvent molecules. We present Brownian dynamic simulations and theoretical models of these materials based on the hypothesis that Brownian motion, hard core repulations, and the free energy penalty for variations in the fluid volume surrounding each particle dominate their structure and dynamics. In particular, we adopt a non-pairwise additive potential energy that is proportional to the square of the deviation of the Voronoi volume surrounding the particles from its mean value. Based on this model we will determine the steady shear rheological properties as a function of the Peclet number and a dimensionless ratio of voronoi potential energy to thermal energy (k_BT). In addition, we will determine the static and dynamic scattering functions in the absence and presence of imposed shear flows. The Brownian dynamics results will be discussed in the context of experimental measurements on NOHMs. We show that NOHM's dynamics are influenced by a large osmotic pressure resuting from the Voronoi constraint energy that resists long ranged volume fraction variations.

Tuesday 11:15 C106 SC18

The shear and extensional rheology of nanoparticle-polymer suspensions and its effect on liquid transfer during gravure printing

Sunil Khandavalli, Ashwin Sankaran, and Jonathan Rothstein
University of Massachusetts, Amherst, MA, United States

Roll-to-roll patterning of small-scale features on a rapidly moving web is an industrially important process with a wide array of commercial applications both old and new. Examples including magazine printing and more recently the pattering of flexible electronics. Among the many existing web coating techniques for large-scale fabrication, slit die and gravure coating are the most commonly used. In gravure coating, an engraved roller with a regular array of shallow cavities/cells is used to pick up fluid from a bath. It is then passed through a flexible doctoring blade in order to meter off excess fluid before printing the fluid onto a flexible substrate. We will present an experimental investigation into the effect that addition of nanoparticles and polymer can have on the dynamics of liquid transfer from an idealized gravure cell to a flat rigid substrate. A detailed study of the shear and extensional rheology of series of aqueous systems containing both silica nanoparticles and PEO will be presented. The effect of both nanoparticle size and concentration as well as polymer molecular weight and concentration on rheology and gravure coating will be presented. The deformation and stretching of the resulting liquid bridges, the motion of the contact line within the gravure cell and the total amount of fluid removed from the gravure cell will be presented as a function of the imposed stretch rate, the fluid rheology, the geometry of the gravure cell and the wettability of both the top plate and the gravure cell. The performance of viscoelastic, shear thickening and shear thinning systems will be compared directly to Newtonian fluids.

Tuesday 11:40 C106 SC19

Effects of temperature and sonication on the rheology and microstructure of nano-crystalline cellulose (NCC) aqueous suspensions

Sadaf Shafiei-Sabet[1], Wadood Y. Hamad[2], and Savvas G. Hatzikiriakos[1]
[1]Chemical and Biological Engineering, University of British Columbia, Vancouver, BC V6T 1Z3, Canada; [2]FPInnovations, Vancouver, BC V6S 2L9, Canada

The rheological properties and microstructure of nano-crystalline cellulose (NCC) aqueous suspensions have been studied at different concentrations. Above a critical concentration (3 wt.%), the suspension phase separates to liquid crystalline and isotropic domains where the fingerprint texture appeared and the viscosity profile showed a three-region behavior, typical of liquid crystals. By further increase in concentration, a gel structure is formed where the viscosity profile showed a single shear thinning behavior over the whole range of investigated shear rates. The effects of ultrasound energy (sonication) and temperature on the rheological properties and microstructure of these suspensions were studied using polarized optical microscopy combined with rheometry (optical rheometry). It was found that the amount of applied ultrasound energy affects the microstructure of suspensions and the pitch of chiral nematic domains and changes the viscosity profile especially at low shear rates. The viscosity of biphasic suspensions at intermediate and high shear rates decreased with increasing temperature while the viscosity at low shear rates showed a sudden increase at a critical temperature indicative of some structure rearrangements. Applicability of

Cox-Merz rule was also studied for these suspensions, showing that suspensions deviate from this rule after a critical concentration. This critical concentration is found to be affected by sonication.

Symposium EM

Electric and Magnetic Field Effects in Rheology

Organizers: Aditya Khair and Yuriko Renardy

Tuesday 10:00 C107 EM6

Effects of environmental parameters on the electrospinnability and fiber morphology of polyethylene oxide

Ljiljana Palangetic and Christian Clasen
CIT, KU Leuven, Heverlee, Belgium

Electrospinning is a technique in which an electric field is used for producing nanometer scale fibers. Even though widely investigated, the method is still challenging due to the large number of affecting parameters. Next to the solution properties and rheology that have been the focus of recent investigations, ambient parameters are suspected to be at least as important for the systems spinnability, production reproducibility, and fiber characteristic. This paper focuses on the effects of temperature and humidity on the electrospinning of polymer solutions and the decoupling of the two. For this, a unique climate-controlled electrospinning setup was used that allows setting a flow-through climate in a high voltage environment with temperature control of 0-45°C (± 1°C) and relative humidity up to 90% with precision of 5%. Aqueous polyethylene oxide (PEO) solutions of different molecular weights and concentrations were spun under ambient conditions that span the range of the chamber. The resulting fiber morphologies are correlated to the environmental parameters via continuous diffusion and evaporation kinetic measurements of batch samples of polymer solutions. This has been done for concentration ranges that mimic the profile in the spinning filament at the same ambient conditions at which the electrospinning experiments were carried out.

Tuesday 10:25 C107 EM7

Fiber formation during electrospinning of low molecular weight polymer solutions due to the presence of small amounts of high molecular weight polymer

Naveen K. Reddy[1], Siddarth Srinivasan[2], Ljiljana Palangetic[1], Robert E. Cohen[2], Gareth H. McKinley[3], and Christian Clasen[1]
[1]CIT, KU Leuven, Heverlee, Belgium; [2]Chemical Engineering Department, MIT, Cambridge, MA, United States; [3]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Fiber-spinning has become again a major topic of research interest in recent year due to the possibility to produce micro- to nanometer thin fibers from polymer solutions in the form of thick non-woven fabrics. These fabrics have potential applications in areas such as non-wetting and breathable clothing, wound dressing and template for growing artificial skin etc. Several techniques have been invented or rediscovered in order to reach fibre diameters on the nanometer scale; examples are electro-, spray-, or forced-spinning. However, the parameters that control the morphology, as for example the formation of a beads-on-string structure on the spun fibre, are still not clear. Reviewing the literature a strong focus has been on the overlap concentration (C*), and a lot of arguments on the spinnability relate to the capability of a solution to form entanglements and exhibit a sufficient (extensional) viscosity. On the other hand it has been shown that a polydisperse polymer solution gives fibers at concentrations well below C*. Within the current paper we are demonstrating how the concentration dependent spinnability can be linked to an extensibility averaged molecular weight of the polymer. The resulting extensional critical concentration is verified from spinning experiments of a series of blends of well-characterized PMMA samples consisting of high concentration low molecular weight (Mw) polymer and low concentration high Mw polymer such that the effective Mw is similar to that of a polydisperse sample.

Tuesday 10:50 C107 EM8

Tethered nanoparticles in oligomer with controllable electrostatic forces

Yu H. Wen, Kerianne Dobosz, and Lynden Archer
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

We report rheology and nanostructure of ionic nanoparticle suspensions in which tunable steric and electrostatic forces co-exist. Particles co-functionalized with polyethylene glycol oligomers and a metal salt are the focus of the current report. Rheology and small-angle X-ray scattering reveal a transition to a jammed, elastic state at low nanoparticle loadings. The results show that both the surface charge-density and valency profoundly impact the stress and strains at the yield point, as well as the infinite frequency elastic modulus. By fitting the low-q structure factor using a charged sphere model, we show that the rheology is a consequence of strong attraction between nanoparticles. Additionally, using X-ray photon correlation spectroscopy (XPCS) we characterize the diffusion of the particle cores and show that electrostatic interactions have a profound influence on the cage dimensions.

Tuesday 11:15 C107 EM9

Visualizing 2-D phase transitions with paramagnetic colloids

Sibani Lisa Biswal
Chemical and Biomolecular Engineering, Rice University, Houston, TX, United States

Paramagnetic colloids placed in a rotating magnetic field can be induced to create an isotropic 2-D interaction potential from 5kBT to 40kBT. Various 2-D thermodynamic phases are observed in a colloidal suspension at different field strengths. Quantitative aggrement is found between theory for dipolar interactions and experiments. Theory to account for the induced dipole due to neighboring particles will be described. The effective three-body potential of a dilute trimer system is measured to account for many-body effects in the system. The system allows for detailed visualization of melting dynamics of 2-D systems.

Tuesday 11:40 C107 EM10

Engineering improved magnetorheological (MR) fluids with the addition of non-magnetizable particles

Benjamin T. Wilson and Daniel J. Klingenberg
Chemical and Biological Engineering, University of Wisconsin, Madison, WI 53703, United States

MR fluids are suspensions of magnetizable particles whose rheological properties are altered when exposed to magnetic fields. Active research areas include developing methods to enhance the field-induced rheological properties and decreasing the density and the cost. One possible method for achieving these goals is to add non-magnetizable particles to the suspension. Replacing some of the magnetizable particles with non-magnetizable particles can lead to both reduced density and reduced cost of MR fluids. In addition, experimental and simulation results indicate that adding non-magnetizable particles can also increase the field-induced yield stress.

The focus of this study has been to better understand the mechanisms of the enhanced yield stress using particle-level simulations. More specifically, we will describe new simulation results that probe the effects of added non-magnetizable particles on the microstructure of MR fluids in steady shear. We will also describe how the presence of non-magnetizable particles influences the behavior of MR fluids in small and large amplitude oscillatory shear flow.

Symposium SA

Self-Assembling, Associating and Gel-Like Systems

Organizers: Kendra Erk and Surita Bhatia

Tuesday 10:00 C101 SA1

Enormous elongation of (SIS)n type multiblock copolymers

Hiroshi Watanabe and Yumi Matsumiya
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Styrene-Isoprene (SI) block copolymers behave as thermoplastic elastomers if the S blocks form glassy spherical domains connected with flexible I blocks. This elastomeric feature is observed for the simplest SIS triblock copolymers but the elongational limit and strain recovery are enhanced for (SIS)n-type multiblock copolymers. Rheological experiments revealed that a (SIS)n undecablock (n = 5) containing I-selective solvent, n-tetradecane, exhibits the enormous elongation (up to the stretch ration of 90) associated with slow but complete strain recovery. On the basis of SAXS data, the enormous stretch is attributable to elasto-plastic deformation through pull-out of S blocks from their domains and reorganization of those domains, and the full strain recovery, to the elasticity of strands of copolymer chains (connected at the S domains) that survive even during/after this deformation.

Tuesday 10:25 C101 SA2

A numerical study on the structure and rheology of transient self-associating polymer networks

Mark Wilson[1] and Arlette Baljon[2]
[1]Department of Computational Science, San Diego State University, San Diego, CA, United States; [2]Department of Physics, San Diego State University, San Diego, CA, United States

We employ a simulation of telechelic polymers, using a hybrid molecular dynamics Monte Carlo (MD/MC) algorithm. Within the simulation, functionalized end groups, at both ends of the polymer chain, form reversible bonds according to MC rules, while the spatial position of the polymers is dictated by MD. The system is studied under an applied oscillatory shear at a temperature below the micelle transition. Hence, the chains self-assemble to form a transient network. The nodes of this network are formed by aggregates of end groups. Bridges between aggregates are formed by one or more polymers. The structure of this self-associating polymer network changes in response to the applied stress. The utility of the simulation is in the ability to identify these microstructural changes. Our results indicate that the system undergoes a continual restructuring of the network, as a result of the rupture and healing of bonds between the functionalized end groups. The system slowly develops towards configurations that include more bridges containing a larger number of polymer chains. Moreover, aggregates become more tightly packed. Temporal correlations between structural properties and the applied shear are presented.

Tuesday 10:50 C101 SA3

The rheological and molecular similarity of failure interfaces resulting from fracture and shear banding instabilities in model physically associating polymer gels

Kendra A. Erk[1] and Kenneth R. Shull[2]

[1]School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States; [2]Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60202, United States

Model physically associating polymer gels deformed in shear over a wide range of reduced shear rates displayed evidence of extreme strain localization occurring in the form of bulk fracture and shear banding instabilities (*Langmuir*, 2012, v. 28, p. 4472-4478). To inform our understanding of the microscopic structural rearrangements driving this macroscopic response of the gel, the nonlinear stress responses and flow fields observed by particle tracking velocimetry were combined with results from sliding friction scaling analysis and prior knowledge of the well-defined structure and stress relaxation mechanisms of the gel. Compared to previous studies of nonlinearity in soft materials, the work described here benefits from studying thermally reversible physical networks composed of triblock copolymer dissolved in a midblock-selective solvent, resulting in the formation of a polymer gel with a well-defined molecular structure and wide range of accessible relaxation times.

Flow visualization results directly confirmed the occurrence of shear-induced cohesive fracture at high shear rates and shear banding at low shear rates. Scaling analysis results suggested that for both the fracture and shear banding instabilities, deformation was confined to a localized shear zone within the gel with thickness comparable to the gel's mesh size, the smallest structural length scale in the network. Additionally, the observed sliding friction response at large values of strain (*i.e.*, power-law shear thinning rheology) was found to be independent of the applied shear rate. **Thus the failure interfaces for both the fracture and shear banding instabilities appeared to be rheologically and molecularly similar, comprised of dangling polymer molecules moving through a solvent-rich environment.** Instructive comparisons will be made to results from traditional sliding friction experiments of gelatin and silicone gels and molecular dynamic simulations of opposing layers of polymer brushes in shear.

Tuesday 11:15 C101 SA4

Strong and tough hybrid hydrogels composed of physical and covalent networks

R. A. Weiss and Jinkun Hao

Dept. of Polymer Engineering, University of Akron, Akron, OH 44325-0301, United States

Neutral hybrid hydrogels consisting of physical and covalent crosslinks were synthesized from dimethyl acrylamide (DMA), 2-(N-ethylperfluorooctane sulfonamido) ethyl methacrylate (FOSM)and 2-hydroxyethyl acrylate (HEA). The HEA were converted to cimmamate groups by reaction with cinnamoyl chloride and covalent crosslinks were formed by exposing the cinnamate groups to UV light. The physical network was formed by ~6 nm FOSM nanodomains. These hybrid hydrogels absorbed up to 270% water and exhibited fracture toughness, measured by single-edge notch tensile testing, of up to 200 J/m^2. The tensile properties achieved were 50 - 200 kPa modulus, 200 - 550 kPa ultimate stress and 500 - 600% elongation, depending on the hydrogel compostion. The compression modulus was 0.4 - 5 MPa. The hybrid hydrogels did not fracture in compression up to strains of 85% and stress > 35 MPa. The hybrid hydrogels were viscoelastic The dynamic and loss shear moduli exhibited frequency dependences that became stronger as the temperature approached the Tg of the hydrophobic nanodomains, ~ 45°C. The viscous response of the physical network also became stronger at 45°C and higher, which was attributed to hopping of the FOSM groups from one nanodomain to another as a consequence of the stresses exerted on them by the network chains. That provided relatively high energy dissipation, with tan δ reaching values as high as 0.6. The shear moduli values were relatively high for a hydrogel, 30 - 400 kPa, which was a consequence of the multifunctional physical crosslinks produced by the hydrophobic nanodomains. The physical crosslinks provided most of the crosslink density of the hydrogels, but the addition of the covalent crosslinks increased the modulus of the hydrogels.

Tuesday 11:40 C101 SA5

Developing a constitutive framework for predicting large deformations of simple and thixotropic elasto-viscoplastic materials

Christopher J. Dimitriou and Gareth H. McKinley

Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Elasto-viscoplastic (EVP) materials are typically characterized by a linear viscoelastic behavior at low stresses and a critical stress (or yield stress) above which the material exhibits irreversible flow. The goal of this work is to develop a general thermodynamically-consistent and frame-invariant class of tensorial constitutive models that can capture the nonlinear deformation regime of these materials. A distinguishing feature of this framework is the incorporation of isotropic and kinematic hardening processes (from the metal plasticity literature) to capture transient viscoplastic flow. These hardening mechanisms describe a transformation of the material's yield surface as a result of imposed deformations. The isotropic hardening/softening mechanism is related to a general class of phenomenological thixotropy models that are commonly encountered in the rheology literature. These models track the evolving material structure using an internal parameter (or hidden variable). For certain limits, this model in this work can be reduced to a simple EVP material, such as the Elastic Bingham (EB) model with no thixotropic behavior.

Experiments are performed on a simple Carpobol gel and a thixotropic model crude oil. Several experimental protocols are considered to determine values of the model fitting parameters. These tests include measurement of the steady flow-curves, Large Amplitude Oscillatory Shear (LAOS), and measurements of stress overshoots following start-up of a steady imposed shear rate. An internally consistent set of constitutive parameters is shown to capture the material response under all of these scenarios. We also explore the effects that thixotropic behavior may have on the stability of steady shear flows in these materials. In-situ velocimetric measurements (Rheo-PIV) of the model crude oil under steady shear show that the presence of a non-monotonic region in the flow curve coincides with pronounced temporal fluctuations in measurements of the local shear rate within the sample.

Symposium EF

Emulsions, Foams and Interfacial Rheology

Organizers: Sachin Velankar and Petia Vlahovska

Tuesday 10:00 C105 EF15

Drop circulation and liquid-liquid extraction in Hele Shaw flow

Christine C. Roberts[1], Scott A. Roberts[2], Rekha R. Rao[2], and Martin B. Nemer[1]

[1]Thermal Fluid Experimental Sciences, Sandia National Laboratories, Albuquerque, NM 87185-0346, United States; [2]Thermal and Fluid Processes, Sandia National Laboratories, Albuquerque, NM 87108, United States

Microfluidic devices are high shear, controlled environments that are useful for studying interfacial mass transport. A thin flow-focusing channel is used to generate monodisperse aqueous phase droplets with drop diameter to channel height ratios ranging from 0.5 to 2. Liquid streamlines within the droplets are inferred by particle tracking, revealing a fountain flow recirculation pattern. Larger droplets that are more confined in the channel exhibit a recirculation in the plane of the chip, whereas unconfined droplets do not. Two-phase flow of droplets in a rectangular channel is also simulated using an arbitrary Lagrangian-Eulerian (ALE) finite element method, allowing investigation of the 3-D droplet flow patterns. Knowledge of the recirculation pattern is then applied to understand species mass transfer from the droplet fluid. Quantitative mass transfer measurements are obtained using high speed imagery and spectrophotometry for various flow rates and droplet sizes. The effects of coalescence on mass transfer are also investigated.

This research is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Tuesday 10:25 C105 EF16

Using the conformal decomposition finite element method to model microfluidic flows and droplet formation

Rekha R. Rao, David R. Noble, Christopher Brotherton, Christine C. Roberts, and Scott A. Roberts

Thermal and Fluid Processes, Sandia National Laboratories, Albuquerque, NM 87185-0836, United States

Here we present results from flow and droplet formation in microfluidic devices using a novel algorithm for modeling capillary free surface flow known as the Conformal Decomposition Finite Element Method (CDFEM). CDFEM is a hybrid moving boundary algorithm, which combines ideas from Eulerian methods (diffuse interface level set methods, extended finite element methods) and arbitrary-Lagrangian Eulerian (ALE) moving mesh methods. A level set field is used to determine the location of the fluid-fluid interface. The original mesh is then dynamically decomposed to add mesh lines on the interface, facilitating the application of boundary conditions. This is a sharp interface method, where it is possible to apply jumps in material properties and field variables at the phase boundary. Surface tension is applied with a Laplace-Beltrami operator. Three classic benchmark problems will be used as a formal verification study: 1) A static bubble, 2) A buoyant drop rising in a tube, and 3) A Rayleigh-Taylor instability. Droplet formation and flow in a flow microfocusing microfluidic device is demonstrated. In two-dimensions, the method predicts the correct trends for capillary number as a function of drop size as seen in experiments, but can never be quantitative. In three-dimensions, we can produce droplets but must artificially reduce the amount of surface tension since numerical issues arise for these low capillary number problems such as mass loss and spurious velocity currents. Methods to ameliorate these issues will be discussed as will next steps in the modeling effort.

* 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. This work was supported by a Laboratory Directed Research and Development Project.

Tuesday 10:50 C105 EF17

Linear stability of oscillating pinned bubbles in interfacial rheological measurements

Anthony Kotula[1] and Shelley Anna[2]

[1]Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States; [2]Depts. of Chemical Engineering and Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

The rheological properties of complex fluid-fluid interfaces are important to the stability and bulk rheology of emulsions and foams. A common class of methods used to measure interfacial rheological properties involves recording the pressure jump across a dilating bubble or droplet pinned at the tip of a small capillary. We have implemented a similar method of measuring interfacial dilatational response in a microtensiometer that uses small (radius ~10-5 m) droplets. Unlike a freely suspended sphere, which would oscillate in a radially symmetric manner, the deformation of pinned bubbles depends on both the radius of the capillary and the radius of the interface. In this study, we show that the geometry of the pinned bubble can affect the linear stability of that interface in response to sinusoidal pressure oscillation. We determine the stability criterion for a variety of interfaces using existing rheological models, including the Boussinesq-Scriven model for a Newtonian interface. We also show how these instabilities are affected by surfactant adsorption from the bulk solution. These criteria can be used to generate stable pressure-controlled oscillations of bubbles pinned at a capillary in order to accurately measure interfacial rheological properties.

Tuesday 11:15 C105 EF18

Rheological properties of methane hydrate slurries formed from AOT + water + oil emulsions

Eric B. Webb, Carolyn A. Koh, E. D. Sloan, Amadeu K. Sum, and Matthew W. Liberatore
Department of Chemical and Biological Engineering, Colorado School of Mines, GOLDEN, CO, United States

A unique high pressure rheology apparatus is used to study the *in situ* formation and flow properties of methane hydrates formed from water-in-oil emulsions composed of water, dodecane, and aerosol OT surfactant (AOT). AOT emulsions have high stability (order of months), well characterized composition, and yield reproducible results compared to hydrate studies in water-in-crude oil emulsions. Viscosity increases rapidly upon hydrate formation, and then slowly decreases. If significant unconverted water remained after the initial formation event, then viscosity increases for a time as methane slowly dissolves and converts the remaining water to hydrate. In addition to transient formation measurements, yield stresses and flow curves are measured over 16 experiments. Hydrate slurry viscosity and yield stress increase with increasing water volume fraction, increasing initial pressure, decreasing temperature, and decreasing shear rate. Hydrate slurry viscosity and yield stress are most sensitive to temperature, followed by water volume fraction, initial pressure, and formation shear rate.

Tuesday 11:40 C105 EF19

High pressure rheology of Alaska heavy oil saturated with methane

Ala Bazyleva, Babajide Akeredolu, and Matthew W. Liberatore
Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO 80401, United States

Viscosity, μ, of Ugnu heavy oil (North Slope of Alaska, USA) saturated with methane was measured from temperature of 0 to 60°C, pressure from 15 to 1800 psi, and shear rate of 0.1 to 500 s^{-1} using a high-pressure rheology apparatus constructed as part of this work. Under saturated conditions, the oil behaves as a Newtonian fluid. A two-variable Antoine-type correlation, $\mu = f(T,p)$, with 6 fitting parameters was developed using 48 points on a (p,T,μ)-diagram. The influence of temperature, pressure, and methane concentration was analyzed, and important regularities in the viscosity change with the varying parameters were established, which can be used for prediction of viscosity trends for other live oils. Since produced oil is accompanied by sand and water, their influence on the viscosity of the Ugnu oil saturated with methane at 1500 psi was also studied. The relative viscosity of the Ugnu oil + water system at temperatures from 2 to 60°C was shown to increases almost linearly with increasing water concentration from 0 to 20 wt% following the Einstein viscosity model. Although possible in the timescale of days, hydrate formation at temperature below 13°C (thermodynamic CH_4-hydrate formation temperature at 1500 psi) did not interfere the rheological measurements for the system. Due to rapid sand particle sedimentation in the methane-saturated Ugnu oil during pre-measurement stages, the impact of sand concentration on the live oil viscosity could not been evaluated. The presented research created a basis for simulating in situ flow behavior of the Ugnu oil.

Tuesday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Tuesday 1:30 C106 SC20

Dynamics of micelle-nanoparticle interactions in the shear templating of colloidal crystals

Bryan A. Rolfe[1], Jaehun Chun[2], and Yong L. Joo[1]
[1]Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States; [2]Interfacial Science & Rheology, Pacific Northwest National Laboratory, Richland, WA, United States

Experiments by Pozzo and Walker (2007) demonstrated shear ordering of binary nanoparticle block copolymer micelle crystals and its potential in the development of new nanostructured materials. Specifically, they have shown that nanoparticles occupying interstitial sites within a micelle crystal affect a low-shear, long-range order and that the shear type and rate are important to the crystal structure. However, the connection between macroscopic variables and the resulting micelle/nanoparticle structure is not well understood. To elucidate this relationship, we present new results illustrating the important role of micelle-nanoparticle dynamics in obtaining ordered nanoparticle structures. Our approach employs a coarse-grained molecular dynamics (CGMD) simulation with an explicit solvent that preserves hydrodynamic effects. Self-assembly of amphiphilic block copolymers into spherical and elongated micelles occurs within the framework of our simulations by appropriate tuning of the interaction parameters. As with experiments, type (simple or oscillatory) and strength of the applied shear are shown to be important in affecting both micelle morphology and the large-scale structure formed. Nanoparticle positioning within these micelle structures is further shown to be influenced by the micelle-nanoparticle dynamics dictated by the length of the micelle corona. The rheology and spatial order in our simulations is quantified for comparison to experimental work in the literature. We also qualitatively compare the observed micelle-nanoparticle dynamics to similar simulation studies of grafted polymers and other soft colloids.

Tuesday 1:55 C106 SC21

Vibration-assisted convective assembly and deposition for monolayer particle coatings from suspension

Gilchrist James, Tanyakorn Muangnapoh, and Alexander L. Weldon
Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, United States

A novel strategy for improving a convective deposition of aqueous binary suspensions of colloidal microspheres and nanoparticles was experimentally examined and reported. By adding a substrate vibration, an enhancement in deposited film qualities was observed. Moreover, by using this technique, it was easier and faster to obtain monolayer structures. In this experiment, we varied the amplitudes of substrate vibration between 0-330 microns. The quality of thin films was characterized by using a confocal laser scanning microscope and an image analysis. The motion of an interfacial liquid surface and the change in an evaporate rate due to a substrate vibration played an important role in an improvement of the deposition process. The monolayer structures formed from this rapid process can be used in a variety of optical, chemical, and biochemical sensing applications such as a LEDs device, a membrane separation and a cell capturing.

Tuesday 2:20 C106 SC22

Passive microrheology of two-dimensional colloidal crystals

Thomas G. Mason
Dept. of Chemistry, Dept. of Physics, UCLA, Los Angeles, CA 90077, United States

We present passive microrheology measurements of the anisotropic linear viscoelastic moduli of two-dimensional colloidal crystals of thermally excited lithographic platelets in water. In particular, we consider a hexagonal rotator crystal and a rhombic crystal of square microplatelets that have effectively hard interactions and diffuse in a plane. We perform high-precision video particle tracking of the positions and orientations of all particles in our microscopic field of view, enabling us to calculate and study self-motion of single particles as well as collective motion involving two or more particles. We connect these mean square displacements, which are spatially anisotropic, to appropriate linear viscoelastic properties of the crystals. Our results show that care must be taken when attempting to use rotational mean square displacements in the prediction of a crystal's elasticity via passive microrheology.

Tuesday 2:45 C106 SC23

Particle tracking of square platelet colloids in a two-dimensional crystal

Kenny Mayoral[1], Xiaoming Zhu[1], Dimitri Bikos[1], Kun Zhao[1], and Thomas G. Mason[2]
[1]Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, CA 90095, United States; [2]Dept. of Chemistry, Dept. of Physics, UCLA, Los Angeles, CA 90077, United States

Measuring the rheological properties of compressed two-dimensional (2D) systems of exotic shaped colloids is interesting, yet presents many challenges. We have developed an advanced particle tracking routine designed for passive microrheology measurements of square platelet colloids with hard interactions which have been osmotically concentrated in two-dimensions enough so that they form a colloidal crystal. Using optical video microscopy, we have recorded the entropically driven fluctuations of a rhombic crystal of square microplatelets. Specifically, in each video frame, our analysis routine identifies points on the edges of each square colloid, orthogonally fits points on the edges to determine the position and orientation of each colloid in the crystal to a high degree of precision. By repeating this analysis on a series of frames, we obtain precise trajectories and translational and rotational mean square displacements, which can then be used via passive microrheology to predict the anisotropic elasticity of the crystal.

Tuesday 3:35 C106 SC24

Aging in colloidal systems: Analogies with Kovacs' structural recovery experiments

Gregory B. McKenna, Xiaojun Di, and Xiaoguang Peng
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

The aging of colloidal systems has generally been investigated in experimental conditions in which the concentrated suspension is "shear melted" and the evolution of the dynamics monitored either rheologically or by diffusing wave spectroscopy. However, it has been argued by our group that such experiments are not truly aging experiments but look more like the superposition of small strains on a large deformation history, similar to aging following mechanical rejuvenation. True aging of molecular glasses as defined by Struik implies that there is a change from an equilibrium thermodynamic state such as a volume-temperature-pressure point to a non-equilibrium state in which pressure remains constant, temperature is "jumped" to a temperature below the glass transition and the volume evolves with time towards equilibrium. The changes in dynamics accompanying the volume changes are considered as aging. To better test the analogy between colloidal glasses and molecular glasses we have taken thermosensitive particle dispersions and, by changing temperature, can perform concentration jumps through the colloidal glass transition regime in direct analogy to the temperature jump in molecular glasses. Using diffusing wave spectroscopy and rheology we can monitor the changing dynamics and find that they are similar to what one might find in a molecular glass, but are different in detail. For example, in the memory experiment documented by Kovacs for two-step temperature histories, the molecular glass exhibits non-monotonic volume recovery that is mirrored in the dynamics. The position of the maximum in the recovery curves depends upon the details of the first step, i.e., temperature below Tg and the length of time for the volume recovery prior to the second step. In the colloidal system, following the equivalent two-step concentration jump, while a memory is observed, it seems that the memory is independent of the first step conditions. The full catalog of Kovacs-type of experiments will be discussed.

Tuesday 4:00 C106 SC25

Analysis of gel yielding of thixotropic drilling fluids by means of rheometric tests

Cezar O. Negrao, Diogo E. Andrade, and Admilson T. Franco
Ppgem - Lacit, Federal University of Technology - Paraná, Curitiba, Paraná 80230901, Brazil

Drilling fluids usually gels at rest in order to avoid cuttings to lie over the drill bit when flow is interrupted. At flow start-ups, the pumping pressure rises above the circulation pressure so as to overcome the gel strength. Due to its thixotropic effect, the gel viscosity remains high for a while after flow start-up. The gelation may have significant importance, specially, in deep waters where high pressures and low temperatures take place. In the current work, different types of rheometric tests, such as controlled shear rate, shear stress and oscillatory tests, were conducted to analyse drilling fluid yielding. The results show that the gel yield stress depends not only on the shear rate but also on the shear strain. An algebraic constitutive equation that accounts for both shear rate and hystory is proposed to predict the gel yield stress. This equation is quite useful to model pressure peaks that take place during drilling fluid flow start-ups.

Tuesday 4:25 C106 SC26

Role of interparticle attraction in yielding behavior of microgel suspensions

Zhen Shao[1], Ajay S. Negi[2], and Chinedum O. Osuji[1]
[1]Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, United States; [2]Physics, Indian Institute of Science Education and Research Bhopal, Bhopal, Madhya Pradesh, India

The yielding behavior of colloidal suspensions is a strong function of the nature of the particle-particle interactions in the system. Due to electrostatic interactions between negatively charged carboxylic acid groups, suspensions of Carbopol micro-gel particles behave as repulsive systems at elevated pH where the acid groups are well deprotonated. This electrostatic repulsion may be screened at sufficiently high ionic strength, resulting in a net attractive interaction between particles and the formation of colloidal gels due to particle aggregation. We examined the yielding behavior of Carbopol suspensions in the transition from a soft jammed glassy suspension to an attractive colloidal gel by varying the ionic strength of the suspensions through salt (NaCl) addition with large amplitude oscillatory strain sweep tests. A clear transition from simple one peak of loss modulus at yield strain to two peaks of loss modulus shown near yield strain in strain sweep tests is found with

increasing NaCl concentration. The trace of peak shifting indicates that the first peak in attractive systems shares the same origin as the single peak in repulsive systems. We speculate that attractive systems yield with network rupture which combines bond rupture and topological rearrangements (cage-breaking) at intermediate strains ~30%. Local densification of particles is induced right after yielding, resulting in the formation of dense clusters. The eventual breakup of these clusters at higher strains gives rise to the second peak in the loss modulus. The magnitude and location of the two peaks in the loss modulus show remarkable differences in their reversibility, that is, in their dependence on sample history. The irreversibility of the first peak as well as results of oscillatory pre-shear tests and oscillatory time sweep tests support the speculation that densification happens near yielding. The present findings provide a perspective of the multistage yielding behavior of colloidal suspensions with attractive interactions.

Tuesday 4:50 C106 SC27

The medium amplitude oscillatory shear (MAOS) of semi-dilute colloidal dispersions

James W. Swan and Norman J. Wagner
Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States

We study the response of semi-dilute colloidal dispersions under Medium Amplitude Oscillatory Shear (MAOS). Using an excluded annulus model of the hard-core repulsion and hydrodynamic interactions among the particles, we determine the linear response of a colloidal dispersion in the pair limit - varying the relative strength of hydrodynamic forces. Through comparison with experiments, this model proves to be a sensitive probe of the ratio of the hard-core and hydrodynamic radii in semi-dilute, mono-disperse colloidal dispersions. By extending the linear response solution asymptotically, we calculate the normal stress differences and predict the scaling of the third harmonic stress response. Both of these are indicative of nonlinearity in the dispersion rheology. Importantly, the influence of hydrodynamic forces, both in magnitude and in character, on the MAOS of semi-dilute dispersions is made explicit through comparison of such rheological properties for different relative strengths of the fluid mediated interactions among the particles. We show that hydrodynamic forces have a considerable effect on nonlinear, oscillatory rheology, particularly at high frequencies.

Tuesday 5:15 C106 SC28

Structural and mechanical manipulation of colloidal gels by shear

Nick Koumakis[1], Rut Besseling[2], Wilson C. K. Poon[2], John F. Brady[3], and George Petekidis[1]
[1]IESL, FORTH, Heraklion, Greece; [2]School of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom;
[3]Div. of Chem. and Chem. Eng., California Institute of Technology, Pasadena, CA, United States

The structural and rheological properties of intermediate volume fraction colloidal gels are examined during steady rate shear flow as well as after cessation using rheology, confocal microscopy and Brownian Dynamics simulations. Experimentally, the gels consist of model hard sphere particle dispersions of f=0.44 with the addition of non-adsorbing linear chains, while BD simulations are conducted by using a potential-free algorithm for hard sphere interactions [1] with the superposition of a depletion attraction. Experiments show that gels yield in two steps during a start-up test by initially breaking bonds and subsequently breaking/restructuring clusters. With increasing rate, the first stress overshoot weakens while the second becomes stronger [2]. Through structural analysis of the steady state, with rheo-confocal imaging and simulations, we find that variation of the applied shear rate alters the microscopic structure both under shear and during gel reformation after flow cessation. Large rates produce disperse particles and the total breakage of structures at rest, which after cessation evolve with time into strong solids with relatively homogeneous structures. However, smaller rates show large inhomogeneous structures under flow, which do not evolve after cessation and additionally exhibit reduced elasticity and as such are weaker solids. Thus by tuning the way a gel is sheared, one may vary the final strength and structure of the resulting gel.

[1] Foss, D. R. and Brady, J. F. Journal of Rheology 44(3), 629-651 (2000); [2] Koumakis, N. and Petekidis, G. Soft Matter 7, 2456-2470 (2011).

Symposium PS

Polymer Solutions and Melts

Organizers: Randy Ewoldt and Suraj S. Deshmukh

Tuesday 1:30 C107 PS10

Globule formation and breakup in dilute solutions of flexible polymers

Rangarajan Radhakrishnan and Patrick T. Underhill
Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

Polyelectrolytes, polymers in poor solvents, polymers mixed with particles and other systems with effective attractive interactions show formation of globules/structures in equilibrium or in flow. We have used a coarse-grained model with short ranged attractions and repulsions to study such systems. Polymers were modeled as a charged bead-spring chain interacting with oppositely charged colloidal beads. Neglecting hydrodynamic interactions between beads, we study the formation of compact structures called globules. The first passage times of globule formation was calculated at different shear rates, and it was found under certain conditions that increasing the shear rate decreases the mean first passage time for globule formation. At other conditions, shear flow causes the globules to break, similar to the globule-stretch transition of polymers in poor solvents. The importance of rotation in shear was analyzed by studying globule formation in oscillatory shear and oscillatory elongational flows.

Tuesday 1:55 C107 PS11

Extracting fundamental materials properties from rheological measurements

Folarin Latinwo and Charles M. Schroeder
Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

A long-standing problem in complex fluids has been the determination of fundamental materials properties (e.g. elasticity) from dynamic far-from-equilibrium measurements (e.g. transient stresses). We recently developed a framework to extract information about polymer elasticity from trajectories of conformational changes of single molecules induced by fluid flow [1]. In our approach, we applied tools from non-equilibrium statistical mechanics namely the Jarzynski relation [2] to complex fluids via Brownian dynamics (BD) simulations of bead-spring models of polymer molecules. The relation allows for the calculation of free energy changes from work distributions of arbitrarily far-from-equilibrium processes and has been applied as originally conceived only to single molecule studies. In our current work, we demonstrate the further application of this new tool to complex fluids by determination of free energy changes from transient bulk stresses. Using BD simulations of bead-spring models of dsDNA and polystyrene molecules in various flow types (shear and extensional) and standard expressions for the stress tensor (e.g. Kramers-Kirkwood), we make a connection between stresses, work distributions of bulk measurements and the generalized Jarzynski relation [3]. In doing this, we developed a formalism to extract new fundamental information such as free energies (which intrinsically defines a system) from previously existing measurements.

[1] Latinwo, F. and Schroeder, C.M., in preparation; [2] Jarzynski, C., Phys. Rev. Lett. 78, 2690--2693 (1997); [3] Hatano, T. and Sasa S.I., Phys. Rev. Lett. 86, 3463-3466 (2001).

Tuesday 2:20 C107 PS12

When does polystyrene become a polymer?

Yangyang Wang[1], Alexander L. Agapov[2], Fei Fan[2], Adam P. Holt[3], and Alexei P. Sokolov[2]
[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States; [2]Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States; [3]Department of Physics, University of Tennessee, Knoxville, TN 37996, United States

The molecular weight (M) dependence of zero-shear viscosity (η_0) of linear polymers has been the subject of numerous studies. For polymers with relatively high molecular weight, it is now well established that $\eta_0 \sim M$ for unentangled polymers, and $\eta_0 \sim M^{3.4}$ for entangled polymers. In the case of unentangled polymers, the molecular weight dependence of zero-shear viscosity can be explained by the Rouse Model, whereas the scaling for entangled polymers can be understood on the basis of the reptation idea. However, the crossover from small-molecule to polymeric behavior has received relatively little attention. The present study closely examines the linear viscoelastic properties of low-molecular-weight narrow-distribution polystyrenes. A sharp transition of molecular weight dependence of zero-shear viscosity is observed around a critical molecular weight of approximately 5000 g/mol, which corresponds to 50 repeating units. This small-molecule-to-polymer transition is in agreement with earlier studies by other experimental techniques. The presented analysis demonstrates that the dynamic bead size of polystyrene is significantly larger than the traditionally defined Kuhn segment. Other possible theoretical implications are also discussed.

Tuesday 2:45 C107 PS13

Viscoelastic and dielectric tests of segmental dynamics in type-B polymers

Yumi Matsumiya and Hiroshi Watanabe
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Type-B polymers have permanent electrical dipoles perpendicular to its backbone, and its segmental dynamics is dielectrically active. The slowest dielectric dispersion observed for these polymers, often called α-dispersion, is related to glass transition phenomenon. For series of type-B polymers, such as polystyrene (PS), 1,2-polybutadiene (PB), poly(*p-tert*-butylstyrene) (PtBS), each having molecular weight M ranging from several hundreds to ten thousand, viscoelastic and dielectric measurements were conducted at various temperatures form glass transition temperature to the temperature where the terminal relaxation was observed. Dielectric terminal relaxation was exclusively attributed to α-relaxation mode for all polymer samples, while viscoelastic terminal relaxation was assigned to the glassy mode (segmental mode) for the samples with M below M*, and to rubbery mode (global mode) for those with M above M*, where M* denotes a critical molecular weight for emergence of rubbery mode. Time-temperature superposition held for segmental relaxation in the viscoelastic and dielectric data, and their shift factors coincided with each other for respective polymer samples. Dielectric segmental relaxation time τ_ε was longer than the viscoelastic relaxation time τ_G for all polymer samples, but the relaxation mode distribution was almost identical for the dielectric and viscoelastic relaxation processes. From the above data, the effective segment size in the polymer was estimated as the molecular weight where the τ_ε/τ_G ratio became insensitive to M.

Tuesday 3:35 C107 PS14

Stretching self-entangled molecules in planar elongational fields

Benjamin Renner and Patrick S. Doyle
Chemcial Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Entanglements between long polymer strands in bulk solution give rise to a wealth of rheological properties, and the underlying physics of such systems has been studied in great detail. By comparison, the physics of a highly *self-entangled* single molecule, a system seen in proteins and viral capsid DNA, have been largely unexplored. Here, we present the first experimental inquiry into the dynamics of highly self-entangled single chains undergoing the transition to stretch in an applied elongational field. We use fluorescently labeled DNA as a model polymer, examining extension dynamics in an electrophoretic planar elongational field. We find that highly self-entangled molecules lie in an arrested state for many decades of Henky strain prior to transitioning to an elongated state, a phenomenon that lies in stark contrast to equilibrium chains where the vast majority undergo the coil-stretch transition within a single decade of Henky strain. We show that for self-entangled molecules, the mean time spent in such arrested states scales with applied strain rate. Furthermore, during the rapid stretching process, we show that localized self-entanglements, or "knots," are clearly present in the initially self-entangled chains, and these small entanglements are able to slow the stretching rate of the chain when compared to chains without such "knots."

Tuesday 4:00 C107 PS15

Viscoelastic and structural properties of dendrimers and hyperbranched polymers undergoing planar elongational flow from nonequilibrium molecular dynamics simulation

Elnaz Hajizadeh[1], Billy D. Todd[1], and Peter J. Daivis[2]
[1]Mathematics Discipline, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia; [2]Applied Physics, RMIT University, Melbourne, Victoria 3001, Australia

Dendrimers and hyperbranched polymer melts with different molecular weights have been simulated using a coarse-grained model and nonequilibrium molecular dynamics simulation techniques. In order to determine flow-induced changes in the structural properties of dendrimers and hyperbranched polymers, various parameters were calculated at different strain rates. The radii of gyration, which is the trace of the tensor of gyration, were calculated to characterize the size of the polymer under deformation. The tensor of gyration was analyzed and ratios of different eigenvalues were calculated. Results indicated that dendrimers and hyperbranched molecules have a prolate ellipsoid shape under elongation, and they tend to align along the elongation direction at higher strain rates. As hyperbranched polymers, especially dendrimers, have compact, highly branched architecture and layers of beads have increasing densities that might lead to an unusual distribution of mass, the distribution of beads within the molecule was also studied. At high strain rates, as the molecules are stretched in the flow, the distribution of mass becomes broader and the average distance of bead from the core increases with the strain rate. The distribution of terminal groups was also investigated to understand the spatial arrangement of these groups, which is very important for applications, such as drug delivery. The results indicate significant backfolding of terminal groups throughout the interior of the molecule. Rheological properties, including extensional viscosity and first and second normal stress coefficients, were calculated at a wide range of strain rates and were compared to the rheological behaviour of linear polymers with the same molecular weights. Elongational viscosity as a function of strain rate showed three distinctive regions comparable with exsisting theoretical models, which contains initial strain-thinning behaviour followed by a moderate strain-thickening region and a pronounced thinning tail.

Tuesday 4:25 C107 PS16

Dynamics and rheology of dilute and entangled polymer solutions from molecular dynamics simulations

Yutian Yang, Shikha Nangia, and Radhakrishna Sureshkumar
Syracuse University, Syracuse, NY, United States

Dynamics and rheology of polymer solutions are investigated using Molecular Dynamics simulations in presence of explicit solvent mediated interactions. In order to circumvent the exorbitant computational costs associated with fully atomistic simulations, coarse-grained (CG) molecular models and corresponding force fields are employed to describe the polymer, solvent and the underlying physico-chemical interactions. The CG models are validated by comparison of their predictions for certain structure parameters such as persistence length as well as radial distribution functions for the monomeric units. Computational advantages of CG MD allow us to perform simulations that span up to tens of microseconds for single molecules and concentrated systems with entanglements. We will present results for the dynamics of single poly ethylene oxide (PEO) chains in shear flow. The effects of chain length and shear rate on the conformational statistics, e.g. tumbling frequency, orientation distribution functions, will be discussed and compared to the predictions of stochastic dynamics. For entangled systems, simulation results for the mean square displacement of the polymer segments as a function of time, diffusion coefficient, viscosity, and relaxation moduli will be presented and compared with the predictions of reptation theory.

Support from the National Science Foundation through grants CBET-1055219 and CDI 1049489 is gratefully acknowledged.

Tuesday 4:50 C107 PS17

Adsorption of single polymer molecules in shear flow near a planar wall

Sarit Dutta, Kevin D. Dorfman, and Satish Kumar
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Adsorption of homopolymers from a dilute solution to a planar wall in the presence of shear flow is studied using a bead-spring dumbbell model. The bead-bead and bead-wall interactions are described by generalized Lennard-Jones potentials. A kinetic theory incorporating bead-wall hydrodynamic interaction is developed in order to obtain an analytical expression for the steady-state dumbbell concentration profile. The concentration profile exhibits an exclusion zone in the immediate vicinity of the wall, is followed by a peak, and finally approaches the bulk concentration far from the wall. Using the analytical expression, the amount adsorbed and the equivalent film thickness are studied as a function of flow strength and the parameters characterizing the bead-wall interaction potential. Shear flow causes migration of the dumbbells due to bead-wall hydrodynamic interaction, which leads to desorption. On increasing the flow strength, the quantity adsorbed and the film thickness decrease until complete desorption occurs. The dependence of the flow strength required for desorption on the model parameters is also studied and a scaling law is derived for the strong-interaction limit. Brownian dynamics simulations are performed to verify the predictions from the kinetic theory. Although the theory makes a number of simplifying assumptions, it captures many of the key features seen in the simulations.

Tuesday 5:15 C107 PS18

The effects of non-conservative forces, compressibility, hydrodynamic interaction and inertia in the microrheology of viscoelastic materials

Andrés Córdoba, Jay D. Schieber, and Tsutomu Indei
Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL, United States

The dynamic modulus G* of a viscoelastic medium is often measured by following the trajectory of a small bead subject to Brownian motion in a method called passive microbead rheology. In recent work we expanded its applicability into higher frequencies [PRE 85, 021504 (2012)] and under non-equilibrium circumstances for example in an optical trap, using Brownian dynamics simulations [JOR 56, 185-212 (2012)]. Moreover in two-point passive microrheology the cross-correlations of two micron-sized beads are used to estimate G*. The two-point technique allows for sampling of larger length scales, which means that it can be used in materials with a coarser microstructure. The modeling formalisms commonly used to relate two-bead cross-correlations to rheological properties neglect inertia effects and underestimate the effect of reflections. A simple dimensional analysis suggests that for a model viscoelastic material there exists a very narrow window of bead separation and frequency range where these effects can be neglected. In a recent work [PoF 24, 073103 (2012)] we proposed an analysis formalism that accounts for medium inertia and high-order hydrodynamic reflections and therefore increases the versatility of the two-point microrheology technique. There has been a recent interest in using two-point microrheology to measure the complex Poisson ratio of biopolymers. However a rigorous analysis of the sensitivity of the technique to the static and dynamic properties of the Poisson ratio is still lacking. In this talk we illustrate the applicability of our analysis to compressible viscoelastic materials. We show that the cross-correlations in the direction parallel to the line of centers is insensitive to compressibility, so may reliably be used to determine G* alone. Although, the cross-correlation in the perpendicular direction may be used to extract a constant Poisson ratio, it is relatively insensitive to its frequency dependence. We consider the example of a composite actin/microtubule network.

Symposium SA

Self-Assembling, Associating and Gel-Like Systems

Organizers: Kendra Erk and Surita Bhatia

Tuesday 1:30 C101 SA6

LAOS rheological characterization of an elasto-viscoplastic gel

Alexandra A. Alicke, Ricardo T. Leite, and Paulo R. de Souza Mendes
Department of Mechanical Engineering, Pontifícia Universidade Católica-RJ, Rio de Janeiro, RJ 22453-900, Brazil

We performed a thorough rheological characterization of a commercially available hair gel (a Carbopol-based solution), to illustrate a novel analysis of large-amplitude oscillatory shear (LAOS) flow test data. The experiments were performed in a rate-controlled rotational rheometer (ARES-G2, TA Instruments) and in a stress-controlled rheometer (AR-G2, TA Instruments). Firstly we performed flow-curve as well as constant-stress and constant-rate transient flow experiments, whose results indicated that the gel under study was an elasto-viscoplastic material, quite elastic below the yield stress and with a low degree of thixotropy. We presented the results of the LAOS flow experiments by means of viscous (stress versus shear rate) Bowditch-Lissajous figures. These figures were obtained for different levels of the stress amplitude, encompassing ranges both below and above the gel yield stress. For each fixed value of the stress amplitude, results were obtained for a wide range of the oscillation frequency. The LAOS results showed that, when the stress amplitude is below the yield stress, the material response to a sinusoidal oscillation is always also (phase-shifted) sinusoidal. Above the yield stress, however, the response departs dramatically from the sinusoidal one at lower frequencies, but recovers the sinusoidal response at large enough frequencies. To analyze the LAOS results, the material is firstly assumed to behave like a Jeffreys (or Oldroyd-B) model whose parameters (relaxation and retardation times) vary with the stress level.

Allowing the relaxation time to diverge when the material is fully structured, such a model is capable of representing a mechanical behavior ranging from the elastic solid up to the Newtonian liquid. The LAOS results were employed to determine the relaxation and retardation times as functions of the stress amplitude. These functions give all the information needed to thoroughly understand the mechanical behavior of the material in shear.

Tuesday 1:55 C101 SA7

Low-dimensional rheological fingerprints of a transient polymeric hydrogel in LAOStrain (large-amplitude oscillatory shear strain)

N. Ashwin Bharadwaj and Randy H. Ewoldt
Mechanical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States

Material functions associated with nonlinear rheology cover a high-dimensional space, but a theoretical framework has been established for low-dimensional intrinsic material functions from oscillatory shear. These intrinsic nonlinearities, defined from an asymptotic power-function expansion of the nonlinear response, are only a function of the imposed frequency. Here we survey available analytical solutions for these intrinsic signatures of constitutive model responses to imposed large-amplitude oscillatory shear strain (LAOStrain) and translate them into the language of intrinsic Chebyshev coefficients to allow for comparison and conceptual interpretation. We consider the corotational Maxwell model, Giesekus model, and other specific models for polymer melts, rod-like polymer solutions, and emulsions. We also derive a new analytical result for a transient nonlinear-elastic network model. For all these models, the two linear viscoelastic material functions are always positive with similar frequency-dependent signatures. In contrast, the four frequency-dependent asymptotic nonlinearities are distinct between models, with sign changes and different functional dependencies on frequency. We experimentally measure the four frequency-dependent LAOStrain intrinsic nonlinearities for a physically crosslinked polymeric hydrogel (PVA-Borax). From the library of analytically obtained rheological fingerprints, a constitutive model with similar trends is qualitatively identified and its nonlinear parameter quantitatively fit.

Tuesday 2:20 C101 SA8

Self-assembly and gelation of conjugated polymers towards enhancing charge transport in organic photovoltaics

Gregory Newbloom[1], Katie Weigandt[2], Pablo de La Iglesia[1], and Danilo Pozzo[1]
[1]Chemical Engineering, University of Washington, Seattle, WA 98195, United States; [2]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, WA 20899, United States

Engineering the multi-scale structure of conjugated polymers is crucial for improving the efficiency of low-cost and light-weight organic photovoltaic devices (OPVs). We have developed a systematic approach to improve charge transport by inducing polymer self-assembly and gelation through solvent quality reduction. At high concentrations many conjugated polymers, such as poly(3-hexylthiophene) (P3HT), can form thermoreversible elastic networks of interconnected fibers. The interconnectivity of these networks lead to a continuous, 3-dimensional path for charge transport which is ideal for the bulk heterojunction structure of OPVs. This talk will describe our recent determination of the gelation and re-dissolution mechanisms for P3HT using simultaneous combinations of rheology, small angle neutron scattering and dielectric spectroscopy.[1] In situ and simultaneous structure-property measurements can enable the understanding of complex self-assembling systems, which in this case allow us to formulate new structure-property relationships for this important class of materials.

Reference: [1] Newbloom, G. M.; Weigandt, K. M.; Pozzo, D. C., Soft Matter 2012, 8, 8854-8864.

Tuesday 2:45 C101 SA9

Flow induced crystallization and gelation of P3HT

Jeong J. Wie, Ngoc A. Nguyen, Colin D. Cwalina, and Michael E. Mackay
University of Delaware, Newark, DE, United States

The rheological properties of poly(3-hexylthiophene) (P3HT) solutions were investigated in a non-volatile solvent, 2-ethylnaphthalene, at various P3HT concentrations. A mild viscosity increase was noted during shear for lower concentration P3HT solutions over 24 h, yet, the viscosity increase was greater than if the sample was not sheared at all over the same time period. In this case, crystalline fibrils with large aspect ratios were formed during shear. Crystallization was determined to be dictated by Brownian motion and mediated by shear or in other words Brownian motion brought the molecules together while shear removed dangling molecules to allow more perfect crystallization. Higher concentration P3HT solutions produced a significant viscosity increase, up to two orders of magnitude, during shear. Again, if a similar solution was merely aged without shear a much lower viscosity increase was noted. Simple calculations show that the fibril concentration was above the percolation threshold at the higher concentration accounting for the large viscosity increase. Finally, a mixture of P3HT and the electron acceptor in bulk heterojunctions, phenyl-C61-butyric acid methyl ester or PCBM, was also studied. The viscosity increase was much larger for the blend than the neat components suggesting the rheopectic phenomenon was catalysed by the PCBM and it was hypothesized a molecular crowding effect occurred that induced more perfect P3HT crystallization.

Tuesday 3:35 C101 SA10

Superposition rheometry of a wormlike micellar surfactant solution

Sunhyung Kim, Jan Mewis, Jan Vermant, and Christian Clasen
Department of Chemical Engineering, KU Leuven, Heverlee 3001, Belgium

The use of oscillatory measurements to explore the non-linear response of materials has been the subject of intense interest, with recent focus on large amplitude oscillatory motions. However, the use of superposition of an oscillatory motion onto a steady state shear flow has been shown to be a method which probably yields a better insight into the underlying mechanisms of the non-linear response [1]. Such an oscillation can be applied both orthogonal and parallel to the main flow direction, which gives insight into the tensorial nature of the stress and the microstructural anisotropy. In the present work the nonlinear properties of a wormlike micellar solution (WLM) were studied experimentally by means of superposition measurements using a simple modification of a commercial strain controlled device. The experimental results are compared with analytical solutions of the Giesekus model, which was chosen both for its suitability to describe the WLM response, and for being one of the simplest continuum models, which nevertheless incorporates an anisotropic microstructure, using the concept of a deformation-dependent tensorial mobility. The fluid response is described in terms of rate-dependent relaxation times and changes in the high frequency plateau moduli, which characterize the structural evolution of WLM with increasing deformation rates. Especially the orthogonal superposition gives quantitative and clear information about the causes of nonlinear behavior of flowing materials in a straightforward way.

[1] Tanner RI, Simmons JM (1967) Combined simple and sinusoidal shearing in elastic liquids. Chemical Engineering Science 22: 1803-1815.

Tuesday 4:00 C101 SA11

Elastic instabilities in a microfluidic cross-slot flow of wormlike micellar solutions

Amy Q. Shen, Neville Dubash, and Perry Cheung
University of Washington, Seattle, WA 98195, United States

We present a series of experiments involving an elastic instability that occurs with the flow of wormlike micellar solutions in a microfluidic cross-slot device. We use four different concentrations of aqueous solutions of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal); two highly viscoelastic and two weakly viscoelastic. Flow in the microfluidic cross-slot device is examined using birefringence and PIV measurements. With all of the solutions we observe the formation of birefringent bands along the outflow axis, the intensity of which increases with the flow rate. In the two highly viscoelastic solutions, as the flow rate increases, the instability results in flow transitioning from a stable symmetric flow to a stable asymmetric flow, to an unsteady asymmetric flow. With the weakly viscoelastic solutions the instability results in the flow transitioning directly from a stable symmetric flow to an unsteady flow. The critical Weissenberg numbers at which the transitions occur, increase with increasing elasticity number (defined as the ratio of the Weissenberg number to the Reynolds number). With the two highly viscoelastic solutions we also observe the formation of lip vortices along the walls of the inlet channels. The critical Weissenberg numbers for the formation of this secondary flow do not behave consistently when compared with the critical Weissenberg numbers for the elastic instability.

Tuesday 4:25 C101 SA12

Extensional flow SANS of cetylpyridinium chloride wormlike micelles

Katie Weigandt[1], Ronald L. Jones[1], Paul Butler[1], and Tatiana Perevozchikova[2]
[1]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, WA 20899, United States;
[2]University of Delaware, Gaithersburg, MD 20899-8451, United States

Structural transitions associated with extensional flow, while common to many processes, remain relatively understudied. Small angle neutron scattering (SANS) is a powerful tool for probing the nano- and micro-structure of a wide range of materials. This technique is frequently used in combination with specialized sample environments to measure altered structures of materials as a result of shear deformation. More recently, a cross-slot flow cell has been designed to generate stagnation flows that enable the characterization of altered structure that arises as a result of extensional flow. In this talk, we will present recent results from extensional flow SANS experiments on wormlike micelle and protein solutions.

Tuesday 4:50 C101 SA13

Microstructure and rheology of a flow-induced structured phase in wormlike micellar solutions

Joshua J. Cardiel[1], Alice Dohnalkova[2], Neville Dubash[1], Ya Zhao[1], Perry Cheung[1], and Amy Q. Shen[1]
[1]University of Washington, Seattle, WA 98195, United States; [2]Environmental Molecular Sciences Laboratory,EMLS, Pacific Northwest National Laboratory, PNNL, Richland, WA 98015, United States

Surfactant molecules can self-assemble into various morphologies under proper combinations of ionic strength, temperature, and flow conditions. In particular, cylindrical micelles in the presence of salts can form flexible and elongated wormlike micelles. Wormlike micelles have exhibited the ability to form multi-connected micellar networks by changing the ionic strength or flow conditions. The rheological properties (zero shear viscosity, relaxation time and elastic modulus) of wormlike micellar solution are strongly affected by the formation of micellar connections. We consider the flow of two wormlike micellar solutions through a microfluidic device, with focus on their microstructural and rheological transitions. These aqueous solutions include different ratios of the cationic surfactant cetyltrimethyl amonioum bromide (CTAB) and sodium salicylate salt (NaSal). One solution is weakly viscoelastic and shear thickening (CTAB = 50 mM). Whereas, the other is strongly viscoelastic and shear thinning (CTAB = 100 mM). When subject to strain rates ($O(10^4)s^{-1}$)and total strain ($O(10^3)$) we observed the formation of a permanent flow-induced structured phase (FISP) in both micellar solutions. The high stretching and local micellar concentration fluctuations in the microdevice induce an increment in the end-cap energy, which lowers the energy required to form wormlike micellar connections. As a result, FISP with highly entangled and multi-connected wormlike micellar bundles form. Further, we observed that the rheological properties of the shear thickening micellar solution are one order of magnitude smaller than those of its FISP, while the rheological properties of the shear thinning solution are one order of magnitude larger than those of its former FISP. This opposite trend indicates that the microstructural evolution of a wormlike micellar solution can yield significant rheological property changes.

Tuesday 5:15 C101 SA14

Nonequilibrium thermodynamic modeling of the shear banding phenomenon of concentrated wormlike micellar solutions

Natalie Germann[1], L. Pamela Cook[1], Antony N. Beris[2], and Norman J. Wagner[2]
[1]Mathematical Sciences, University of Delaware, Newark, DE, United States; [2]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States

Colloidal systems such as concentrated wormlike micellar solutions can exhibit flow instabilities that result in the formation of shear bands. Using the generalized bracket approach of nonequilibrium thermodynamics [1], we have developed a new model for concentrated wormlike micellar solutions. Following the Vasquez-Cook-McKinley (VCM) approach [2], the micellar population was modeled by a two-species representation of Hookean dumbbells. Those micelles that are longer than the statistical average in the equilibrium state of rest form species A, and those that are shorter, species B. One constituent, species A, is allowed to break in half to form two constituents, species B, which themselves can recombine to form one constituent of species A. The breakage and reformation kinetics are assumed to be affected by the viscoelastic contributions to the free energy of the micellar system and are described employing an extension to the nonequilibrium treatment of chemical reaction kinetics for media with an internal structure [1]. This represents an improvement of the VCM model to be thermodynamically consistent. In this talk, we present the full version of the constitutive model that also takes into account flow-induced concentration changes due to Fickian diffusion and stress-induced migration. Sample calculations performed in the concentric Taylor-Couette system will be discussed and compared with predictions of the VCM model and experimental data. Special emphasis will be placed on the transient development of the shear bands and the impact of the different types of diffusion processes on the rheological properties.

References: [1] A.N. Beris and B.J. Edwards, Oxford University Press, 1994. [2] P.A. Vasquez, G.H. McKinley, L.P. Cook, J. Non-Newt. Fluid Mech. 144 (2007) 122-139.

Symposium SG

Solids and Glasses

Organizers: Craig Maloney and Chinedum Osuji

Tuesday 1:30 C105 SG1

Boundary layer in yield stress fluids: How some liquid flows depend on the deformation in the solid regions

Philippe Coussot, Thibaud Chevalier, Xavier Chateau, and Stéphane Rodts
Laboratoire Navier, Université Paris-Est, Champs sur Marne, France

Yield stress fluids such as concentrated colloids, emulsions, foams, are jammed systems which behave as liquids if they are submitted to a sufficiently large stress, and as solids otherwise. In usual situations the stress is heterogeneous throughout the material so that "solid" regions coexist with "liquid" regions. In simple uniform flows (e.g. in straight conduits or open channels, in concentric cylinders, etc) the stress field is known so that the shape of the solid-liquid interface can be determined and its exact position is found from boundary conditions (e.g. velocity, force, torque). For all uniform flows it is found that the thickness of the liquid region tends to zero for creep flows, i.e. when the flow rate tends to zero. Thus the solid-liquid interface reaches the boundaries when the velocity tends to zero, which means that the liquid region tends to disappear for creep flows. This result seems natural as in that case the material behavior tends to that of a simple plastic material the deformations of which, beyond the yield limit, are generally described by shear localization in a thin region. For more complex flows such as the injection or the displacement of an object through a yield stress fluid we show that the situation is not so simple. Slightly complex (i.e. non-uniform) flows of yield stress fluids can exhibit an almost uniform (liquid) region which cannot be described with usual assumptions. The most surprising point is that for sufficiently slow flows the thickness of this region is independent of the flow rate. We deduce that the formation and characteristics of this liquid region are also governed by the transient deformations of the surrounding material in the solid regime. This means that yield stress fluid flows in complex geometries, even well-developed, can be described properly only by taking into account, at any time, the stress field both in the solid and the liquid regions.

Tuesday 1:55 C105 SG2

Complex yielding of simple hard sphere glasses under oscillatory shear

Nick Koumakis[1], John F. Brady[2], and George Petekidis[1]
[1]IESL, FORTH, Heraklion, Greece; [2]Div. of Chem. and Chem. Eng., California Institute of Technology, Pasadena, CA, United States

Yielding of hard sphere glasses under large amplitude oscillatory shear has been studied by experimental rheology and Brownian Dynamics simulations. By varying the frequency of oscillation we probe the interplay between Brownian relaxation and shear-induced structural changes. The stresses, structure and microscopic particle displacements are probed by a experiments and simulations. Two frequency regimes are revealed: At low frequencies where Brownian motion is dominant yielding takes place in a single step during which microscopically particles escape their cage assisted by Brownian motion. In this regime, in agreement with the conventional understanding of yielding of repulsive colloidal glasses dynamic strain sweeps probing the 1st harmonic of G' and G" indicate a single peak of the latter at (or near) their crossover. At high frequencies the yielding mechanism is related with shear induced particle collisions causing cage breaking with the maximum energy dissipation marked by a G" peak at strains beyond the G', G" overlap. In this regime, Lissajous plots indicate a reduced stress within the oscillation period related with a persistent anisotropy of the structure after strain reversal. Intermediate frequencies present a complex yielding behavior influenced by both mechanisms that leads to a double peak in G" that has not been reported before in HS glasses. We further quantify the nonlinear response by the higher harmonics present in the stress signal. While at low frequencies the strength of higher harmonics reaches a constant value at high strains, in the intermediate and high frequency regime a non-monotonic behavior is detected with characteristic large amplitude strains exhibiting apparent harmonic response.

Tuesday 2:20 C105 SG3

Spatially correlated stresses in soft-particle suspensions

Craig E. Maloney[1] and Kamran Karimi[2]
[1]Civil and Environmental Engineering, CMU, Pittsburgh, PA 15213, United States; [2]CMU, Pittsburgh, PA 15213, United States

We study the spatial correlations in the stress field in simulations of dense, soft-particle suspensions. The suspensions are athermal and confined at volume fractions, f, above the random close packing point, f_c, so that stress and viscoelasticity arise from the deformation of particles at contact. We measure the anisotropy in coarse-grained stress e_s and shear modulus e_m as functions of coarse-graining scale, R. e_s can be collapsed onto a master curve after rescaling R by a characteristic length scale ? and e_s by an anisotropy magnitude A. Both A and ? accelerate as f approaches f_c from above, consistent with a divergence at f_c. In contrast to e_s, e_m shows no characteristic length scale, but has a nontrivial power-law form, $e_m \sim R^{-0.62}$, over almost the entire range of R at all f. These results suggest that the so-called force chains present in the spatial structure of the quenched stress may be governed by different physics than the anomalous elastic response near jamming.

Tuesday 2:45 C105 SG4

Comparison of failure strength vs. consolidation stress data and associated error limits from different shear cells when testing the reference material BCR-116 Limestone powder

Robert G. McGregor
Brookfield Engineering Laboratories, Moddleboro MA, MA 02346, United States

The prediction for flowability of powders in gravity discharge from hoppers has traditionally been measured using a shear cell. The Jenike Shear Cell is a long-established instrument used for this purpose. ASTM D6128 describes the test method and the type of data that is generated. BCR-116 Limestone powder is the only reference material currently used in the powder industry to test shear cell performance when measuring flow behavior. The performance data for flowability of the BCR-116 Limestone powder is measured using a Jenike Shear Cell. The test setup procedure and test execution is complicated and therefore best accomplished by an experienced test technician. Each data point requires a fresh sample of powder. More than 40 separate tests can be required to generate a single flow curve. The Brookfield Powder Flow Tester uses the same sample of powder to run the complete test automatically without operator involvement. Test data from the calibration data sheet provided with the BCR-116 Limestone powder will be compared against test data from 7 separate Brookfield Powder Flow Testers. Repeatability and reproducibility of the Brookfield test data will be calculated.

Tuesday 3:35 C105 SG5

The colloidal glass transition as rheological inverse of gelation

H. Henning Winter
University of Massachusetts Amherst, amherst, MA 01002, United States

After many years of modeling the colloidal glass transition and gelation, the difference between gels and soft glasses is still in dispute. This is where experimental rheology can help since, as will be shown, gels and glasses exhibit inverse viscoelasticity on the Liquid Side near the Liquid-to-Solid Transition (LS-LST). Two model systems of known linear viscoelasticity were chosen to exemplify the two material classes: (1) a crosslinking PDMS represents gelation (using chemical gelation instead of physical gelation) and (2) a concentrated colloidal suspension represents the soft glass transition. The longest relaxation time and the zero shear viscosity diverge for both materials, which look very similar in this way. However, the relaxation time spectrum H(tau) and its expression as complex modulus, with components G' and G", provide clear distinctions between gelation and the colloidal glass transition. While the long-time component of the relaxation time spectrum follows a powerlaw in time for both material types near LS-LST, H= A tau^n, their powerlaw exponent n is of different sign (inverse behavior): negative n for the critical gel (material at the gel point) and positive n for the colloidal glass transition. The powerlaw spectrum is cut off by the diverging, longest relaxation time (called "alpha relaxation time" for the glass) in the approach of the liquid-to-solid transition from the liquid side. Further examples will be shown in order to test the proposed distinction between chemical/physical gels and glasses (colloidal and molecular). In summary, relaxation data provide a clear distinction between these two classes of materials.

Tuesday 4:00 C105 SG6

Symmetric aging behavior upon temperature up and down jumps of a soft glassy nano-clay suspension

Tanmay Dhavale and Yogesh M. Joshi
Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Utter Pradesh, India

Soft glassy materials undergo physical aging wherein they reduce potential energy as a function of time in search of the thermodynamic equilibrium state. The physical aging is accompanied by enhancement of relaxation time and modulus as a function of time elapsed since glass transition. Moreover the rate of physical aging increases with increase in temperature. Interestingly these characteristic features of physical aging are similar to that observed in polymeric glasses where physical aging accompanies specific volume relaxation. Classical experiments by Kovacs (Adv. Polym. Sci., 3, 394, 1964) demonstrated that specific volume relaxation of polymeric glasses upon step up and step down change in temperature follows asymmetric paths. Interestingly recent work of McKenna and coworkers (Phys. Rev. Lett. 106, 095701, 2011) on thermosensitive soft colloidal glass also reported similar nonlinearity leading to asymmetry upon step up and down temperature jumps. In this work we employ a model soft glassy suspension of nanoclay: Laponite, that shows strong increase in elastic modulus and relaxation time as a function of time. Interestingly unlike polymeric glasses and other colloidal glassy systems, soft glass of Laponite suspension shows symmetric behavior of structural evolution upon temperature step up and down jumps. We model this behavior and compare the same with a rate of crosslinking reaction upon temperature up and down jumps.

Tuesday 4:25 C105 SG7

Exploring the nature of strain hardening in uniaxial extension of polymer glasses in absence of strain localization

Panpan Lin and Shi-Qing Wang
Department of Polymer Science, University of Akron, Akron, OH 44325, United States

In uniaxial extension, ductile polymer glasses undergo initial elastic deformation, strain softening, neck propagation, and eventually "strain hardening". The study of "strain hardening" can be complicated by the emergence of necking. We use several strategies to prevent the strain localization and elucidate the nature of the stress buildup in the "strain hardening" regime. The origin of the strain hardening has been elusive because both plastic and anelastic deformation take place in the post-yield regime. We use a combination of tensile tests and in situ temperature measurements to demonstrate that there is significant energy storage during the extension and the mechanical stress largely originates from the straining of a chain network.

Tuesday 4:50 C105 SG8

Rheologically based strategies for long term durability of sealants

Christopher C. White, Donald Hunston, and Kar Tean Tan
Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

The unique properties of polymers enable modern building design. These unique properties are also the greatest vulnerability as they are most susceptible climate induced changes in properties. For example, buildings of steel, glass, and marble dominate the landscape. These materials have different coefficients of thermal expansion. In order to make these building airtight over the expected range of temperatures encountered, an elastomeric sealant is used as a air and moisture barrier in the designed gap. This gap will expand and contract as the building thermally cycles through the day or seasons. The elastomer will maintain an air tight seal as the gap dimensions change. What strategies do material designers use to maintain the seal as the building thermally cycles? This presentation will examine a range of survival strategies from three perspectives: the early formation of the elastomeric networks, the stress dissipation strategies, and finally how are these strategies reflected in the standards and codes used to evaluate sealants.

Tuesday 5:15 C105 SG9

Using a 20 Ma fossil resin to test the super-Arrhenius behavior of glass forming systems

Jing Zhao and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

20 Ma fossil amber offers the opportunity to investigate the dynamic behavior of glass-forming materials far below the nominal glass transition and in the equilibrium condition. This is important in the context of classic theory (e.g. Adam-Gibbs) in which the equilibrium dynamics are extrapolated by, for example, the Williams, Landel and Ferry (WLF) or Vogel-Fulcher-Tammann (VFT) expressions to diverge at a finite temperature (super-Arrhenius behavior). It is also timely as there are new theories which do not give such a finite temperature divergence, hence challenging the idea of an "ideal" glass transition. By performing stress relaxation experiments from ambient temperature to above the glass transition temperature of amber in a step-wise fashion, we can measure upper bounds to the equilibrium relaxation time at each temperature. In all of our experiments, when we are in this upper bound condition (T=Tf'), we find that the material response deviates dramatically from the expectation of the classic theory. The results seem consistent with more modern ideas, such as that of Dyre, et al[1,2], Mauro, et al[3] or

Chandler and co-workers[4,5], in which the diverging time scale signature of complex fluids disappears. These results suggest that such apparent divergence and its interpretation in terms of an ideal glass transition need to be reconsidered.

References: 1. J. C. Dyre, N. B. Olsen, and T. Christensen, Phys. Rev. B 53, 2171 (1996); 2. J. C. Dyre, Rev. Mod. Phys. 78, 953 (2006); 3. J. C. Mauro, Y. Yue, A. J. Ellison, P. K. Gupta and D. C. Allan, PNAS, 106. 19780 (2009); 4. Y. S. Elmatad and D. Chandler and J. P. Garrahan, J. Phys. Chem. B 113. 5563 (2009); 5. Y. S. Elmatad and D. Chandler and J. P. Garrahan, J. Phys. Chem. B 114. 17113 (2010).

Wednesday Morning

Symposium PL

Plenary Lectures

Wednesday 8:30 C102-C104 PL3

Drag reduction and the dynamics of turbulence in simple and complex fluids

Michael D. Graham
Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, United States

At low speed, flow in a pipe or over an aircraft is smooth and steady. At higher speeds, it becomes turbulent -- the smooth motion gives way to fluctuating eddies that sap the fluid's energy and make it more difficult to pump the fluid through the tube or to propel the aircraft through the air. For flowing liquids, adding a small amount of very large polymer molecules or micelle-forming surfactants can dramatically affect the turbulent eddies, reducing their deleterious effects on energy efficiency. This phenomenon is widely used, for example in the Alaska pipeline, but it is not well-understood, and no comparable technology exists to reduce turbulent energy consumption in flows of gases, in which polymers or surfactants cannot be dissolved. The most striking feature of this phenomenon is the existence of a so-called maximum drag reduction (MDR) asymptote: for a given geometry and driving force, there is a maximum level of drag reduction that can be achieved through addition of polymers. Changing the concentration, molecular weight or even the chemical structure of the additives has no effect on this asymptotic value. This universality is the major puzzle of drag reduction.

We describe direct numerical simulations of turbulent channel flow of Newtonian fluids and viscoelastic polymer solutions. Even in the absence of polymers, we show that there are intervals of "hibernating" turbulence that display very low drag as well as many other features of the MDR asymptote observed in polymer solutions. As viscoelasticity increases, the frequency of these intervals also increases, while the intervals themselves are unchanged, leading to flows that increasingly resemble MDR. A simple theory captures key features of the intermittent dynamics observed in the simulations. Additionally, simulations of "edge states", dynamical trajectories that lie on the boundary between turbulent and laminar flow, display characteristics that are similar to those of hibernating turbulence and thus to the MDR asymptote, again even in the absence of polymer additives. Based on these observations, we propose a tentative unified description of rheological drag reduction. The existence of "MDR-like" intervals even in the absence of additives sheds light on the observed universality of MDR and may ultimately lead to new flow control approaches for improving energy efficiency in a wide range of processes.

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Wednesday 10:00 C106 SC29

State diagram of soft colloid / polymer mixtures

Domenico Truzzolillo[1], Dimitris Vlassopoulos[1], and Mario Gauthier[2]
[1]Materials Science & Technology, FORTH and Univ. of Crete, Heraklion, Greece; [2]Chemistry, Univ. of Waterloo, Waterloo, Canada

We investigate the high-volume fraction glassy regime of soft colloid / polymer mixtures , using the star polymer paradigm. We find that the addition of linear polymers at different size ratios leads to softening of the glass and eventually its melting due to depletion. At a certain size ratio, further addition of polymers leads to re-entrant gel. The rheological signatures of the different states are distinct both in the linear and nonlinear responses. Results show that mechanical yielding is a gradual process. The key idea for rationalizing the different states is the combination of osmotic shrinkage of the stars and the depletion effects, both due to the presence of the linear chains. Moreover, heating of the depletion gel leads to its melting, despite its osmotic origin. The reason is the hybrid nature of the star particle which is effectively core-shell, and hence it is suggested that internal particle microstructure greatly affects the rheological properties of soft colloids.

Wednesday 10:25 C106 SC30

Overcoming kinetic barriers to self-assembly: Field-directed colloidal phase transitions

Eric M. Furst, James W. Swan, and Paula Vasquez
Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Suspensions of polarizable colloids are expected to form crystalline equilibrium phases when exposed to a steady, uniform field. However, when colloids become localized this field-induced phase transition arrests and the suspension persists indefinitely as a kinetically trapped, percolated structure. The accomanying fluid-solid transition makes magneto-rheological (MR) fluids useful as shock absorbers, while electro-rheological (ER) fluids can be used as haptic controllers and tactile displays in micro-electronics devices. However, kinetic arrest ultimately prevents the formation of equilibrium phases encoded by the colloidal interactions or particle shape. We demonstrate that, by toggling the field strength at varied frequencies, gels formed in MR fluids can be annealed. This allows the arrested structure to relax periodically to equilibrium. There is a stark boundary as a function of magnetic field strength and toggle frequency that distinguishes arrested states from phase separation. These results demonstrate how kinetic barriers to a colloidal phase transition are subverted through measured, periodic variation of driving forces. Such directed assembly may be harnessed to create novel materials from dispersions of colloids and nanoparticles.

Wednesday 10:50 C106 SC31

Brownian dynamics method for simulation of binding kinetics of patterned colloidal spheres with hydrodynamic interactions

Jun Liu and Ronald G. Larson
Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI 48109, United States

We develop a method of Brownian dynamics (BD) simulation with full hydrodynamic interactions (HI) to study the recognition kinetics between two patterned colloidal spheres. We use a general resistance matrix (12*12) to describe both the far and near-field hydrodynamics of translation, rotation and translation-rotation coupling between the two spheres, adopted from Jeffrey and Onishi (J. Fluid. Mech, 1984, 139, 261), after correcting some translation-rotation and rotation-rotation coupling terms in that paper. We apply the method to the study of specific binding of "patchy" spheres, including effects of depletion attraction and orientation-specific binding, such as that present in "Janus" spheres whose surfaces contain both hydrophobic and hydrophilic faces (as in the work of Chen, et al. Nature 469, 381-384 (2011)). The binding times obtained between two spheres with or without HI by extrapolating to infinite dilution are in good agreement with theoretical predictions from the Smoluchowski equation. In addition, the binding times for pairs of spheres for three cases of surface patterning (uniform-uniform, uniform-Janus and Janus-Janus) are compared with or without rotational motion. Our simulation methodology can readily be extended to allow for prediction of binding kinetics and self-assembly of multiple spherical particles with anisotropic interactions, where both translational and rotational hydrodynamic interactions need to be accurately accounted for.

Wednesday 11:15 C106 SC32

Tuning rheological properties and structure of thermoreversible organohydrogels based on O/W nanoemulsions

H. Burak Eral, Harry Z. An, Eric R. Safai, and Patrick S. Doyle
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Recently, our group reported the synthesis of a novel class of organohydrogels based on water-in-oil nanoemulsions containing poly(ethylene glycol) functionalized at both ends with slightly hydrophobic acrylate groups (PEG-DA) that act as a thermosensitive gelator[1]. These nanoemulsions show a thermoreversible fluid-to-gel transition from a low viscosity Newtonian fluid to a remarkably high moduli gel (~ 100 kPa). The fluid-to-gel transition occurs for a wide range of system parameters (PEG-DA concentrations, droplet sizes, oil volume fractions, etc.). We hypothesized that the onset of such gelation is triggered the formation of inter-droplet bridges due to partitioning of the acrylate end-groups to the oil/water interface1. In this talk, we report an in-depth look into the underlying physical mechanism of this transition by carefully tuning the system composition and studying the viscoelasticity using oscillatory shear experiments. Our findings show that the fluid-to-gel transition can be finely controlled by adjusting the length of the gelator (end-functionalized PEG, in this case), as well as the volume fraction of oil and PEG-DA. This interesting class of soft matter inspires a range of unique application possibilities, including orthogonal encapsulation and release for drug delivery[2], and strong, reversible, thermosetting matrices for tissue engineering.

[1] Helgeson, M.E., Moran, S., An, H.Z., and Doyle, P.S., "Mesoporous organohydrogels from thermogelling photocrosslinkable nanoemulsions", Nature Materials 11, 344-352 (2012))

[2] An, H.Z., Helgeson, M.E., and Doyle, P.S, "Nanoemulsion Composite Microgels for Orthogonal Encapsulation and Release", Advanced Materials, 24, 28, 3895-3899 (2012)

Wednesday 11:40 C106 SC33

Microstructural processes during LAOS yielding of nanoemulsion gels

Juntae Kim, Yongxiang Gao, and Matthew E. Helgeson
Chemical Engineering, UC Santa Barbara, Santa Barbara, CA 93117, United States

The transition to flow in colloidal gels is known to depend significantly on their network microstructure. However, little is understood about the differences in yielding between gels with the homogeneous structure typically found in dilute suspensions, and those with heterogeneity characteristic of more concentrated systems. In this work, we use nanoemulsion "organohydrogels" [Helgeson et al., Nature Materials, 2012, 11(4): 344-352] as a model system to explore these differences, whereby the interdroplet attractions can be dynamically tuned through a thermoresponsive polymer, allowing for the formation of gels with either homogeneous or heterogeneous cluster-scale microstructure. Large-amplitude oscillatory shear (LAOS) measurements reveal that the non-linear response homogeneous shows an abrupt transition from elastoplastic strain softening to viscoplastic shear thinning during the yielding, whereas for heterogeneous gels it occurs over a range of strain amplitude at nearly constant values of the fundamental moduli. To probe the microstructural origins of this behavior, we present the first combined studies of rheo-small and ultra-small angle neutron scattering on soft colloidal gels, providing detailed structural information on length scales ranging from the primary particle size to several microns. We find that, in general, yielding arises from a "top-down" cascade of microstructural processes, beginning with large-scale rupture of weak cluster bonds near the yield point, further cluster bond rupture and suspension beyond the yield point, and finally densification and breakage of clusters en route to terminal flow. The broad yielding transition in heterogeneous gels is related to the progressive melting of heterogeneous cluster-cluster correlations. These results demonstrate the critical influence of large-scale microstructure on the yielding of attractive suspensions.

Symposium PS

Polymer Solutions and Melts

Organizers: Randy Ewoldt and Suraj S. Deshmukh

Wednesday 10:00 C107 PS19

Partitioned plate geometry to perform large amplitude oscillation shear (LAOS)measurements on polymers

Aloyse J. Franck
R&D, TA Instruments, New Castle, DE 19720, United States

Highly viscous fluids such as polymer melts have been successfully tested using dynamic mechanical analysis at small deformations. However at the onset of the non-linear mechanical response at larger strains, melt fractures can occur making oscillatory measurements at large deformations unreliable i.e. impossible as the sample is ejected from the gap. Sample fracturing starts at the sample rim and propagates to the center of the plate-plate i.e. cone - plate geometry with increasing time and/or increasing strain amplitude. In order to reduce the effect of sample fracturing, the partitioned plate/cone geometry, a concept developed by J. Meissner (J.Rheol, 1989) to measure the second normal stress difference is used. A newly developed partitioned plate/cone geometry has been designed to fit the standard FCO on the ARES-G2. It consists of a stationary 25mm ring connected to the transducer base with a standard geometry size shaft. The 10mm diameter center plate is attached to a small rod which runs through the hollow shaft and is directly connected to the torque transducer. LAOS experiments at various frequencies and strain ranges have been performed on PDMS and LDPE to evaluate the new test geometry. The results show that steady state oscillation is obtained within a few cycles of oscillation. At higher strains, after an initial phase of steady state oscillation the stress amplitude increases and then decreases continuously. The deviation from steady state oscillation can be visually correlated with melt fracture occurring at the sample rim. With increasing strain amplitude, the steady state region is steadily reduced and at large strain, only a few cycles are available to evaluate the sample response.

Wednesday 10:25 C107 PS20

Non-linear rheology of model branched polymer systems under large amplitude oscillatory shear (LAOS)

Brendan C. Blackwell[1], Randy H. Ewoldt[1], Johannes M. Soulages[2], and Andy H. Tsou[2]
[1]Mechanical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States; [2]Exxonmobil Corporate Strategic Research, Clinton, NJ, United States

Long chain branching (LCB) has long been recognized to play a central role for many commercial products (polyolefins, elastomers, lubricants) and processes (extrusion, film blowing, fiber spinning). Nonetheless, identification of specific LCB topology has remained a challenging task to date. Recent research efforts have allowed for qualitative differentiation between different families of long chain branched molecules, such as combs, stars, dendrimers, or pompom architectures. However, a current challenge is to find a quantitative analytical technique capable of differentiating the geometrical details of the branching topology, such as the number and length of dangling arms, density of branch points, or quantity of branched molecules present. In this talk, we study the use of nonlinear shear rheometry to characterize molecular topology and microstructural architecture. We use an inventory of well-defined branched model polyethylenes with unique molecular architectures. These branched polyethylenes are blended into an essentially linear polyethylene matrix. We study the non-linear rheological response using deformation-controlled Large-Amplitude Oscillatory Shear Strain (LAOStrain). The LAOStrain technique probes the nonlinear viscoelastic response as a function of frequency and strain amplitude, systematically surveying a broad range of deformation timescales and amplitudes. We make use of higher-harmonic Chebyshev coefficients in the nonlinear shear stress response to show the potential of LAOS as an analytical tool for fingerprinting the nonlinear behavior of viscoelastic materials and thereby probing the molecular topology and microstructural architecture of LCB systems.

Wednesday 10:50 C107 PS21

Theory of low-dimensional asymptotic material functions from large-amplitude oscillatory shear (LAOS)

Randy H. Ewoldt and N. Ashwin Bharadwaj
Mechanical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States

Rheological material functions are used to form our conceptual understanding of a material response. For a nonlinear rheological response, the possible deformation protocols and material measures span a high-dimensional space. Here we use asymptotic expansions to outline low-dimensional measures for describing leading-order nonlinear responses in large-amplitude oscillatory shear (LAOS). These intrinsic nonlinear material functions are only a function of oscillatory frequency, and not amplitude. Such measures have been suggested in the past, but here we clarify what measures exist and give physically meaningful interpretations by using the deformation-domain (Chebyshev coefficient) framework. Both strain-control (LAOStrain) and stress-control (LAOStress) protocols are considered, and nomenclature is introduced to encode the physical interpretations. We introduce non-integer power expansions, and demonstrate their applicability with two common generalized Newtonian fluid models (Cross and Carreau-Yasuda). Finally, we measure experimentally the four intrinsic shear nonlinearities of LAOStrain for a polymeric hydrogel (PVA-Borax). We observe integer asymptotic scaling of all four measures. The magnitudes and signs of the intrinsic nonlinear fingerprints are used to conceptually model the mechanical response and to infer molecular- and micro-scale features of the material.

Wednesday 11:15 C107 PS22

Temperature rise in large-amplitude oscillatory shear flow from shear stress measurements

A. Jeffrey Giacomin[1], R. Byron Bird[2], and Hyung Min Baek[1]
[1]Rheology Research Center and Mechanical Engineering Dept., University of Wisconsin - Madison, Madison, WI 53706, United States; [2]Rheology Research Center, Chemical and Biological Eng. Dept., University of Wisconsin - Madison, Madison, WI 53706, United States

Recently, we derived the temperature rise in a viscoelastic fluid undergoing large-amplitude oscillatory shear flow (LAOS) using the corotational Maxwell model [Giacomin, A.J., et al., Physics of Fluids (in press)]. The results of this derivation are used to estimate the temperature rise a priori. In the present paper, we show how to calculate the temperature rise in any liquid after measuring the shear stress response to LAOS. Specifically, if the measured response is represented by a Fourier series of odd harmonics, we can then combine this Fourier series with the equation of energy, written in terms of temperature, to calculate the temperature rise. We can thus use this calculation to see if the temperature requirement of the current standard for oscillatory shear flow testing [BS ISO 6721-10:1999] is satisfied. Our work proceeds without the choice of a constitutive equation, and can thus be used to estimate the temperature rise a posteriori for any LAOS measurement on any fluid.

Wednesday 11:40 C107 PS23

A comparison of mechanical hole burning and Fourier transform rheology of polymer solutions

Nabila Shamim and Gregory B. McKenna
Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

In prior work we examined the non linear viscoelastic response of polystyrene solutions having different concentrations and molecular weights using Mechanical Spectral Hole Burning (MSHB). While MSHB is thought to be related to dynamic heterogeneity in complex fluids, the information gained from such experiments has never been compared to Fourier Transform Rheology (FTR), another probe of fluid nonlinearity. Here we undertake an investigation of the MSHB and FTR behaviors of polybutadiene and polystyrene solutions with the goal of examining similarities and differences in how these methods "fingerprint"[1] the nonlinear response. For example the vertical holes in the MSHB experiments vary in intensity with the square of the sine wave pump amplitude. We find that the same is true of the third harmonics in the FT Rheology. These will be discussed in detail at the meeting.

Reference: 1. Kyu Hyun, et. al., A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS), Progress in Polymer Science, 2011; 36: 1697-1753.

Symposium SA

Self-Assembling, Associating and Gel-Like Systems

Organizers: Kendra Erk and Surita Bhatia

Wednesday 10:00 C101 SA15

Elastic turbulence in micellar solutions

Marc A. Fardin[1], Gareth H. McKinley[2], Sandra Lerouge[3], and Sebastien Manneville[1]
[1]Physics, Ecole Normale Superieure de Lyon, Lyon, France; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; [3]Physics, Universite Paris Diderot, Paris, France

In the past twenty years, shear-banding flows have been probed by various techniques, such as rheometry, velocimetry and flow birefringence. In micellar solutions, many of the data collected exhibit unexplained spatiotemporal fluctuations. Recently, we have shown that those fluctuations can originate from a purely elastic instability of the shear-banding flow. In some cases, the flow of micellar solutions can exhibit elastic turbulence, with our without shear-banding. I shall review the current state of our understanding on such cases.

Wednesday 10:25 C101 SA16

Diffusive effects on the transient and steady state shear response of the VCM model for wormlike micellar mixtures

Lin Zhou[1], Gareth H. McKinley[2], and L. Pamela Cook[3]
[1]Mathematics, New York City College of Technology, New York, NY 11201, United States; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; [3]Mathematical Sciences, University of Delaware, Newark, DE 19716, United States

Wormlike micelles are known as 'living polymers' because they can break and reform continuously. Imposed shear or extensional stresses can enhance the breakage rate and couple the external stress field to the microscopic dynamics. The VCM (Vasquez, Cook and McKinley) model is a two-species kinetic theory model of wormlike micelles that incorporates this coupling in the breakage and reforming mechanisms of the ``worms". This model has been used successfully to describe flows of wormlike micellar mixtures in different deformation histories including Taylor-Couette shear, pressure-driven channel flow, and also extensional flow.

In this talk, transient and steady state responses of the VCM model under start-up of steady shear are discussed. In particular, the important role that diffusive processes in the stress and number density play during the formation of shear bands, in the transient stress response, and in the shape of the steady-state flow curve are examined. The transient response of the model can be divided into four distinct regions which include; (i) initial propagation of an elastic shear wave, (ii) viscoelastic stress overshoot, (iii) nucleation and growth of the shear band as the shear stress plateaus, followed by (iv) a long slow diffusive period as the shear-band migrates and the stress relaxes to a final steady profile. The long time effect of the diffusion is a focus of the work, and the model predictions are compared with recent experimental results. Computationally, a conformal mapping strategy (adaptive method) is used to control the spatial discretization so that the shear-band 'kink', (i.e. the sharp transition region in the velocity profiles between the bands of dissimilar shear rate), remains well resolved even for small diffusion constants.

Wednesday 10:50 C101 SA17

Novel simulation method for the rheology of semi-dilute threadlike micellar solutions

Weizhong Zou and Ronald G. Larson
Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI 48105, United States

We report an extension of Cates and coworkers' model for the rheology of entangled thread-like micelles that includes not only reptation, breakage and recombination, primitive path fluctuations, and Rouse modes, which have been included in the Cates model, but also constraint release, and bending modes, which had not been included. Our method also includes correlations in micelle length that extend through multiple breakage/recombination cycles, not included in previous approaches. We also allow for the possibility of both tight and loose entanglements. Using a fast "pointer" algorithm that only tracks the ends of un-relaxed regions along each micelle, we achieve fast simulations of large ensembles containing thousands of micelles, to obtain accurate averages without pre-averaging or neglecting correlations. With a modified Genetic Algorithm, we make the transformation of our simulation results from the time domain to the frequency domain. The model can span across several regimes of behavior depending on the relative rate of reptation, primitive path fluctuation, and breakage/recombination, and is suitable for predicting the behavior of experimental solutions of threadlike micelles.

Wednesday 11:15 C101 SA18

Flow induced irreversible gelation of non-ionic surfactants in a microfluidic device with microposts

Ya Zhao[1], Joshua J. Cardiel[1], Lige Tonggu[2], Liguo Wang[2], and Amy Q. Shen[2]
[1]Mechanical Engineering, University of Washington, SEATTLE, WA, United States; [2]University of Washington, Seattle, WA 98195, United States

Recently, it has been shown that it is possible to induce purely flow-induced irreversible gelation from cationic wormlike micellar solutions. In this work, we report a generalized flow induced microfluidic approach to produce irreversible gel from a nonionic surfactant system. This nonionic irreversible gel formation is brought about via a mixed shearing/extensional flow in which the fluid experiences very high strain rates and total strains via a microfluidic device. We use a dilute aqueous non-ionic surfactant system consisting of polyoxyethylene (20) sorbitan monooleate (Tween-80) and Monolaurin (25% in weight of Tween 80 and 2% in weight of Monolaurin). This non-ionic surfactant system can form a mixture of spherical and rod-like micelles at low surfactant concentrations. They are frequently used in protein bio-pharmaceutical formulations and cosmetic industries.The irreversible gel aggregates are floc-alike nanoporous structures with 1-2 um in diameter, formed from rod-like bundles, imaged by the Scanning Electron Microscopy (SEM) and Transimission Electron Microscopy (TEM).The rheological properties of Tween80/ML precursor and their corresponding gel aggregates are investigated by both bulk rheology and microrheology. The precursor shows slightly shear thinning behavior at large shear rates and the weakly viscoelastic properties of the gel aggregates is due to the lack of ionic strength in the wormlike micelles of nonionic surfactant. This nontoxic and biodegradable nanoporous gels formed from Tween80/ML system can be applied in biosensing, drug delivery, and bioencapsulation areas.

Wednesday 11:40 C101 SA19

Rheological properties of commercial body washes: The effects of salts and perfume raw materials

Xueming Tang[1], Peter H. Koenig[2], Shawn D. McConaughy[2], Mike R. Weaver[2], and Ronald G. Larson[1]
[1]Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States; [2]Procter and Gamble, Cincinnati, MI 48109, United States

We report systematic measurements and modeling of the rheological properties of two commercial body wash formulas, including the effects of salts and perfume raw materials (PRMs) at different temperatures. The two formulas, named BCP1 and PC51WB, are composed of sodium lauryl ether sulfate, cocamidopropyl betaine, PRMs, and salts. Formula PC51WB has longer surfactant head group and tail group distributions than formula BCP1. As the concentration of NaCl increases, the viscosity and elasticity of the body washes increase to a maximum and then decrease. It is proposed that micellar shape changes from spherical to threadlike as the salt concentration increases, and above the viscosity maximum the micelles become branched. The addition of PRMs modifies the viscoelasticity of body wash in a way that can be rationalized based on the hydrophobicity index of the perfume, logP, and their chemical structures. The loss modulus versus frequency curve passes through a common fixed point as either the salt or PRM concentration changes. The possibilities of generating "master curves" for different salt concentrations, PRM concentrations, and temperatures are discussed. Micellar characteristic lengths and times, and scission energies are extracted from the rheological data using Cates' model for elongated micelles. Formula PC51WB with longer head group and tail group distributions exhibits shorter micellar lengths, smaller scission energies, and smaller maximum zero shear viscosities.

Symposium BS

Rheology in Biological Systems

Organizers: Charles M. Schroeder and Isidro (Dan) E. Zarraga

Wednesday 10:00 C105 BS1

Asymmetric vesicle instabilities in uniaxial and planar extensional flows

Andrew Spann[1], Hong Zhao[2], and Eric Shaqfeh[2]
[1]Institute for Computational and Mathematical Engineering, Stanford University, Stanford, CA 94305, United States; [2]Chemical Engineering, Stanford University, Stanford, CA 94305, United States

The process in which a liquid drop placed in an extensional flow stretches into a dumbbell shape with a long thin neck and eventually breaks up has been covered extensively. Motivated by recent experimental observations, we study a seemingly analogous problem with vesicles, which are deformable but incompressible membranes that conserve area and volume. We begin with vesicles in an unbounded uniaxial extensional flow which are given general radial perturbations from an initially stable symmetric equilibrium state. For dumbbell-shaped prolate vesicles with low enough reduced volumes (< 0.74 at matched inner/outer viscosity) we find a critical capillary number beyond which an asymmetric perturbation mode will grow, resulting in the dumbbell shape becoming asymmetric as fluid flows from one dumbbell to the other and a long cylindrical neck forms. Using an axisymmetric spectral boundary integral method, we simulate this instability and observe the same growth rate predicted by the most unstable mode in a linear stability analysis of stationary perturbed shapes. We additionally demonstrate a fully 3D simulation using a boundary integral method with Loop subdivision surfaces that shows good agreement with the spectral results. We use this 3D method to simulate planar extensional flow and compare and contrast the stability results between planar and uniaxial extensional flow. We describe the effects of non-matched inner and outer fluid viscosities on the flow instability. Our simulations help elucidate a mechanism for this instability

based on a competition between internal pressure differentials in the vesicle resulting from the membrane bending force and ambient flow. We compare and contrast this transition to the classic drop breakup transition.

Wednesday 10:25 C105 BS2

Brownain dynamics simulation of discrete red blood cell model based on kinetic theory with constraints

Kyung Hyo Kim
Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States

The Brownian Dynamic simulation allows predicting the movement of biological cells with the consideration of forces such as hyodrodynamic, the Brownian, intermolecular, and constraint forces. Instead of considering blood as continuum fluid or using an empirical constitutive equation, we can use kinetic theory where the stress tensor and the stochastic differential equation (SDE) of motion depend on the configuration of the microstructure of the fluid. Blood is considered as a suspension of deformable red blood cells (RBC) in a dilute solution of Newtonian fluid. A discrete model of bead-spring RBC based on kinetic theory with a geometrical holonomic constraint is constructed. The constraints using Lagrange multiplier method describes the effect of the biological cell conserving its overall size throughout the motion of flow while allowing the shape to deform. We present our method and demonstrate its applicability to study rheology of biological cells and further study of blood flow. To demonstrate the capability of the method, the minimalist bead-spring-ring model to represent the RBC was simulated. A simple linear Hookean spring is used to give flexibility to deform. The model is tested under shear and shear free flow. An assumption was made that the friction tensor is isotropic. The rheological material properties obtained are qualitatively in agreement clearly showing shear-thinning effect of viscosity in shear flow. The two-constraint model was set to have constant area and constant total length of the connected springs. The two-constraint model gives more restriction to deformation than one-constraint method where the constraint is only an area, and yet still has some degree of flexibility. We can also observe Fahraeus-Lindqvist effect in the capillary flow with this study where the viscosity drops as the vessel diameter decreases.

Wednesday 10:50 C105 BS3

Modeling the concentration distribution of a low-Reynolds number suspension of vesicles and red blood cells in wall-bounded shear flow

Vivek Narsimhan, Hong Zhao, and Eric Shaqfeh
Chemical Engineering, Stanford University, Stanford, CA 94305, United States

We develop a nonlocal, kinetic theory to predict the concentration distribution of a suspension of vesicles or red blood cells in a wall-bounded Couette flow. This model balances the wall-induced hydrodynamic lift on deformable particles with the flux due to binary collisions, which we represent via a second-order kinetic master equation. Our theory is not self-sufficient, as it requires data (simulation or experimental) on the details of a binary collision process and the hydrodynamic lift of a single particle in a wall-bounded shear flow. Nevertheless, it represents a significant improvement in terms of time savings and predictive power over current large-scale numerical simulations of suspension flows. Our model predicts a depletion of particles near the channel wall (ie, the Fahraeus-Lindqvist effect), followed by a near-wall formation of particle layers. We quantify the effect of channel height, particle volume fraction, viscosity ratio, and capillary number on the occurrence of both of these phenomena. The concentration profiles from our theory agree reasonably well with those computed from boundary integral simulations. Additionally, our predictions of the Fahraeus-Lindqvist effect match quite well with in-vitro and in-vivo studies of red blood cell flow. We conclude by discussing how to extend our theory to Poiseuille flows and pulsatile flows that are typically observed in the microcirculation.

Wednesday 11:15 C105 BS4

Response of endothelial cells to stagnation point flows

Maggie A. Ostrowski[1], Ngan F. Huang[2], Travis W. Walker[1], John P. Cooke[3], Alexander R. Dunn[1], and Gerald G. Fuller[1]
[1]Chemical Engineering, Stanford University, Stanford, CA 94305, United States; [2]Department of Cardiothoracic Surgery, Stanford University, Stanford, CA, United States; [3]Department of Cardiovascular Medicine, Stanford University, Stanford, CA, United States

Human blood vessels are lined with a single cell layer called the endothelium. This mechano-sensitive layer senses and responds to the hydrodynamic forces of the blood flow. Under conditions of steady shear stress, endothelial cells orient parallel to the direction of blood flow and provide a healthy, tight barrier that protects against vessel diseases such as atherosclerosis. Vascular disease occurs preferentially in locations where vessels curve, branch or bifurcate. This geometry results in unsteady flow patterns with impinging and upwelling flows, and stagnation points that are thought to cause an unhealthy endothelial cell layer prone atherosclerosis. Although the subject of intense interest, the underlying molecular mechanisms connecting complex flow to vascular disease remain incompletely understood. To investigate the behavior of endothelial cells exposed to a complex flow, we built a submerged impinging jet device that produces a stagnation point flow. This device allows us to observe the behavior of endothelial cells in this flow environment on the hours/days timescale with a live-cell imaging microscope. We observe dramatic changes in cell migration, orientation, and crowding as a function of Reynolds number. Our observations also reveal a remarkable ability of endothelial cells to sense and respond to spatial gradients in fluid shear. We discuss these results in the context of human physiology and disease.

Wednesday 11:40 C105 BS5

Mechanical phenotyping of tumor cells using a microfluidic cell squeezer device

Zeina S. Khan[1], Nabiollah Kamyabi[1], Souad Sennoune[2], Raul Martinez-Zaguilan[2], and Siva A. Vanapalli[1]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]Health Sciences Center, Texas Tech University, Lubbock, TX, United States

Studies have indicated that cancer cells have distinct mechanical properties compared to healthy cells. We are investigating the potential of cell mechanics as a biophysical marker for diagnostics and prognosis of cancer. To establish the significance of mechanical properties for cancer diagnostics, a high throughput method is desired. Although techniques such as atomic force microscopy are very precise, they are limited in throughput for cellular mechanical property measurements.

To develop a device for high throughput mechanical characterization of tumor cells, we have fabricated a microfludic cell squeezer device that contains narrow micrometer-scale pores. Fluid flow is used to drive cells into these pores mimicking the flow-induced passage of circulating tumor cells through microvasculature. By integrating high speed imaging, the device allows for the simultaneous characterization of five different parameters including the blockage pressure, cell velocity, cell size, elongation and the entry time into squeezer.

We have tested a variety of in vitro cell lines, including brain and prostate cancer cell lines, and have found that the entry time is the most sensitive measurement capable of differentiating between cell lines with differing invasiveness. Surprisingly, we have found that the entry times of more invasive cell lines can be larger than for less invasive or benign cells, indicating that they are stiffer. We have also examined the effects of cytoskeletal disruption using chemotherapy drugs on cancer cells with the cell squeezer.

Wednesday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Wednesday 1:30 C106 SC34

Mechanistic insights into flow induced segregation in blood and other multicomponent suspensions

Amit Kumar and Michael D. Graham
Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, United States

Blood is a multicomponent mixture comprising mostly of red-blood-cells (RBCs) along with trace amounts of other components, primarily leukocytes and platelets. Under physiological flow conditions both the leukocytes and the platelets segregate near the walls of the blood vessel, a phenomenon commonly known as margination, while the RBCs tend to migrate away from the walls. The key physical differences between RBCs, leukocytes, and platelets are their relative size and rigidity: the leukocytes are larger than RBCs, while the platelets are smaller; both are considerably stiffer than RBCs. However, how these differences in properties lead to the observed segregation behavior is poorly understood. In this work we focus on the model system of a fluid-filled elastic capsule mixture in which individual components differ in size and rigidity. Using detailed boundary integral simulations we delineate the effect of both of these key properties on the flow induced segregation behavior and relate these to the observations of leukocyte and platelet margination in blood flow. To gain a mechanistic understanding of these results, we introduce a novel hydrodynamic-Monte Carlo simulation technique, which incorporates two of the main ingredients of flow dynamics in confined suspensions: the wall-induced migration and hydrodynamic pair collisions. The model quantitatively characterizes the role of wall-induced migration and different types of pair collisions on the segregation behavior in various parameter regimes like volume fraction, stiffness ratio and size ratio. In particular, the model clarifies the important role played by heterogeneous collisions, i.e. collisions between two different species in a mixture. The insights and tools presented in this talk will be helpful, e.g., in designing drug delivery particles for optimal vascular wall targeting and for designing microfluidic devices for separating/enriching trace components of blood.

Wednesday 1:55 C106 SC35

Porous media model and collective behavior of colloidal particles trapped at a fluidic interface

Eric Shaqfeh, Gerald G. Fuller, and Shenghan Yan
Chemical Engineering, Stanford University, Stanford, CA 94305, United States

It is well known that charged colloidal particles may form an effective two dimensional suspension at a fluidic interface. Research toward the understanding of the dynamics and collective behavior of these suspended particles is at the core of engineering Pickering emulsions. Many experiments have been performed where two particle laden interfaces have been brought into close contact in a controlled manner and various observations, including particle ``bridging", have been made in an attempt to understand the stabilization mechanism of interfacial particles in a Pickering emulsion. One of the most interesting observations is the tendency for the particles on one interface to ``evacuate" and those on the other interface to ``aggregate" during the close approach of the surfaces. In this work, we propose to understand the mechanism of particle evacuation-aggregation via a combined experimental and theoretical approach. First, we performed real-time experiments where two particle-laden water-decane interfaces were brought into contact. We then developed a Brownian dynamics simulation of the evacuation-aggregation including the important relevant interparticle interactions that we presumed were important in describing the phenomena. In this simulation, we have incorporated both reasonable electric inter-particle interactions from available literature studies and flow interactions via a porous media model that relates the particle velocity to the local surface coverage through the effective permeability of a porous media. Thus the flow effects are captured in a mean field sense. The BD simulations were able to capture the evacuation/aggregation qualitatively and, in most instances, quantitatively. In particular the diameter of the evacuated area decreases with increasing surface coverage in both simulations and experiments, and we will describe the physical mechanisms leading to this behavior by analyzing the particle force balance in the BD simulations.

Wednesday 2:20 C106 SC36

Hydrodynamic migration of soft spheres and rods in microflow

Yeng-Long Chen[1] and Chia-Wei Hsu[2]
[1]Institute of Physics, Academia Sinica, Taipei, Taiwan; [2]Department of Physics, Harvard University, Cambridge, MA, United States

We investigate the cross-stream migration of soft particles near walls under shear and Poiseuille flow in low Reynolds number flow. Near no-slip surfaces, asymmetric flow field induced by the elastic deformation of soft particles such as DNA and blood cells is known to cause the particles to migrate away from the walls. At moderate particle Reynolds numbers, fluid inertia can also cause the particles to move away form the high stress region and migrate away from the walls. We examine particle migration due to these different contributions and study the dependence of the migration velocity on the particle size, shape, and elasticity. The migration effect leads to non-Newtonian suspension rheology.

Wednesday 2:45 C106 SC37

Simulation of a non-Newtonian dense granular suspension in a microfluidic contraction

Gustaf E. Mårtensson[1], Andreas Mark[2], and Thomas Kurian[1]

[1]R&D, Micronic Mydata AB, Täby 18303, Sweden; [2]Fraunhofer-Chalmers Research Centre, Göteborg 41296, Sweden

The success of a solder paste jet printer is based on the uninterrupted flow of fluid, specifically dense fluid suspensions, inside the printing head. It is well known that the flow of dense suspensions are prone to jamming and sedimentation effects, which both could entail detrimental failure modes in the printing heads, see Parry and Millet (2010). The purpose of this study is to develop a novel simulation framework and to show that it captures the main effects such as mass flow and partial jamming in a cylindrical duct test configuration. The granular suspension is a generic solder paste with 20 um metal alloy particles immersed in a flux. The simulations are performed with IBOFlow, see Mark and Rundquist (2011), a multi-phase flow solver developed at the Fraunhofer-Chalmers Centre. The granular suspension is modeled by a two-fluid model discretized in an Euler-Euler framework. The averaged momentum equations from Enwald et al. (1996) is solved together with the common continuity equation generating a shared pressure field. Explicit constitutive equations for the interfacial momentum transfer model from Gidaspow (1994) and the particle pressure from Zenit et al. (1997) and Kulkarni et al. (2010) are employed. To capture the shear thinning effects of the non-Newtonian suspensions, a Carreau model is utilized. To study how the fluid flow affects the local volume fraction and partial jamming in the duct, simulations are performed for different applied pressure drops. For both particle pressure models, the resulting mean bulk velocities are compared with experiments with good agreement and partial jamming is observed. Hence, it is concluded that the proposed framework is suitable to model and simulate the granular suspension in a micro fluid contraction.

Wednesday 3:35 C106 SC38

Fast evaporation of spreading droplets of colloidal suspensions

Kara L. Maki and Satish Kumar

Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

When a coffee droplet dries on a countertop, a dark ring of coffee solute is left behind, a phenomenon often referred to as "the coffee-ring effect". A closely related yet less-well-explored phenomenon is the formation of a layer of particles, or skin, at the surface of the droplet. In this work, we explore the behavior of a mathematical model that can qualitatively describe both phenomena. We consider a thin axisymmetric droplet of a colloidal suspension on a horizontal substrate undergoing spreading and rapid evaporation. The lubrication approximation is applied to simplify the mass and momentum conservation equations, and the colloidal particles are allowed to influence droplet rheology through their effect on the viscosity. By describing the transport of the colloidal particles with the full convection-diffusion equation, we are able to capture depthwise gradients in particle concentration and thus describe skin formation, a feature neglected in prior models of droplet evaporation. The highly coupled governing system of equations is solved using a finite-difference scheme based on a moving overset grid method. Whereas capillarity creates a flow that drives particles to the contact line to produce a coffee-ring, Marangoni flows can compete with this and promote skin formation. Increases in viscosity due to particle concentration slow down droplet dynamics, and can lead to a significant reduction in the spreading rate.

Wednesday 4:00 C106 SC39

Microfluidic generation of droplets with a high-loading of nanoparticles for drug delivery to the lungs via microgel particles

Robert K. Prud'homme

Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States

Microfluidic approaches for controlled generation of colloidal clusters, e.g., via encapsulation of colloidal particles in droplets, have been used for the synthesis of functional materials including drug delivery carriers. Most of the studies, however, use a low concentration of an original colloidal suspension (< 10 wt%). Here we demonstrate microfluidic approaches for directly making droplets with moderate (10-25 wt%) and high (> 60 wt%) particle concentrations. Three types of microfluidic devices, PDMS flow-focusing, PDMS T-junction, and microcapillary devices, are investigated for direct encapsulation of a high concentration of polystyrene (PS) nanoparticles in droplets. In particular, it is shown that PDMS devices fabricated by soft lithography can generate droplets from a 25 wt% PS suspension, whereas microcapillary devices made from glass capillary tubes are able to produce droplets from a 67 wt% PS nanoparticle suspension. When the PS concentration is between 0.6 and 25 wt%, the size of the droplets is found to change with the oil-to-water flow rate ratio and is independent of the concentration of particles in the initial suspensions. Drop sizes from ~12 to 40 μm are made using flow rate ratios Qoil/Qwater from 20 to 1, respectively, with either of the PDMS devices. However, clogging occurs in PDMS devices at high PS concentrations (> 25 wt%) arising from interactions between the PS colloids and the surface of PDMS devices. Glass microcapillary devices, on the other hand, are resistant to clogging and can produce droplets continuously even when the concentration of PS nanoparticles reaches 67 wt%. We believe that our findings indicate useful approaches and guidelines for the controlled generation of emulsions of microparticles that are filled with a high loading of nanoparticles and which are useful for drug delivery applications.

Wednesday 4:25 C106 SC40

The collective dynamics of confined rigid spheres and deformable drops

Michael Loewenberg[1], Jerzy Blawzdziewicz[2], Pieter J. Janssen[3], Mathew D. Baron[4], Eligiusz Wajnryb[5], and Patrick D. Anderson[6]
[1]Chemical and Environmental Engineering, Yale University, New Haven, CT 06520-8286, United States; [2]Mechanical Engineering, Texas Technical University, Lubbock, TX 79409-1021, United States; [3]SABIC Innovative Plastics, Rotterdam, The Netherlands; [4]Economics, Princeton University, Princeton, NJ 08544, United States; [5]Inst Fundamental Technol Res, Polish Academy of Science, Warsaw PL-02106, Poland; [6]Eindhoven Univ Technology, Eindhoven 5600 MB, The Netherlands

The evolution of linear arrays of rigid spheres and deformable drops in a Poiseuille flow between parallel walls is investigated to determine the effect of particle deformation on the collective dynamics in confined particulate flows. We find that linear arrays of rigid spheres aligned in the flow direction undergo a particle-pairing instability and are unstable to lateral perturbations. Linear arrays of deformable drops, in addition to the pairing instability, exhibit other dynamical features, including formation of transient triplets, cascades of pair-switching events, and formation of pairs with equal interparticle spacing. Particle deformation also stabilizes drop arrays to lateral perturbations. These pairing and alignment phenomena are qualitatively explained in terms of hydrodynamic far-field dipole interactions (insensitive to particle deformation) and quadrupole interactions (deformation induced). We suggest that quadrupole interactions underlie the spontaneous formation of droplet strings in confined emulsions under shear [Phys. Rev. Lett., 2001, v86, p1023].

Wednesday 4:50 C106 SC41

Microfluidic fabrication of non-spherical endoskeleton droplets

Marco Caggioni, Jessica Lenis, and Patrick T. Spicer
Complex Fluids Microstructures, Procter & Gamble, West Chester, OH 45069, United States

In consumer products, cosmetics, and medicines many benefits are delivered by deposition of emulsion droplets onto hair, skin, or other tissues. During formulation of such products the droplet stability and specific interactions with targeted substrates are optimized to maximize delivery. Particle shape is a parameter that adds utility and complexity to colloids but is typically exploited only for solid materials. We show that a non-spherical shape can also be imparted to emulsion droplets, provided an elastic endoskeleton is present. A simple physical model shows that the elongated droplet structures are stable as a result of a balance between interfacial tension and the endoskeleton elasticity. The addition of the endoskeleton can be achieved by crystallization of a portion of the droplet phase during cooling of an initially hot oil-in-water emulsion. Multiple endoskeleton droplets can be easily produced by a microfluidic device that combines the ability to produce droplets, control their temperature, and modify their shape. Non-spherical endoskeleton droplets still possess properties of simple emulsions, like the ability to coalesce with liquid and wet solid substrates of interest. Such unique anisotropic droplet materials can be used as building blocks for new supracolloidal structures with fascinating properties.

Symposium PS

Polymer Solutions and Melts

Organizers: Randy Ewoldt and Suraj S. Deshmukh

Wednesday 1:30 C107 PS24

A new large-strain uniaxial extension rheometer for polymer melts

Martin Sentmanat
Xpansion Instruments, Tallmadge, OH, United States

Details of a newly developed large-strain uniaxial extension rheometer are provided. The new extensional rheometer has been designed as a detachable fixture for accommodation within the environmental testing chamber of commercial combined motor & transducer (controlled stress) and separate motor & transducer (controlled strain) rotational rheometers and is capable of achieving Hencky strains of greater than 7.5, almost double that of existing extensional rheometer fixtures, per motor revolution. Validation results are presented for a number of linear and branched polymer melts in uniaxial extension over a broad range of temperatures and Hencky strain rates.

Wednesday 1:55 C107 PS25

Creep measurements confirm steady flow after stress maximum in extension of branched polymer melts

Nicolas J. Alvarez, José Manuel Román Marín, Qian Huang, and Ole Hassager
Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs Lyngby 2800, Denmark

The presence of a stress maximum followed by steady flow in uniaxial extension was first reported by Rasmussen and co-workers for long branched polymers [1]. The measurements were carried out on a filament stretching rheometer (FSR) operating at a constant rate of deformation for a commercial low density polyethylene (Lupolen 3020D). Typically, Hencky strains larger than four are required to establish a steady tensile stress. However in many extensional flow devices, sample inhomogeneity will prevent control of the kinematics at approximately the same Hencky strain, such that a steady flow cannot be observed. Therefore, the validity of the observations of Rasmussen has been a subject of

debate. In this work, we have adapted for the first time a FSR to operate in constant stress (creep) mode. Since creep is very effective at obtaining steady flow, we have applied the creep protocol to Lupolen 3020D in order to confirm the steady state measured in constant rate of deformation. The novel creep measurements presented here definitively support previous observations of a stress maximum and confirms the steady state measured previously by Rasmussen et al. [1].

[1] H.K. Rasmussen, J.K. Nielsen, A. B. and Hassager, O., J. Rheol. 49, 369-381 (2005).

Wednesday 2:20 C107 PS26

Stress relaxation of entangled polymer melts and solutions following uniaxial extension

Qian Huang[1], Yumi Matsumiya[2], Olga Mednova[3], Henrik K. Rasmussen[4], José Manuel Román Marín[1], Nicolas J. Alvarez[1], Kristoffer Almdal[3], Hiroshi Watanabe[2], and Ole Hassager[1]

[1]Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs Lyngby 2800, Denmark; [2]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan; [3]Department of Micro- and Nanotechnology, Technical University of Denmark, Kgs.Lyngby 2800, Denmark; [4]Department of Mechanical Engineering, Technical University of Denmark, Kgs.Lyngby 2800, Denmark

Experiments on entangled polymer solutions [1] showed that the extensional steady state viscosity initially decreased with increasing the strain rate; but when the strain rate became higher than the inverse Rouse time, it started to increase. In contrast, experiments on polymer melts [2] showed the steady state viscosity decreased monotonically even at the rate higher than the inverse Rouse time. The tube model [1, 3] reasonably described the above behavior of polymer solutions. However, it could not capture the monotonic thinning of polymer melts. Recently Yaoita et al. [4] analyzed the stress relaxation data of polymer melts and solutions both following uniaxial extension. From those data they evaluated the magnitude of stretch/orientation-induced reduction of monomeric friction and used it in their simulation. The simulated results satisfactorily described the monotonic thinning for the polymer melts and the thinning followed by thickening seen for the solutions. However, that work was based on very limited experimental data.

Our previous work on polystyrene melts and solutions has shown that the extensional viscosity is very different in the two systems even when they behave similarly in linear viscoelasticity. In order to further investigate the molecular origin of the difference, in this work we measured the stress relaxation by using a filament stretching rheometer. We compared a nearly monodisperse polystyrene melt of 285kg/mole with its solutions of different concentration. We also examined a polystyrene solution that has the same number of entanglements per chain as the 285kg/mole melt. The results showed that the polystyrene melts and solutions also behave differently in the stress relaxation after fast uniaxial extension. Possible reasons will be discussed on site.

[1] Bhattacharjee et al., Macromol.35: 10131-10148 (2002); [2] Bach et al., Macromol.36: 5174-5179 (2003); [3] Bhattacharjee et al., J. Rheol.47: 269-290 (2003); [4] Yaoita et al., Macromol.45: 2773-2782 (2012).

Wednesday 2:45 C107 PS27

Melt rheology and extensional flow-induced crystallization of poly(1-butene)

Rossana Pasquino, Naveed Ahmed, and Nino Grizzuti

Department of Chemical Engineering, University of Naples, Napoli, Napoli 80125, Italy

Crystalline elastomers are olefin polymers or co-polymers, where the typical mechanical properties of crystalline materials (high rigidity and high stress-to-break) are associated with those of an elastomer (high deformability, high ductility). The above properties can be modulated by suitably changing the degree of order of the monomer distribution along the polymer chain. This has been made possible in recent years by the development of metallocene and post-metallocene homogeneous catalysts. In this paper we focus our attention on syndiotactic Poly(1-butene) (sPB) and investigate both its linear viscoelastic rheology in the melt state and its crystallization behavior under application of extensional flow. All measurements have been carried out on a ARES strain controlled rheometer equipped with a plate-plate geometry for linear viscoelasticity and with the SER extensional tool for flow-induced crystallization. The linear viscoelasticity of molten sPB is found to be quantitatively very similar to its atactic counterpart (aPB). In particular the plateau moduli and, correspondingly, the molecular weight between entanglements of the two polymers are essentially the same. This result is quite different from previous measurements on syndiotactic Polypropylenes (sPP) of varying degree of stereo-regularity. Flow-induced crystallization experiments at room temperature (where the SPB quiescent crystallization kinetics is very slow, order of days) show that extensional flow has a strong effect in accelerating the crystallization kinetics of sPB. Experiments indicate that a multi-fold increase in the crystallization rate can be obtained even at very small values of stretch and stretching rate.

Wednesday 3:35 C107 PS28

X-ray scattering investigation of structural relaxation in an ordered block copolymer melt in uniaxial extensional flow

Erica M. McCready and Wesley R. Burghardt

Northwestern University, Evanston, IL, United States

The structural dynamics of an ordered styrene-ethylene butylene-styrened triblock copolymer have been studied in uniaxial extensional flow using in situ x-ray scattering. Experiments were performed in a custom instrument consisting of an SER extensional flow fixture housed in a convection oven designed to facilitate x-ray access. Use of synchrotron radiation provided sufficient time resolution to study the structural response during inception of uniaxial flow, and as a function of time following flow cessation. The sample studied here exhibits hexagonally packed cylindrical microdomains of polystyrene embedded in a poly(ethylene butylene) matrix. Application of extensional flow produces multiple structural effects, including deformation of the microphase-separated morphology, and a complex reorientation process in which elongated PS microdomains progressively orient along the stretching axis. A series of experiments was run in which samples were stretching to varying Hencky strains, allowing investigation of the nature of structural relaxation from a variety of flow-induced structural states induced during extensional flow. Significant differences in structural relaxation are found depending on the total applied extensional strain. Specifically, relaxation occurs more slowly when flow is stopped at small Hencky strains, where the structural response is dominated by a nearly affine deformation of the microphase separated structure. Larger strains appear to induce more substantial structural perturbations to the deforming samples, and more rapid relaxation of flow-induced deformation and orientation is observed when flow is stopped under these circumstances.

Wednesday 4:00 C107 PS29

Breakdown of time-temperature superposition in transient responses of entangled melts to startup extension

Hao Sun and Shi-Qing Wang

Department of Polymer Science, University of Akron, Akron, OH 44325, United States

It is well known that entangled polymeric materials obey the time-temperature superposition principle in the rheological characterization of both linear viscoelastic and nonlinear behavior in steady state. Here we report the first observations of the violation of the time-temperature superposition principle during startup uniaxial extension of entangled polymer melts. Specifically, we find that at relatively low temperature, but still 20 to 40 degrees above the glass transition temperature, the stress responses of well entangled polymer melts to startup extension do not match at the different temperatures under the same Weissenberg number that is evaluated according to their linear viscoelastic characteristics (LVC). Their shear rheology such as capillary rheometry still seems to obey the WLF relationship derived from the LVC. The interpretation and implication of this new violation of the tTs principle will be discussed in this presentation. The phenomenon confirms that polymer rheology may not be treated at the level of the classical bead-spring picture, on which all popular theoretical descriptions are based.

This work is supported, in part, by a grant from the National Science Foundation (DMR-1105135).

Wednesday 4:25 C107 PS30

Ultra-high strain extensional rheometry of polymer melts

Joao M. Maia and Ricardo Andrade

Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, United States

Usually, when studies on uniaxial extension of polymer melts are performed the main concern is the achievement of the largest possible deformation with a homogeneous stretching of the sample at any given deformation rate. Therefore, it is necessary to ensure that the correct experimental conditions are achieved, which, more often than not, is not the case. In fact, despite a wealth of work available in the open literature that highlights the importance of correctness of the experimental method, many researchers still disregard basic experimental phenomena such as, for example, the almost certain discrepancy between the nominal and the true strain rates being imposed on the sample, poor sample preparation, inadequate sample dimensions and the effects of sample sagging. In this work we build on previous works by our group and use our new CSER, a dual Controlled-Stress/Rate Extensional Rheometer based on the Meissner principle but small enough to fit in the oven of a standard rotational rheometer, to highlight the importance of truly controlling the strain rate in rate-controlled experiments in order to achieve ultra-high deformations in uniaxial extension of polymer melts. This can only be achieved by coupling the ability of the CSER to achieve very strains (something the SER fixture cannot do, for example) with visually accessing the sample during deformation and using a feedback control loop to keep the desired rate constant. By using the control loop to compensate for the deviations in the expected cross-section evolution over time it is possible to minimize or even eliminate both slip at the rollers and the planar component of the deformation known to be present when relatively wide samples are used, e.g., to prevent sagging in SER-type devices. With proper experimental care we have been able to perform true constant rate experiments in various polymers up to Hencky strains in the range of 6 to nearly 9, depending on the polymers. The latter case corresponds to a linear deformation of approximately 8,000.

Wednesday 4:50 C107 PS31

A control scheme for filament stretching rheometers with application to polymer melts

José Manuel Román Marín, Nicolas J. Alvarez, Qian Huang, and Ole Hassager

Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs.Lyngby 2800, Denmark

In the classical controlled deformation extensional experiment, a constant rate of extension is imposed and the stress is monitored as a function of time. In many cases achieving a steady flow under constant rate of extension is only possible if sufficiently large values of Hencky strain are attained (~4). Despite the fact that such strains are in principle accessible by many of the currently used extensional rheometers, steady flow conditions cannot be observed due to inhomogeneities in the sample and the lack of an active control scheme. In this work, we present the details of a scheme for controlling the kinematics of deformation in a filament stretching rheometer [1]. The scheme proposed here consists of a feed-back and a feed-forward term. It is simple to implement, robust and has been recently adapted to operate in stress-controlled (creep) mode. The performance is demonstrated on a commercial low density polyethylene.

[1] Marin, J.M.R. et al., J. Non- Newtonian Fluid Mech. (2012).

Symposium SA

Self-Assembling, Associating and Gel-Like Systems

Organizers: Kendra Erk and Surita Bhatia

Wednesday 1:30 C101 SA20

Mechanical behavior of nanostructured block copolymer micelle solutions and particle loaded systems

Vicki A. Cheng, Melissa Dao, and Lynn M. Walker
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Self-assembled block copolymer templates are used to control the nanoscale structure of materials that would not otherwise order in solution. In this work, we have developed a technique to use close-packed cubic mesophases of a thermoreversible block copolymer (PEO-PPO-PEO) to impart spatial order on dispersed nanoparticles and globular proteins. The interstitial spaces of these micellar crystals are used to template nanoparticles with hydrodynamic diameters ranging on the order of 1-10 nm. The result of this templating is spatially ordered nanoparticle arrays embedded within the block copolymer nanostructure. Studying the transport of these nanoparticles indicates that the structure of the block copolymer generates composites with very different dynamics. The two extremes are systems in which the particles diffuse as if in a polymer solution and systems in which diffusion is essentially hindered completely. In this work, the macroscopic mechanical properties of the gel-like solutions of these cases are compared to understand the relevant lengthscales in the system.

Wednesday 1:55 C101 SA21

Dynamics and microstructure of metallo-supramolecular networks obtained from polyethylene-oxides

Hadi Goldansaz, Dietmar W. Auhl, and Christian Bailly
BSMA, Université Catholique de Louvain, Louvain-la-Neuve 1348, Belgium

Supramolecular polymers are large synthetic molecules, which can self-assemble into well defined architectures via highly directional non-covalent interactions to form macromolecules with desired configurations and properties. Metal-ligand coordination chemistry has been used to prepare a wide range of stimuli-responsive supramolecular architectures with varying hierarchical structures based on the diversity of metal-ligand systems and ease of tuning the interaction strength [1]. In this study poly ethylene-oxide (PEO) is employed as a model polymer system to test the dynamics and stimuli responsive behavior of the transient metallo-supramolecular networks. The strength and characteristic terminal relaxation time of the network proved to be enormously sensitive to the metal ion concentration. Investigations on the terpyridine end-functionalized supramolecular PEO networks using Nickel(II) chloride salt revealed that formation of the metal-bis-terpyridine complexes is favored up to the stoichiometric concentration of the metal ions and mono-complexes are formed at superior concentrations which lead to a decrease of viscoelastic properties of the network [2]. However this trend is replaced at concentrations higher than 2 times the stoichiomety in which very strong gel like behavior is observed that exhibits several orders of magnitude higher elasticity and viscosity by comparing with the stoichiometric composition. Combined rheological, dielectric and microstructure studies illustrated that interactions between Ni(II) ions and polymeric precursor backbone are responsible for such dramatic gel-like behavior, in which metal ions act as physical cross linking agents.

1. J. D. Fox and S. J. Rowan, Macromolecules (2009), 42, 6823; C. Mugemana, J.F. Gohy, C.A. Fustin, Lungmuir (2012) 28, 3018. 2. P. Guillet,C. Mugemana, F.J. Stadler, U.S. Schubert, C.A. Fustin, C. Bailly, J.F. Gohy, Soft Matter (2009) 5,3409.

Wednesday 2:20 C101 SA22

Self-assembly of novel dendronized polymers and cetyltrimethylammonium p-toluenesulfonate

Evis K. Penott-Chang[1], Karolaine N. Silva[1], Alejandro J. Müller[1], Julio C. Cuggino[2], Marcelo Calderón[3], Cecilia I. Alvarez[2], and Miriam C. Strumia[2]
[1]Universidad Simón Bolívar, Caracas, Venezuela; [2]Universidad Nacional de Córdoba, Córdoba, Argentina; [3]Freie Universität Berlin, Berlin, Germany

The interaction of novel dendronized polymers (PLn) containing amide and carboxyl groups with the cationic surfactant CTAT were explored by solution rheometry. When a small amount of PLn, with two different molecular weights, was added to an entangled wormlike micelles solution, a synergistic viscosity enhancement was observed. The highest association tendency with CTAT was found for PL1 (dendronized polymer with the lowest theoretical molecular weight) at the maximum polymer concentration before phase separation (i.e., 100 ppm). The solution viscosity at low shear rates could be increased by an order of magnitude upon addition of 100 ppm of PL1 to a 20 mM CTAT solution. For this mixture, the fluid obtained was highly structured and exhibited only shear thinning behavior from the smallest shear rates employed. These PL1/CTAT mixtures exhibited an improved elastic character (as determined by dynamic rheometry) that translated in a much longer value of the cross-over relaxation time and a pronounced thixotropic behavior which are indicative of a strong intermolecular interaction. In the case of the polymer with a higher theoretical molecular weight, PL2, its association with CTAT leads to an extraordinary doubling of solution viscosity with just 0.25 ppm polymer addition to a 20 mM CTAT solution. Evidence (GPC and DLS) indicates that PLn show a strong tendency to self-aggregate in aqueous solutions, however the addition of any PLn to water did not cause any increase in viscosity up to concentrations of 1000 ppm, thus, in view of the synergistic increases in viscosity obtained, it seems likely that the CTAT-PLn interactions are favored over the PLn-PLn interactions in aqueous solution.

Wednesday 2:45 C101 SA23

Surfactant-activated microgels

Krishnan Chari, Raymond Hsu, Prachur Bhargava, Brian Figura, Wayne Yang, Jung-hyun Park, Ted Clifford, Murat Kadir, and George Benedikt
Lubrizol Advanced Materials, Inc., Cleveland, OH, United States

Microgels are used as rheology modifiers in a broad range of industrial, pharmaceutical, personal and home care applications. Commercial microgels typically comprise chemically crosslinked polymers with a pH-responsive moiety. Free-flowing dispersions of these polymers may be mixed with other ingredients in a formulation and then neutralized. Upon neutralization, the polymers swell to form a close-packed network of swollen crosslinked particles imparting rheological features such as yield stress, viscosity, shear-thinning and optical clarity. Well-known examples of pH-responsive microgel rheology modifiers are crosslinked polyacrylic acid polymers and alkali-swellable emulsion (ASE) polymers based on ethyl acrylate and methacrylic acid. However, pH-responsive microgels suffer from the disadvantage that desired properties are obtained only over a limited span of pH and significant changes in properties are observed in the range of pH values close to the pKa. Although crosslinked microgels with a sulfonic acid group instead of a carboxylic acid group have been prepared in order to overcome this problem, these ionic microgels are not effective at the high levels of surfactant commonly used in personal and home care formulations. Here we describe a new class of nonionic (non-polyelectrolyte) microgels comprising crosslinked amphiphilic copolymers of alkyl acrylates and hydroxyalkyl esters that are activated by surfactant instead of pH. We discuss the mechanism of action of these materials as a combination of swelling of individual polymer particles by surfactant micelles and surfactant-mediated interaction of the swollen microgels using dynamic light scattering (DLS), dynamic rheology and proton NMR. We demonstrate that it is possible to tailor the composition of the copolymers to combine a high degree of swelling with the mechanical rigidity and inter-particle interactions needed to achieve a high yield stress. In contrast to ASE polyelectrolyte polymers, uniform properties are obtained over a broad pH range.

Wednesday 3:35 C101 SA24

Microstructure and rheology of a thermoreversible gel under large amplitude oscillatory shear (LAOS) deformation using time-resolved oscillatory rheo-small-angle neutron scattering (tOr-SANS)

Jung Min Kim, Aaron Eberle, Amanda Kate Gurnon, and Norman J. Wagner
Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States

Large amplitude oscillatory shear (LAOS) rheology is an effective way of studying the nonlinear dynamics of complex fluids. Typically, strain controlled LAOS measurements are interpreted in terms of the resulting stress as a function of strain and strain rate. From the rheological results an interpretation is made about the underlying microstructure of the sample and how it is affected by the imposed deformation. However, this approach remains largely qualitative and indirect due to both the lack of structural information and numerical tools to quantify the structure. Here, we present a new method for a direct, quantitative study of the microstructure under LAOS deformation in the framework of the alignment factor, Af. We use a model thermoreversible adhesive hard-sphere system composed of octadecyl-coated silica particles suspended in n-tetradecane. With temperature the particle potential is controlled and the system is shifted from behaving as a near hard-sphere to an adhesive hard-sphere system leading to aggregation and ultimately a dynamical arrest transition to macroscopic gelation. Time-resolved oscillatory rheo-small-angle neutron scattering (tOr-SANS) measurements in the 1-3 plane are performed by stroboscopically probing the structural evolution as a function of time during LAOS. Under strong shear, the 2D scattering pattern of the system in the gelled state exhibits a strong anisotropy commonly known as a "butterfly" pattern, which corresponds to the stretching of the microstructure along the flow direction. The first structure-Lissajous plots of this model system are presented in terms of an order parameter and Af as a function of instantaneous strain and strain rate. This new analysis demonstrates a novel method for simultaneously measuring the rheology and microstructure during a time-dependent deformation (LAOS).

Wednesday 4:00 C101 SA25

Ultrafast ultrasonic imaging of carbon black gels under large amplitude oscillatory shear

Christophe Perge, Vincent Grenard, Thomas Gibaud, Nicolas Taberlet, and Sebastien Manneville
Physics Laboratory, Ecole Normale Superieure de Lyon, Lyon 69007, France

Attractive colloidal gels display a solid-to-fluid transition as shear stresses above the yield stress are applied. This shear-induced transition is involved in virtually any application of colloidal gels. It is also crucial for controlling material properties. Still the yielding transition is far from fully understood. For instance we find that gels stressed below the apparent yield stress inferred from small-amplitude oscillatory shear can eventually flow if given enough time. Moreover classical rheology experiments do not provide any local insight on such "delayed yielding". In particular, the loss modulus may dominate the storage modulus only because the sample has yielded close a wall while it remains solidlike in the bulk. To go beyond simple rheology experiments we use a high-frequency ultrasonic scanner to image the local displacements of opaque attractive colloidal gels (carbon black gels) under large amplitude oscillatory shear. We find that yielding is both heterogeneous in time and space and we isolate various yielding mechanisms as a function of the amplitude and frequency of the applied oscillatory stress. The amplitude dependence of the yielding behavior hints toward activated processes in line with recent models and the frequency dependence could be explained in terms of self-healing processes within the gel.

Wednesday 4:25 C101 SA26

Gelation through colloidal assembly at liquid interfaces

Jessica A. Witt and Ali Mohraz
Chemical Engineering and Materials Science, University Of California, Irvine, Irvine, CA 92697, United States

Gelation is commonly defined as a rheological transition from a liquid-like material to a viscoelastic solid. In colloidal suspensions, this transformation is typically a result of attractive interparticle interactions. In this talk, a number of alternative routes to colloidal gelation that are based on particle assembly at liquid interfaces will be discussed. The first system involves a two-phase liquid mixture with particles that have a three-phase contact angle ? > 90°. The obtuse contact angle leads to bridging of dispersed droplets by a cohesive monolayer of particles, and gelation results from a percolating three-dimensional particle/droplet network. The second system involves a suspension of neutrally wetting (? ~ 90°) particles in a binary liquid mixture undergoing spinodal decomposition. The particles adsorb to the fluid interface upon phase separation and become jammed when the interfacial area is reduced such that it can only accommodate a monolayer of touching particles. Gelation is then a consequence of particle jamming at the liquid interface. The third system contains a suspension of colloidal particles with a range of contact angles (? = 90°) in the same binary liquid mixture. During spinodal decomposition, the neutrally wetting colloids adsorb to the fluid interface and the remaining particles preferentially partition into one of the liquid phases. Secondary nucleation and growth then results in droplet bridging within the corresponding fluid domains. Gelation is therefore due to a combination of particle jamming at the spinodal interface and the bridging of droplets within the domains. The microstructural origins of gel-like rheology in these systems are explored via quantitative confocal microscopy and bulk rheometry, and will be discussed. Finally, the potential technological applications of these novel multi-phase materials will be reviewed.

Wednesday 4:50 C101 SA27

Mechanics and microstructure of self-assembled molecular gels

Nikola Dudukovic and Charles Zukoski
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Anisotropic or patchy interactions between nanoparticles may result in low volume fraction stiff gels. Here we explore gel formation in suspensions of ~1.5 nm particles which form at extremely low concentrations (<0.001 wt%). One specific type involves hydrophobic peptide based molecules - Fmoc-diphenylalanine (Fmoc-FF). We find that when water is added to a Fmoc-FF/DMSO solution, gels are formed along a line of increasing Fmoc-FF concentration with decreasing water concentration. Rigid (G' > 105 Pa) space filling gels are observed at Fmoc-FF concentrations as low as 0.1 wt%. Gelation in these systems is associated with formation of fibrils that branch to fill space. Here we report on the kinetics of gelation and demonstrate that these gels are reversible in the sense that they can be disrupted mechanically and rebuild strength over time. Small angle X-ray scattering studies covering over three decades in q-space are used to characterize the solution structure above and below the gel transition. We attempt to understand the gelation process as arising from increasing strength of attraction between Fmoc-FF molecules with increasing water concentration. We present studies of gelation kinetics and the mechanics of the resulting gels.

Symposium BS

Rheology in Biological Systems

Organizers: Charles M. Schroeder and Isidro (Dan) E. Zarraga

Wednesday 1:30 C105 BS6

A multi-scale view of platelet adhesion in high shear

Sean Fitzgibbon and Eric Shaqfeh
Chemical Engineering, Stanford University, Stanford, CA 94305, United States

Overall platelet function is an important factor in stopping blood loss, but it is still relatively poorly understood. After a trauma, low red blood cell concentration, or hematocrit, is correlated with significant increases in bleeding time, while a lowered platelet concentration has no discernible effect on bleeding time. Using a large scale Stokes flow simulation, Zhao partially explain this correlation with RBC induced velocity fluctuations acting on platelets in the bulk. We extend their work by investigating the dynamics of platelets in shear once they have marginated to the near-wall region. We simulate fluid forces using the boundary integral equations of Stokes flow, while RBC fluctuations are accounted for with an autoregressive process fit to Zhao et al's data. We represent platelet receptors with a stochastic creation annihilation process, using literature values for parameters when available. To fill in the rest of our model, we directly compare to Kenny's recent series of experiments watching platelets roll and adhere to von Willibrand Factor coated surfaces in a microfluidic device called the *dynamic platelet assay*. Using our model we infer underlying physics from the experimental observables, further expanding our understanding of platelet adsorption in flow.

Wednesday 1:55 C105 BS7

Stability and bifurcation in a simple model for shape changes in discoidal high-density lipoprotein

Eliot Fried[1] and Yi-chao Chen[2]
[1]Mechanical Engineering, McGill University, Montreal, Quebec H3A 0C3, Canada; [2]Mechanical Engineering, University of Houston, Houston, TX, United States

High-density lipoproteins (HDL) remove cell cholesterol and thereby provide protection from atherosclerosis. HDL can adopt a various shapes, including discoidal and spheroidal. Although conversions between these shapes are believed to influence the functionality of HDL, the mechanisms underlying these conversion are not understood. Experimental evidence and molecular dynamics simulations have led to the proposition of an analog model involving an elastic loop spanned by a soap film, corresponding respectively to the major protein component of the HDL and the lipid molecules. Perhaps surprisingly, the literature appears to contain only one very recent work on the problem of an elastic loop spanned by a soap film. We reconsider the formulation of that problem and obtain a boundary-value problem for a vector field that parametrizes both the bounding loop and the spanning surface. Working with the first and second variations of the relevant free-energy functional, we conduct detailed bifurcation and stability analyses.

Wednesday 2:20 C105 BS8

Rapid isolation of viable circulating tumor cells from patient blood samples

Andrew D. Hughes[1], Jeffrey C. Mattison[1], John D. Powderly[2], Bryan T. Greene[3], and Michael R. King[1]
[1]Biomedical Engineering, Cornell University, Ithaca, NY 14853, United States; [2]Carolina BioOncology Institute, PLLC, Huntersville, NC 28078, United States; [3]BioCytics, Inc, Huntersville, NC 28078, United States

Circulating tumor cells (CTC) disseminate from a primary tumor, travel throughout the circulatory system, and can ultimately form secondary tumors at distant sites. Currently CTC counts can be used as predictors of disease severity and direction. A potential use for CTC in the clinic would be develop personalized therapies. To this end, the isolation process should not cause harm to captured cells, and contamination by other cell types, particularly leukocytes, must be avoided as much as possible. Many of the current techniques, including the sole FDA-approved device for CTC enumeration, destroy CTC as part of the isolation process. A biomimetic microfluidic device to capture viable CTC is described, consisting of a surface functionalized with E-selectin glycoprotein in addition to antibodies against epithelial markers. To enhance device performance a nanoparticle coating was applied consisting of halloysite nanotubes. The halloysite nanotube coating significantly enhances device performance by promoting stronger adhesion of fast moving cells, providing increased surface area for protein adsorption, and repelling contaminating leukocytes. The nanotube coating imparts these advantages without altering the fluidic properties that drive the rapid selectin-specific isolation. This device has been successfully used to capture cancer cells from the blood of metastatic cancer patients. Captured cells are maintained for up to 15 days in culture following isolation. In addition, this device has been used to capture viable CTC from both diluted whole blood and buffy coat samples. Ultimately, we describe a technique with functionality in a clinical setting to develop personalized cancer therapies.

Wednesday 2:45 C105 BS9

Location-dependent intracellular particle-tracking using a cell-based coordinate system

Shada Abuhattum, Diana Goldstein, and Daphne Weihs
Biomedical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

The focus of many particle-tracking experiments in the last decade has been intracellular mechanics. In living cells, the analysis of particle motion in is difficult as probes are actively transported within heterogeneous and changing microenvironments. Specifically, regions in the cell exhibit different probe-particle transport, relating to active processes and dynamic local structure. Regions in the cells may respond differently to environmental changes or following treatment making location dependence crucial. Hence, to reveal location dependence of particle transport and cell responses, we introduce a cell-specific polar coordinate system. The polar coordinates are defined by nucleus location and orientation and provide relative location of particles in the cytoplasm. To demonstrate the utility of the approach, we compare cells following ATP depletion with untreated cells. The scaling of the mean square displacement (MSD) showed a marked reduction in activity driving particle transport in the cells. However, it is only by combining the MSD with our approach that we reveal that the combined mechanical response and reduction in activity are actually uniform across the cell cytoplasm. Hence, our approach can reveal new information on the location-dependent mechanics and responses of living cells.

Wednesday 3:35 C105 BS10

Measuring the viscoelasticity of living cells with a cell monolayer rheometer

Claire M. Elkins and Gerald G. Fuller
Chemical Engineering, Stanford University, Stanford, CA 94305, United States

The mechanical properties of living cells are related to a variety of critical cellular functions such as intracellular transport, locomotion, and cell differentiation. Thus a number of biological fields would benefit from a rapid and accurate method to measure the viscoelasticity of living cells. Our research involves the construction of a novel cell monolayer rheometer capable of efficiently measuring the average mechanical properties of an entire cell population. In this rheometer cells are deposited between two collagen-coated coverslips and allowed to adhere to both the top and bottom plates. The top coverslip is then sheared while a sensitive force transducer measures the applied stress. This allows measurement of the viscoelastic modulus of the cell population, as well as stress relaxation and creep behavior. The entire apparatus is mounted on a DIC

microscope, allowing visualization of the cells during deformation using both transmitted light and fluorescence. Fluorescently tagged structural proteins are used to track the position of cytoskeletal stress fibers during the shearing process. Combined with the force measurements, visualization of cytoskeletal deformation provides unique insight into cellular mechanics. Our linear cell monolayer rheometer has been applied to investigate a variety of biological systems, such as human fibroblasts in both monolayer and bilayer configurations, epithelial cells found in the human cornea, and human adipocytes containing deformable lipid droplets.

Wednesday 4:00 C105 BS11

Shear behavior of human skin: Large amplitude oscillatory shear and viscoelastic modeling

Gerrit Peters[1], Edwin Lamers[2], and Cees Oomens[2]
[1]Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands; [2]Biomedical Engineering, Eindhoven Universiy of Technology, Eindhoven, The Netherlands

Skin is a complex multi-layered tissue, with highly non-linear viscoelastic and anisotropic properties. Thus far, a few studies have been performed to directly measure the mechanical properties of three distinguished individual skin layers; epidermis, dermis and hypodermis. These studies however, suffer from several disadvantages such as skin damage due to separation and disruption of the complex multi-layered composition and, sometimes, too thin samples. In addition, most studies are limited to linear shear measurements, mostly small amplitude oscillatory shear experiments, whereas in daily life skin can experience high strains, due to for example shaving or walking. To get around these disadvantages and to measure also the non-linear mechanical (shear) behavior, we used through-plane human skin to measure large amplitude oscillatory shear (LAOS) deformation up to strain amplitudes of 0.1. LAOS deformation was combined with real-time image recording and subsequent digital image correlation and strain field analysis to determine skin layer deformations. Results demonstrated that the overall deformation at large strains became highly non-linear, by showing intra-cycle strain stiffening and inter-cycle shear thinning. Digital image correlation revealed that dynamic shear moduli gradually decreased from 8 kPa at the superficial epidermal layer down to a stiffness of 2 kPa in the dermis. These results show that, from a mechanical point of view, skin should be considered as a complex composite with gradually varying shear properties rather than a three layered tissue. The results were used to model each different layer with a non-linear viscoelastic model (non-linear standard model) and from that predict the overall response of the full skin sample.

Wednesday 4:25 C105 BS12

In situ characterization of the rheology of Staphylococcus epidermidis biofilms

Leonid Pavlovsky[1], John G. Younger[2], and Michael J. Solomon[1]
[1]Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States; [2]Emergency Medicine, University of Michigan, Ann Arbor, MI 48109, United States

Staphylococcus epidermidis RP62a (S. epidermidis) is a biofilm-forming bacterium that is an opportunistic pathogen found on medical implants within the bloodstream, such as catheters and prosthetic heart valves. Reducing the disease burden associated with S. epidermidis may require better understanding of the mechanical features that allow it to persist in the bloodstream. To address this connection, we developed a method to grow Staphylococcus epidermidis bacterial biofilms and characterize their rheological properties in situ in a bioreactor incorporated into a parallel plate rheometer. The temperature (37?C) and shear forces (shear rate > 100 s-1 and shear stress of 0.1 Pa) during growth modeled bloodstream conditions. We measured the linear viscoelastic moduli using small-amplitude oscillatory rheology and the yield stress using non-linear creep rheology. The elastic and viscous moduli of the S. epidermidis biofilm were 11±3 Pa and 1.9±0.5 Pa at a frequency of 1 Hz (6.283 rad/s) and that the yield stress was approximately 20 Pa. We modeled the linear creep response of the biofilm using a Jeffreys model and found that S. epidermidis has a characteristic relaxation time of ~750 seconds and a linear creep viscosity of 3000 Pa•s. The effects on the linear viscoelastic moduli of environmental stressors, such as NaCl concentration and temperature, were also studied. We found a non-monotonic relationship between moduli and NaCl concentrations, with the stiffest material properties found at human physiological concentrations (135 mM). Temperature dependent rheology showed hysteresis in the moduli when heated and cooled between 5?C and 60?C. Through these experiments, we demonstrated that biofilms are rheologically complex materials that can be characterized by a combination of low modulus (~10 Pa), long relaxation time (~1000 seconds), and a finite yield stress (20 Pa). This suggests that biofilms should be viewed as soft viscoelastic solids whose properties are determined in part by local environmental conditions.

Wednesday 4:50 C105 BS13

3-D numerical investigation of biofilm dynamics

Qi Wang[1] and Jia Zhao[2]
[1]Mathematics, University of South Carolina, Columbia, SC 29208, United States; [2]University of South Carolina, Columbia, SC 29208, United States

Bacterial biofilms are ubiquitous in nature and often observed in infectious diseases. They are consisted of water, biopolymers, bacteria, and nutrient materials. They are live materials. so, there growth, deformation, and eradication are intimately tied to the live cellular behavior. They are shown to exhibit viscoelastic behavior under stress. In this presentation, we will present a comphrehensive 3-D hydrodynamic mixture model for biofilms accounting, the extracellular polymeric sustance (EPS), bacteria, and solvent as explicit components in the mixture. The transport of the nutrient, antimicrobial substance, and signaling molecules for quorum sensing effect are modeled as well. In addition, we employ an active nematic gel model for the bacteria to account for its motility. We will discuss the hydrodynamic behavior of the mixture under various flow conditions, spatial distributions of various biofilm components, and predict the material's rheological properties. Full 3-D numerical simulations of biofilm dynamics subject to inflow-outflow boundary conditions will be presented as well.

Thursday Morning

Symposium AP

Award Presentations

Metzner Award Presentation

Thursday 8:00 C106 AP1

New directions in single polymer dynamics: Molecular rheology, hybrid biomaterials, and microfluidic trapping

Charles M. Schroeder
Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Polymers underlie an untold number of technologies ranging from consumer products to electronics. Despite tremendous progress in the field, we still lack a full understanding of the flow properties of polymer solutions and melts. To overcome these challenges, my group is developing new molecular-based approaches to study the dynamics of entangled and branched polymer solutions. In this talk, I will discuss two active areas of research: (1) single polymer dynamics of "new" materials, including truly flexible polymers and branched polymers, and (2) microfluidic trapping for 2-D manipulation and analysis of single nanoparticles and single polymer chains. Recently, my lab extended the field of single polymer dynamics to a new class of materials, including flexible and branched polymers based on chemically modified single stranded DNA (ssDNA). Nearly all previous single polymer studies have relied on double stranded DNA, a semi-flexible polymer with markedly different molecular properties compared to flexible chains. We developed a synthesis platform to produce ssDNA (linear, branched, and copolymers) for single polymer experiments, and we are using this system to study chain relaxation from high stretch and chain dynamics in model flows. In related work, we developed a new theoretical framework that allows for calculation of materials properties (such as polymer elasticity) from non-equilibrium measurements (such as dynamics) by extending the Jarzynski equality to the field of complex fluids. In the second part of the talk, I will discuss the "microfluidic trap", which is a fully automated method for 2-D particle manipulation and trapping based on the sole action of fluid flow. Using this method, we demonstrate exquisite control over solution processing of single polymers in the context of a "single polymer rheometer", thereby allowing for new methods of molecular-level characterization of polymers such as large amplitude oscillatory extension (LAOE). Finally, I discuss the development of a microfluidic Wheatstone bridge, which facilitates rapid dynamic sampling of particles in continuous flow systems.

Symposium SC

Suspensions and Colloids

Organizers: Roseanna Zia and Florian Nettesheim

Thursday 8:40 C106 SC42

Rheological properties of bubble suspensions in yield stress fluids

Lucie Ducloué, Thuy Linh Nguyen Thi, Guillaume Ovarlez, and Xavier Chateau
Laboratoire Navier, Université Paris-Est, Champs sur Marne, France

We study experimentally and theoretically the behavior of suspensions of bubbles dispersed in a yield stress fluid. We observed that the overall properties of bubble suspensions depend upon the deformability of the bubbles. For deformable bubbles, the yield stress of the suspension is the same as the yield stress of the suspending fluid and the overall elastic modulus is a decreasing function of the bubble volume fraction. For non-deformable bubbles, the yield stress and the elastic modulus of the suspension increase with the bubble volume fraction. Comparison of experimental data with theoretical modeling shows that the capillary number accounting for the deformability of the bubbles is not the same in the solid-elastic regime and in the liquid-plastic regime: deformability of the suspending fluid must be accounted for by the elastic shear modulus in the elastic regime whereas bubbles deformability should not be taken into account in the plastic regime.

Thursday 9:05 C106 SC43

Gravity-induced flow of yield stress fluids being squeezed on a plane

Andrei Potanin
Colgate-Palmolive, Piscataway, NJ 08855, United States

Experiments and numerical simulations are used to study gravity-induced spreading of various yield stress fluids on a plane. Rheology of the fluids is characterizes by steady shear and transient tests. Spreading is studied using image processing of samples after they are deposited on a plane. Fluids are modeled as yield stress thixotropic materials by Fluent computational software using measured rheological properties. The comparison of experimental spreading results and modeling data allows us to identify rheological properties of the fluids that affect their spreading characteristics.

Thursday 9:30 C106 SC44

Uniaxial extensional flow of a thixotropic yield stress fluid

Yuriko Renardy and Holly V. Timme
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123, United States

The uniaxial elongational flow of a thixotropic yield stress fluid is studied with a viscoelastic constitutive model (Partially Extending strand Convection model, Larson, 1984) combined with a Newtonian solvent with no assumptions about the existence of a yield stress or thixotropy. The PEC model is based on molecular theory for highly branched polymers with side branches that get in the way of fully extending. A class of initial value problems with prescribed tensile stress is addressed. If the relaxation time is large, then there are two time scales which naturally emerge: a fast time scale for elastic deformation and flow, and a long time scale for small changes in the microstructure. The steady state curve for tensile stress vs elongation rate is non-monotone for a certain parameter range. The time-dependent solutions display an interplay of slow and fast dynamics.

Thursday 10:25 C106 SC45

Visco-plastic settling rate models to determine sag potential of non-aqueous drilling fluids

Sandeep Kulkarni, Sharath Savari, Kushabhau Teke, Robert Murphy, and Dale Jamison
Halliburton, Houston, TX, United States

One of the less understood phenomena in invert-emulsion non-aqueous drilling fluids (NAF) is sag that leads to unwanted density variations. Sag is considered to be a static or dynamic phenomenon and can become severe in highly deviated and complex wells. To understand and tackle this issue, there has been a need for experimental techniques and/or empirical methods to predict sag for different well environments and fluid compositions. A method for quantitatively determining the solids settling rate in a NAF under shear is presented in this paper. The method is based on an empirical equation which is modified form of Stoke's Law that considers the effects of viscous as well as visco-plastic properties of the NAF on solids settling rate. For building/validating the empirical equation, the viscosity is measured using conventional oilfield viscometers while the visco-plastic properties of the fluid under shear in the form of the yield stress are measured by applying Herschel-Bulkley or Bingham plastic models to the rheology data. This is combined with experimental data on solids settling rate U(mm/hr) in NAF obtained from a Dynamic High Angle Sag Tester (DHAST) at chosen conditions of temperature, pressure and shear rate. A method to accurately determine sag in the field has been a long-standing need. This model may be used readily for accurate solids' settling rate predictions using the rheology data under relevant conditions of temperature, pressure and shear. The model could serve as a handy tool for mud engineers to evaluate the sag behaviour at given well conditions and to make speedy decisions at the rig site to optimize fluid formulations for sag management.

Thursday 10:50 C106 SC46

Shear thickening and shear-induced agglomeration of chemical mechanical polishing slurries under high shear

Nathan C. Crawford[1], S. Kim R. Williams[2], David Boldridge[3], and Matthew W. Liberatore[1]
[1]Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO 80401, United States; [2]Chemistry and Geochemistry Department, Colorado School of Mines, Golden, CO 80401, United States; [3]Research and Development, Cabot Microelectronics, Aurora, IL 60504, United States

Chemical mechanical polishing (CMP) is a fundamental technology used in the semiconductor manufacturing industry to polish and planarize a wide range of materials for the fabrication of microelectronic devices (i.e., computer chips). During the high shear ($\geq$1,000,000 s^{-1}) polishing process, it is hypothesized that individual slurry particles (~0.1 μm) collide with one another to form large agglomerates (>0.5 μm) that cause the slurry to shear thicken. These agglomerates tend to dig into the material surface triggering defects such as scratches or gouges during polishing, which cost the semiconductor industry billions of dollars in lost production annually. Our goal is to obtain a detailed understanding of the high shear (>10,000 s^{-1}) rheological behavior of CMP slurries and to link changes in particle structure, both temporary and permanent, to the observed shear thickening response. The slurries of interest consist of fumed silica suspended in water with added KOH for electrostatic stabilization at alkaline pH (10-11). A controlled stress rheometer with a parallel-plate geometry at small gaps (<100 μm) measures the non-linear rheological behavior of the high solids slurry (10-35 wt%). Shear thickening behavior was altered by changing the silica concentration and through the addition of monovalent chloride salts. Small-angle light scattering (SALS) was employed *in situ* with rheological characterization to identify the formation, shape, and size of agglomerates generated under shear.

Thursday 11:15 C106 SC47

Rheology of hydrate slurries

Clint Aichele and Peter E. Clark
School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078-5020, United States

Offshore oil production and pipelining is often hindered by the production of hydrates from the gas-oil-brine mixtures that flow from producing wells. These hydrates can and do form plugs that completely block the flow through pipeline systems. The blockages are expensive to remove and have resulted in the complete abandonment of pipelines that could not be safely or economically cleared. Hydrates often form in water-in-oil systems where the oil is saturated with methane and enough natural surfactants in the oil to stabilize the emulsion. Asphaltenes can also contribute to the problem. Methane hydrates require low temperatures and high pressures to form, which makes them difficult to study in the laboratory. We are using model systems based on mineral oil, water, C-5 and C-6 hydrocarbons, surfactants, and oil soluble additives to raise the density of the outside phase to better match the density of the two phases. The resulting system will form a hydrate at or near room temperature and atmospheric pressure. This allows us to study hydrate formation, annealing, stability, and melting without having to deal with high pressures. Data will be presented on the prehydrate emulsion rheology, the growth and evolution of hydrates under shear, the melting or breakdown of the hydrates at elevated temperatures, and the influence of droplet size and size distribution on hydrate formation.

Thursday 11:40 C106 SC48

Study of the rheology and slump retention properties of micro mortars

Xue Chen[1] and Michael Radler[2]
[1]Formulation Science, the Dow Chemical Company, Midland, MI, United States; [2]Dow Construction Chemicals, the Dow Chemical Company, Midland, MI, United States

Rheology is an important tool to understand the flow ability of cement paste and micro mortar. In this study, both the micromortar rheology and slump retention tests were conducted with various levels of water/cement ratios, sand/cement ratios and, superplasticiser (SP) concentrations. Herschel and Bulkley model was applied to derive the rheological parameters (yield stress and plastic viscosity). The effects of the water and sand loadings on micromortar rheology and slump retention tests were investigated. We also presented the correlations between rheological parameters and the application properties in order to predict the flow behavior of cement pastes and micro mortars. An attempt had been made to identify the range of rheological parameters to achieve the desired flow ability of mortar.

Thursday 12:05 C106 SC49

Converging flow rheometry for characterizing ceramic paste formulations

Kurt A. Koppi and Steve R. Lakso
Core R&D, Dow Chemical, Midland, MI 48667, United States

Certain ceramic paste formulations exhibit a yield stress and significant wall slip which renders rheological characterization of such formulations through typical means (e.g. parallel plate rheometry, capillary rheometry) quite challenging. A converging slot rheometer was recently developed to overcome these challenges. The focus of this presentation will be to describe the converging flow rheometry technique including the appropriate data analysis routine to extract rheological material parameters for ceramic paste formulations.

Symposium PS

Polymer Solutions and Melts

Organizers: Randy Ewoldt and Suraj S. Deshmukh

Thursday 8:40 C107 PS32

Shear banding in polymer solutions: Breakdown of the homogeneity assumption

Michael Cromer, Gary Leal, and Glenn Fredrickson
Department of Chemical Engineering, Univeristy of California, Santa Barbara, Santa Barbara, CA 93106, United States

At the International Congress on Rheology in Portugal we revealed the possibility of shear-banded flow in polymer solutions with an underlying monotonic constitutive curve. Under the Helfand-Fredrickson mechanism, polymer concentration moves up stress gradients such that infinitesimal defects can drive the polymer solution away from homogeneity. In this work, we delve further into the analysis of the two-fluid model and the resulting shear-banded profiles. Since the underlying homogeneous curve is monotonic, the selection process for the number of bands is not obvious, unlike for a non-monotonic curve that, in steady-state, chooses two shear rates at constant stress. Indeed, numerical simulations reveal the possibility of multiple (>2) bands that is governed by the ratio of the relevant length scales. In addition, we further examine the nonlinear, subcritical instability, which results in multiple steady-states, as observed in experiment.

Thursday 9:05 C107 PS33

Mesoscale modeling and simulation of transient networks

Yun Zeng[1], L. Pamela Cook[1], Lin Zhou[2], and Gareth H. McKinley[3]

[1]Mathematical Sciences, University of Delaware, Newark, DE 19716, United States; [2]Mathematics, New York City College of Technology, New York, NY 11201, United States; [3]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Many polydisperse entangled materials such as physically cross-linked gels and biopolymer networks exhibit "slow" relaxation process (which are power-law-like rather than exponential). One such class of materials includes concentrated wormlike micellar dispersions. For a range of ratios of counter ion salt concentration to surfactant concentration the linear response of the materials exhibits Maxwellian, exponential, stress decay. As the counter ion concentration decreases the decay is better described by a stretched exponential (Rehage,Hoffmann , Molecular Phys. 1991). Such a power-law-like viscoelastic response can be captured at the macroscale, by a "fractional" Maxwell model. The slow relaxation behavior is due to the distribution of energetic interactions between the entangled worms or other network components at the "mesoscale". In order to understand the dynamics of these fluids, and to avoid inaccurate closure relationships when constructing continuum-scale models, we model and simulate the evolution in the transient network deformation at the mesoscale.

Our modeling efforts begin from stochastic models in which the transient network is composed of inter-connected and dangling bead-spring dumbbells. While simulations following the spring connectors are computationally efficient, in order to understand concentration effects and inhomogeneous flow behavior, it is necessary to track the network topology in time and space. In these meso-scale models the Fokker-Planck equation is formulated for each of the locally attached, and detached, dumbbells, and coupled with a kinetic model for the attachment/detachment processes. Classically, the attachment/detachment rates are governed by exponential distributions. In this work we examine alternative attachment/detachment scenarios which lead to fractional stress relaxation, and we compare the results with experimental results on CPyCl/salt mixtures as well as gluten/water biopolymer networks.

Thursday 9:30 C107 PS34

Influence of rheological properties on the micro-flow in aqueous polymeric solutions during solvent evaporation

Ashkan Babaie[1] and Boris Stoeber[2]

[1]Mechanical Engineering, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada; [2]Electrical and Computer Engineering, Mechanical Engineering, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

The solvent casting of microstructures uses the evaporation of a solvent from a thin film of a polymer solution. The associated fluid mechanics problem is quite complex because several phenomena contribute to the micro-flow generated inside the film while the solvent evaporates. In order to use this process for controlled polymer deposition on a mould surface, the evaporation-driven flow and the associated phenomena such as the Marangoni effect need to be controlled. The present study investigates the evaporation of an aqueous solution of polyvinyl alcohol (PVA) next to a vertical wall in a micro-fabricated mould (8 mm *8 mm *0.4 mm). Confocal microscopy combined with micro particle image velocimetry (PIV) is used to capture the velocity field inside the film during the evaporation process. Our measurements show the evaporation driven flow toward the wall and the Marangoni effect that generates a surface flow away from the wall during solvent evaporation. In addition, a significant recirculation region can be produced that transports the fluid away from the wall along the bottom of the mould. It is observed that the flow behavior is highly influenced by the solution's rheological characteristics such as its viscosity and elasticity and for more viscous solutions no recirculation is observed. The solution's rheology is highly dependent on the polymer's initial concentration and also its molecular weight and can lead to completely different evaporation-driven micro-flow patterns inside the solution film. This is observed through PIV measurements for solutions with different polymer molecular weights (16,000 to 186, 000 Da) and different initial polymer mass concentrations (~5% to 8%), where the general flow patterns and associated velocity magnitudes correlate with the properties of the polymer solutions and the process conditions.

Thursday 10:25 C107 PS35

Dynamics of nanoparticles in non-Newtonian aqueous dispersions

Firoozeh Babaye Khorasani, Ramanan Krishnamoorti, and Jacinta C. Conrad

University of Houston, Houston, TX, United States

Understanding the dynamics of nanoparticles dispersed in non-Newtonian media is required to optimize their transport for applications, including improved hydrocarbon recovery, environmental engineering, drug delivery and polymer and hydrogel nanocomposites. Nonetheless, the transport properties of nanoparticles in soft complex media are poorly understood. Here, we use single-particle tracking to measure the diffusional dynamics of nanoparticles in non-Newtonian aqueous polymer solutions that serve as models of viscoelastic porous media. We track the motion of polystyrene nanoparticles of diameter 400 nm in aqueous solutions of hydrolyzed polyacrylamide whose radii of gyration are comparable to the diameter of the nanoparticles over a wide-range of dilute and semi-dilute concentrations. At all concentrations, the mean-square displacement (MSD) of nanoparticles at long times is linearly proportional to time, indicating diffusive motion. The viscosity extracted from the MSD systematically varies with polymer concentration but is smaller than the zero shear rate viscosity measured at each polymer concentration using bulk rheometry, indicating that the dynamics cannot be explained in the context of microrheology of viscous solutions. Moreover, the distributions of displacements obtained through particle tracking are not adequately described by a single Gaussian function at all lag times. For dilute polymer solutions (i.e., concentration $c <$ overlap concentration c^*), these distributions can be fit by the sum of two

Gaussian functions, suggesting that the nanoparticles diffuse in two different effective media. For semi-dilute solutions (c > c*), the distributions of displacements are best fit by the sum of an exponential, describing the large displacements, and a Gaussian, describing the short displacements. These functional forms along with the lag time dependence of the characteristic displacement of each relaxation mode indicate the emergence of cooperative dynamics between the nanoparticles and the polymers.

Thursday 10:50 C107 PS36

Exploiting viscoelastic fluids for enhanced particle removal

Travis W. Walker, Theresa T. Hsu, Curtis W. Frank, and Gerald G. Fuller
Chemical Engineering, Stanford University, Newark, CA 94560, United States

The introduction and subsequent removal of highly elastic solutions from surfaces has recently allowed industry to effectively remove colloidal, particulate contaminants from high-grade silicon. The advantage of this continuous process over conventional techniques is the noninvasive removal while generating limited nonhazardous aqueous waste. our group investigated the use of polymeric liquids to act as soft adhesives that effectively eliminate particles without damaging the delicate surfaces. To investigate this removal, we studied four different flow types (shear, syphoning, channel, and rinsing) of various rheological fluids to understand the governing physics that allow for removal. We have shown that the presence of a large elongational viscosity is exploited by local extensional flow gradients to overcome the adhesion of the particulate to the surface. We present experiments that show an increase in removal effectiveness for the siphoning flow over the other flow types while providing a theoretical explanation for the difference.

Thursday 11:15 C107 PS37

Chaotic mixing in serpentine channels due to viscoelastically-induced secondary flows

Robert J. Poole[1], Anke Lindner[2], and Manuel A. Alves[3]
[1]School of Engineering, University of Liverpool, Liverpool, United Kingdom; [2]PMMH, ESPCI, Paris, France; [3]Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Porto, Portugal

We report the results of a detailed numerical investigation of inertialess viscoelastic fluid flow through three-dimensional serpentine (or wavy) channels of varying radius of curavtaure and aspect ratios using the Oldroyd-B model. The results reveal the existence of a secondary flow which is entirely absent for the equivalent Newtonian fluid flow (due to the absence of inertia). The secondary flow arises due to the curvature of the geometry and the streamwise first normal-stress differences generated in the flowing fluid and can be thought as the viscoelastic equivalent of Dean vortices. Estimation of the maximum Lyapunov exponents reveal that the secondary flow causes two nearby trajectories to diverge exponentially in time and that the flow is hence chaotic in nature. The effects of radius of curvature ratio, aspect ratio and solvent-to-total viscosity ratio on the strength of the secondary flow are investigated and shown to be self-similar over a wide parameter range using a modified Deborah number.

Thursday 11:40 C107 PS38

Instable flow of high molecular weight polyacrylamide in confined geometry

Julien Beaumont[1], Laetitia Martinie[1], Hugues Bodiguel[1], Hamid Kellay[2], and Annie Colin[1]
[1]University Bordeaux 1, Rhodia LOF, Pessac 33608, France; [2]University Bordeaux1-Laboratoire Ondes Matière d'Aquitaine, Talence 33400, France

At low Reynolds number (Re<1), elastic turbulence develops in polymer solutions flowing in curvilinear flows for Weissenberg numbers Wi beyond a given threshold Wic. Unlike inertial turbulence (Re>>1), elastic turbulence is due to their normal stress anisotropy [Groisman and Steinberg, Nature, 2000]. It has only been shown very recently, both theoretically [Morozov and van Saarlos, Phys. Report, 2007] and experimentally [Bonn et al., PRE 2011], that elastic turbulence could also occur in rectilinear flows, provided that the perturbation amplitude is sufficiently high. In this work, the aim is to characterize the consequences of this turbulence on the velocity profile of high molecular weight Polyaccrylamide solutions flowing in a straight channel. By varying both flow rate and polymer concentration, we are able to explore a wide range of Wi. Flows driven by a controlled pressure are characterized using particle image velocimetry. For Wi < Wic, the measured velocity field is well accounted for by the bulk flow curve of the shear thinning fluid. For Wi > Wic, this prediction is not valid anymore and a high level of fluctuations is observed. In addition, velocity profiles can be described by a logarithmic behavior in areas where the fluid is highly sheared, similarly to what is observed in inertial turbulence in a rectilinear geometry. A model based on an Olroyd B fluid behavior has been developed to explain the experimental profiles observed. We also investigate in which extend such instable fluid behave in a more complex geometry like porous media.

Thursday 12:05 C107 PS39

A weak-coupling expansion for viscoelastic fluid flows

Matthew N. Moore and Michael J. Shelley
Mathematics, Courant Institute, New York, NY 10012, United States

I will discuss a weak-coupling expansion for the computation of viscoelastic fluid flows. The weak-coupling expansion exploits the small ratio of polymeric to solvent viscosity, occurring for example in Boger fluids. As a consequence of the expansion, a leading-order polymeric stress evolves according to a background Newtonian flow, and this stress is used to correct the motion of bodies. We apply the method to a sphere settling through a viscoelastic fluid. In this case, the background Newtonian flow is known exactly, resulting in semi-analytic solutions for the corrected sphere motion. We recover the well-known transient velocity overshoot, and we present some new predictions when the Weissenberg number is larger than one. We extend the classical settling problem to include an oscillatory body-force, and show how the introduction of a second time-scale modifies the body-dynamics.

Symposium SA

Self-Assembling, Associating and Gel-Like Systems

Organizers: Kendra Erk and Surita Bhatia

Thursday 8:40 C101 SA28

Formation and aging behavior of charged vesicle gels

Mansi Seth and Gary Leal
Department of Chemical Engineering, Univeristy of California, Santa Barbara, Santa Barbara, CA 93106, United States

We have previously shown that beyond a critical volume fraction, repulsive interactions between charged vesicles in a suspension can lead to a spontaneous transformation of the vesicle shape and size. Such transformations are enabled by the fluid nature and low bending rigidity of the vesicle membrane, and result in a lowering of the suspension's volume fraction thereby providing a relaxation mechanism in these concentrated suspensions. Here, we study suspensions of charged vesicles made from surfactant bilayers that are in the gel or solid state at room temperature and have a high bending rigidity. We find that upon extrusion, such vesicle suspensions instantaneously transform into 'jammed' suspensions that have a high volume fraction and behave as visco-elastic gels, similar to hard-sphere suspensions in the glass state. We examine mechanisms involved in the formation of such vesicle gels, and in the subsequent aging or relaxation of their microstructure which occurs over time scales that depend upon the surfactant composition and mechanical properties of the constituent vesicles.

Thursday 9:05 C101 SA29

A multidimensional Hebraud-Lequeux model

Michael Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24060, United States

The Hebraud-Lequeux model was formulated for shearing flows of soft glassy materials. We formulate a frame-indifferent tensorial version of the model and analyze its behavior for small velocity gradients in steady homogeneous flow. We prove that, as for the original one-dimensional version of the model, there is yield stress behavior or not depending on a parameter in the model. This is joint work with Julien Olivier, University of Marseille.

Thursday 9:30 C101 SA30

Diamondoid molecular gels

Mengwen Zhang and Charles Zukoski
Department of Chemical and Biomolecular Engineering, University of Illinois, Urbana-Champaign, Urbana, IL 61801, United States

Gels are made from saturated carbon cage structures. These molecules are rendered attractive through acid-base non-covalent interactions of 1-adamantanecarboxylic acid (A1C) with 1-adamantylamine (A1N), which result in a rapid aggregation with crystallization at vanishing concentration. The resulting particles gel at approximately 3% by weight in DMSO, yielding gels with reversible shearing qualities. Strongest gels are formed at a 1:1 mole ratio of 1-adamantanecarboxylic acid (A1C) and 1-adamantylamine (A1N). At 1:1 ratio, the gel's elastic modulus increases as φ^x with x~4. Here we investigate the microstructure determined by WAXS and SAXS and characterize the frequency dependent flow properties of these diamondoid molecular gels. Particular attention is paid to determine the applicability of models for colloidal gelation to these molecular gels.

Thursday 10:25 C101 SA31

The shear rheology and salt induced vorticity banding of graphene oxide

Michael P. Godfrin[1], Fei Guo[2], Indrani Chakraborty[3], Nicholas Heeder[4], Arun Shukla[4], Arijit Bose[3], Robert Hurt[2], and Anubhav Tripathi[5]
[1]Center for Biomedical Engineering, School of Engineering, Brown University, Providence, RI, United States; [2]Chemical Engineering, Brown University, Providence, RI, United States; [3]Department of Chemical Engineering, University of Rhode Island, Kingston, RI, United States; [4]Mechanical Enginering, University of Rhode Island, kingston, RI, United States; [5]Engineering, Brown University, providence, RI, United States

Graphene has been the subject of an immense amount of research over the past decade as it offers outstanding mechanical and electrical properties. Graphene oxide is a form of graphene with charged oxygen-based functional groups that allow easy processing in the aqueous phase. The advantageous properties of graphene oxide are often exploited in solution and thus it is extremely beneficial to understand and furthermore

control the rheology of the material in water. The shear rheology of graphene oxide in aqueous solution has been investigated. Graphene oxide in aqueous solution has been found to have a relative viscosity on the order of ~10,000 at low concentrations (~0.1 mg/mL). It has also been found to be a pseudoplastic material displaying behavior coinciding well with the Carreau-Yasuda model. Furthermore, it was observed that graphene oxide can be induced into vorticity banding flow with the introduction of salts into solution. Although vorticity banding has been reported in a wide array of different materials, this is the first reported observation of vorticity banding in graphene oxide solutions.

Thursday 10:50 C101 SA32

A novel particulate / polymer composite made with xanthan gum

Ross Clark[1], Rachael Abson[2], Sanyasi Gaddipati[2], Sandra Hill[2], Bettina Wolf[2], and John Mitchell[3]
[1]CP Kelco, San Diego, CA 92123, United States; [2]Division of Food Sciences, University of Nottingham, Loughborough, Leicestershire LE12 5RD, United Kingdom; [3]Biopolymer Solution Ltd, Loughborough, Leicestershire LE12 5RD, United Kingdom

Xanthan gum is a highly successful water soluble polymers due to its stability, pseudoplasticity and thickening efficiency. When dispersed in aqueous solution, colloidal xanthan gum molecules form a weakly associated network. Molecularly dispersed xanthan polymer "solutions" have high levels of elastic modulus and extraordinarily high lower Newtonian viscosity values. This makes xanthan gum a popular choice for many applications from oil well drilling to salad dressing.

Dry xanthan gum powder was processed with extrusion which significantly altered its properties. Water dispersions of this treated xanthan gum shows characteristics of both a particulate thickener and one with colloidally dispersed molecules. A portion of the treated xanthan gum is able to swell but not become fully dispersed on a colloidal size scale. Another portion can fully disperse as individual molecules and contributes the usual xanthan gum properties. The mixture of highly swollen gels and associating xanthan gum molecules produces unique benefits.

The composite product shows a higher elastic modulus and increased strain sensitivity. This leads to a shorter, less stringy flow and a more gel-like texture. It is theorized that such systems will also have enhanced diffusivity for small molecules. This could promote better flavor in foods.

Through a combination of microscopy and rheometry, it can be shown that different amounts of salt (higher levels inhibit swelling) and temperature (higher temperature promote swelling) can be used to achieve similar properties. Birefringent microscopy can distinguish the highly swollen particles resulting from the processing.

While many composite materials rely on two different materials; one for the continuous polymeric phase and one for the particulate fiber phase, this system is novel since it is entirely composed of xanthan gum. Extrusion processing can be used to produce functional properties not possible with the untreated xanthan gum.

Thursday 11:15 C101 SA33

Effect of complex formation on the gel transition and strength of xanthan-gelatin mixtures

Ana R. Cameron-Soto and Aldo Acevedo
Department of Chemical Engineering, University of Puerto Rico, Mayagüez 00680, Puerto Rico

Gelatin-polysaccharide mixtures are commonly used in food, pharmaceutical, and household products. The interactions between the biopolymers could be associative or segregative resulting on phase separation, or a molecular suspension of complexes. Rheological measurements are a useful tool to determine the resulting structure of the mixtures, as well as the optimal processing and formulation parameters to obtain the desired properties of the final product. In this work, we determine the effect of xanthan addition on the gelation temperature and gel strength of aqueous gelatin solutions. A drop in the gelation temperature and gel's strength was observed upon addition of xanthan, until it reached a minimum where no gelation was observed. Afterwards, the gel strength and gelation temperature increased. The observed behavior was attributed to the formation of soluble gelatin-xanthan complexes, which decrease the gelling capacity of the mixture. Nevertheless, at a critical concentration the complexes percolate increasing the gel strength. A set of Takayanagi blending rules for composite gels describing the system as a discrete biphasic system were used. Good qualitative agreement was observed between the predicted and experimental values with only four adjustable parameters in three different regions.

Thursday 11:40 C101 SA34

Characterizing the viscoelasticity of soft contact lenses immersed in saline

Charles P. Lusignan, Charles M. Jarman, and William J. Seyboth
Research and Development, Bausch & Lomb, Rochester, NY 14609, United States

Characterizing the mechanical properties of hydrogels can be challenging, and often requires immersion in water to prevent dehydration. Measurements on actual contact lenses pose additional complications due to their non-uniform thickness and spherical shape. Typically, only stress-strain testing is employed to determine Young's modulus. The viscoelasticity of contact lens materials is believed to impact product performance, but the exact relationships are unknown.

In this talk, we will discuss the development of improved experimental techniques to measure contact lens rheology in saline solutions using customized fixtures in an RSA-G2 DMA. Both conventional and silicone hydrogel lens materials were studied. We observe a variety of frequency responses for the storage and loss moduli. To quantify the measurements we develop empirical models for the viscoelastic response. Additionally, we find that time-Temperature Superposition works well and construct Master Curves using both horizontal and vertical shifts.

Thursday 12:05 C101 SA35

Mobile technology for measuring polymer hydration and viscosity

Jason Maxey, Xiangnan Ye, HsinChen Chung, and N. Tonmukayakul
Halliburton, Houston, TX, United States

A common problem in the industrial application of viscosified fluids is the ability to quickly measure adequate viscosification when field conditions do not lend themselves to use of viscometers. Measuring viscosity is critical for ensuring pump pressures will remain within safety and operating specifications, especially during on-the-fly mixing processes when proper polymer hydration is difficult to confirm.

One potential solution to this problem is the use of mobile video technologies to measure rheological properties. Digital video cameras, in the form of cell phones and tablet devices, are becoming near-ubiquitous. These devices have the processing power to analyze videos of simple fluid flows. The monitored flow can be parsed to measure the fluid viscosity using little more than what the operator already carries and without requiring a separate instrument. Application of this approach to measure the viscosity of biopolymer gels, as well as the degree of polymer hydration, is presented.

Symposium BS

Rheology in Biological Systems

Organizers: Charles M. Schroeder and Isidro (Dan) E. Zarraga

Thursday 8:40 C105 BS14

Rheological properties and micro-flows of suspensions of the green micro-alga Chlorella vulgaris

Antoine Soulies[1], Jeremy Pruvost[1], Jack Legrand[1], Cathy Castelain[2], and Teodor I. Burghelea[2]
[1]GEPEA UMR-61, University of Nantes, CNRS, Saint Nazaire, France; [2]LTN, University of Nantes, CNRS, Nantes, France

A systematic study of the (macro) rheological properties of solutions of microalgae (Chlorella vulgaris) in a wide range of volume fractions is presented. As the volume fraction is gradually increased, several rheological regimes are observed. At low volume fractions the suspensions display a Newtonian behaviour and the volume fraction dependence of the viscosity can be well described by the Quemada model. For intermediate values of the volume fraction a shear thinning behaviour is observed and the volume fraction dependence of the viscosity can be described by the Simha model. For the largest values of the volume fraction investigated an apparent yield stress behavior is observed. Increasing and decreasing stress ramps within this range of volume fractions indicate a thixotropic behavior as well. A detailed characterisation of the micro-channel flows within each of the macro-rheological regimes is presented. The rather unexpected flow irreversibility and emergence of yield stress behaviour are explained by the local aggregation of individual cells.

Thursday 9:05 C105 BS15

Effect of rotational diffusion on the collective behavior of swimming microorganisms in viscoelastic fluids

Yaser Bozorgi and Patrick T. Underhill
Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

Hydrodynamic interactions of swimming microorganisms can lead to coordinated behaviors of large groups. The impact of viscoelasticity on the collective behavior of active particles driven by hydrodynamic interactions has been quantified with the inclusion of rotational diffusion. Oldroyd-B, Maxwell, and generalized linear viscoelastic modeled are considered as the constitutive equation of the suspending fluid, inspired by some biological fluids. A mean field assumption is used to model the suspension dynamics near an isotropic state. The onset of instability has been quantified by a linear stability analysis in terms of wavenumber, diffusivities, and constitutive equation parameters. Some key results are in contrast to suspensions in Newtonian fluids. The maximal growth rate can occur at a particular wavelength, and diffusion can act to make the system more unstable. Viscoelasticity can also affect the long time dynamics of the continuum equations.

Thursday 9:30 C105 BS16

Microfluidic inertioelastically-driven particle focusing in flows of non-Newtonian fluids for flow-cytometry and disease diagnostics

Thomas J. Ober[1], Eugene J. Lim[2], Mehmet Toner[3], and Gareth H. McKinley[1]
[1]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; [2]Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; [3]Center for Engineering in Medicine and Surgical Services, Massachusetts General Hospital, Harvard Medical School, Charlestown, MA 02129, United States

It is now well known that inertial forces in flows of Newtonian fluids through microfluidic devices can cause migration of particles to very specific locations in the cross-section of the microchannels (Di Carlo 2009). It has been proposed that this highly robust localization of particles, often called "inertial focusing", can be exploited for biomedical and clinical applications such as high-speed flow cytometry ($Q > 1$ mL/min) and the isolation of rare and diseased cells from the bloodstream. A major stumbling block in the practical realization of this technology, however, is the need to pre-process and dilute whole blood samples, in part because the role of non-Newtonian rheological effects in particle focusing is currently poorly understood.

We implement a technique developed in our previous work (Lim et al. 2012), to better understand the focusing behavior of particles in flows of non-Newtonian fluids, including model rheological fluids like dilute and semi-dilute polyethylene oxide and polyacrylamide solutions, as well as blood itself in order to isolate the effects of viscoelasticity and shear-thinning. We also investigate the interplay of inertial and elastic forces acting on colloidal particles at flow rates near the onset of inertial turbulence (Wi >> 1, Re ~ 2000). A key aim of this research is the construction of an operating diagram in Weissenberg-Reynolds number phase space, which will be valuable in the design of future particle separation devices and ongoing theoretical and numerical modeling work.

Di Carlo, D. "Inertial Microfluidics." Lab Chip 9, 3038-3046. (2009); Lim, E. J. et al. "Visualization of microscale particle focusing in diluted and whole blood using particle trajectory analysis." Lab Chip 12, 2199-2210. (2012).

Thursday 10:25 C105 BS17

Effects of irreversible and reversible clustering on viscosity of concentrated protein solutions

Jai A. Pathak[1], Prasad S. Sarangapani[1], Steven D. Hudson[2], and Kalman B. Migler[2]
[1]MedImmune, Gaithersburg, MD 20878, United States; [2]Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8542, United States

Equilibrium and non-equilibrium clustering are ubiquitous phenomena in soft matter physics and are typically observed in systems ranging from colloidal suspensions to solutions of monoclonal antibodies (mAbs). Such phenomena are central to understanding and preventing irreversible aggregation in addition to controlling viscosity challenges related to formulation and drug delivery of protein therapeutics. Curiously, little work has been done in exploring the cluster size dependence of low-shear viscosity and intrinsic viscosity in protein solutions in a controlled manner. In this work, we carefully control cluster size of reversible and irreversible clusters formed by globular proteins or monoclonal antibodies over a concentration range of 2 mg/mL-500 mg/mL and pH from 3-9. We find a marked dependence of low-shear viscosity on cluster size using custom-designed silicon-based microfluidic viscometers. Measurements of cluster sizes using static light scattering reveal a correlation of low shear viscosity as well as intrinsic viscosity with the average cluster size. We model the composition dependence of viscosity for the case of equilibrium and non-equilibrium clusters using an adaptation of a model recently presented by Minton for protein mixtures.

Thursday 10:50 C105 BS18

Rheology of clustered solutions of therapeutic monoclonal antibodies

P. Douglas Godfrin[1], Eric Yearley[1], Thomas M. Scherer[2], Steven J. Shire[2], Isidro E. Zarraga[2], Norman J. Wagner[1], and Yun Liu[3]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19711, United States; [2]Late Stage Pharmaceutical Development, Genentech Inc., South San Francisco, CA 94080, United States; [3]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, United States

Concentrated therapeutic protein formulations for subcutaneous injection provide a favorable route for drug therapy; however, numerous challenges arise with regards to their delivery and stability. Native reversible protein aggregation or self-association at high concentrations can lead to undesired consequences, such as irreversible aggregation, phase separation, and high viscosities. In particular, the nature of dynamic protein cluster formation and arrangement in monoclonal antibody (mAb) solutions is still not fully understood. We have applied small angle neutron/x-ray scattering (SANS/SAXS), neutron spin echo (NSE), dynamic light scattering (DLS), and rheological measurements to investigate a few therapeutic IgG1 mAbs. The results shed light on the anisotropic protein interactions, structure and dynamics of mAb dynamic clusters in solution. We compare these results to simulations and rheology of a model clustered solution as a basis for understanding the complex mAb behavior.

Thursday 11:15 C105 BS19

Particulate formation from adsorbed protein layers under flow and agitation using neutron reflectivity and scattering

Ronald L. Jones[1], Tatiana Perevozchikova[2], Katie Weigandt[3], and Christopher Roberts[2]
[1]NIST, Gaithersburg, MD 20899-8541, United States; [2]University of Delaware, Newark, DE, United States; [3]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, WA 20899, United States

Particles in biotherapeutics are disadvantageous, as they are believed to be responsible for an adverse immunogenic response in patients, making investigation of factors leading to protein instabilities a high priority. The exposure of protein therapeutics to various interfaces during manufacturing, storage and shipment procedures can be a potential cause of the formation of insoluble particulates observed in final formulations. Using a combination of neutron reflectivity (NR), a channel flow cell with cyclic flows that mimic agitation, and small angle neutron scattering (SANS), we present data on the role of biofilm formation at surfaces on the formation of particulates and protein aggregation in the bulk solution. Surfaces of interest include glass, rubber, and steel found in manufacturing and use of protein based therapeutics. These techniques provide unique and new insight into the long suspected role of solid surfaces on aggregation in concentrated protein solutions.

Thursday 11:40 C105 BS20

Transport properties of human lung mucus

Greg Forest[1], Paula Vasquez[2], David Hill[3], Scott McKinley[4], and John Mellnik[5]
[1]Mathematics, Biomedical Engineering, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250, United States; [2]Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250, United States; [3]Cystic Fibrosis Center, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250, United States; [4]Mathematics, University of Florida, Gainesville, FL 32611-8105, United States; [5]Mathematics, Bioinformatics & Computational Biology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250, United States

The flow and diffusive transport properties of human lung mucus are explored using particle-tracking, passive microrheology. In particular, we use mucus samples from human bronchial epithelial cell cultures. Particle position time series are analyzed first to understand the underlying diffusive processes for different particle sizes and mucus concentrations, followed by an inference of the viscoelastic properties using the Mason-Weitz protocol. Time permitting, we will highlight the data analysis tools of our group.

Thursday 12:05 C105 BS21

Extensional rheology of Mamaku gum solutions

Aditya Jaishankar[1], May Wee[2], Lara Matia-Merino[2], Kelvin KT Goh[2], and Gareth H. McKinley[1]
[1]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; [2]Institute of Food, Nutrition and Human Health, Massey University, Palmerston 11222, New Zealand

Mamaku gum is a biopolymer extract from the fronds of the Black Fern Tree found in the South Pacific Islands. It has traditionally been used by the Maori tribes of New Zealand as a poultice for the treatment of boils and wounds, as a vermifuge and as a cure for diarrhea. Only recently have the rheological properties of this highly-viscoelastic polysaccharide system been investigated. Rheological characterization in steady shear indicates that these gum solutions show intriguing non-linear rheology with shear-thickening seen beyond a certain critical shear-rate, reminiscent of associative polymer solutions [Goh et al., Biomacromolecules, 8:3414-3421, 2007]. In this contribution we present a detailed characterization of the extensional rheology of Mamaku Gum solutions of different concentrations through the use of the Capillary Breakup Extensional Rheometer (CaBER) and the Filament Stretching Extensional Rheometer (FiSER). We find that beyond a critical concentration the solutions are strongly strain hardening and have extremely high extensional viscosities. In order to understand the nature of the intermolecular interactions that generate these pronounced viscoelastic properties, we systematically study the effect of added urea on the extensional rheology of the gum solutions. We find that increasing the urea concentration progressively decreases the relaxation time and extensional viscosity and we relate these changes to disruption of the intermolecular hydrogen bonding present in the transient gum network. Finally we draw parallels between the effects of increasing temperature and increasing urea concentration on the rheology of the concentrated gum solutions by equating their changes in the energy landscape characterizing the physical network through a 'urea-temperature superposition principle'.

Poster Session

Symposium PO

Poster Session

Organizers: Xue (Ida) Chen and Ubaldo M. Córdova-Figueroa

Wednesday 5:30 Conference Center Lower Level PO1

Connecting nanoscale motion and rheology of gel-forming colloidal suspensions

Subramanian Ramakrishnan[1], Robert Leheny[2], and Carissa Redmon[3]

[1]Chemical and Biomedical Engineering, Florida A&M University, Tallahassee, FL 32310, United States; [2]Johns Hopkins University, Baltimore, MD 21218, United States; [3]Florida A&M University, Tallahassee, FL 32310, United States

We report a combined x-ray photon correlation spectroscopy and rheometry study of moderately concentrated suspensions of silica colloids that form a gel on cooling. The suspensions are comprised of silica colloids, 45 nm in diameter, coated with octadecyl-hydrocarbon chains in decalin at colloidal volume fractions ranging from 0.20 to 0.43. During gel formation, the suspensions acquire a shear modulus that increases with time, while the thermal motion of the colloids becomes localized over an increasingly restricted range. The nanometer-scale localization length characterizing this motion obeys an exact relationship with the shear modulus predicted theoretically from mode coupling calculations (K. S. Schweizer and G. Yatsenko, J. Chem. Phys. 127, 164505,2007). This scaling thus demonstrates a direct quantitative connection between the microscopic dynamics and macroscopic rheology. It further indicates the importance of local structure over longer-range correlations in dictating the dynamical and mechanical properties of such gels.A preliminary XPCS study of mixtures of colloidal silica is also reported in this work.

Wednesday 5:30 Conference Center Lower Level PO3

Shear thickening of corn starch suspensions: Does concentration matter?

Nathan C. Crawford and Matthew W. Liberatore

Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO 80401, United States

Suspensions of corn starch and water are the most common example of a shear thickening system. Investigations into the non-Newtonian flow behavior of corn starch slurries have ranged from simplistic elementary school demonstrations to in-depth rheological examinations that use corn starch to further elucidate the mechanisms that drive shear thickening. We have determined how much corn starch is required for the average person to "walk on water" (or in this case, run across a pool filled with corn starch and water). Steady shear rate rheological measurements were employed to monitor the thickening of corn starch slurries at concentrations ranging from 0 to 55 wt% (0 to 44 vol%). The steady state shear rate ramp experiments revealed a transition from continuous to discontinuous thickening behavior that exists at 52.5 wt%. The rheological data was then compared to macroscopic (~5 gallon) pool experiments, in which impact-induced thickening behavior was tested by dropping a 2.1 kg rock onto the suspension surface. Thickening in the "rock drop" study was not observed until the corn starch concentration reached at least 50 wt%. At 52.5 wt%, the corn starch slurry displayed true solid-like behavior and the falling rock "bounced" as it impacted the surface. The corn starch pool experiments were fortified by steady state stress ramps which were extrapolated out to a critical stress value of 67,000 Pa (i.e., the force generated by an 80 kg adult while running). Only the suspensions containing at least 52.5 wt% (42 vol%) thickened to high enough viscosities (50-250 Pa·s) that could reasonably be believed to support the impact of a man's foot while running. Therefore, we conclude that at least 52.5 wt% corn starch is required to induce strong enough thickening to safely allow the average person to "walk on water."

Wednesday 5:30 Conference Center Lower Level PO4

Boundary driven compression of hard sphere suspensions at constant velocity and normal stress

Mu Wang and John F. Brady

Div. of Chem. and Chem. Eng., California Institute of Technology, Pasadena, CA, United States

We study structural and stress evolution of confined hard sphere colloidal suspensions during uniaxial compression achieved by moving one confining wall towards the other via Brownian dynamics simulations. Compression at both constant velocity and at constant normal stress are examined. Structurally, we monitor the order of the system via correlational order parameters and characterize the structures via the pair-distribution function, Voronoi tessellations, *etc*. When $Pe >> 1$, where Pe characterizes the compression rate relative to the time scale for Brownian motion, we find that the moving boundary not only causes geometric frustration by disrupting Brownian relaxation, but also introduces local ordering near the moving boundary. For a given final gap width, minimum ordered structures form at $Pe \sim 1$ for constant velocity compression. For the stress, at constant velocity the normal stress diverges as the gap width reduces. When $Pe > 1$, the normal stress on the confining walls are proportional to Pe, and the stress distribution changes rapidly in a boundary layer near the moving wall. For compression at constant normal stress, the moving wall eventually fluctuates around an equilibrium position, and the structural and stress evolution depend on the wall mobility and *Pe*. Continuum models for both constant velocity and constant stress simulations are developed to describe the interplay between the moving boundary and Brownian motion. Without any fitting parameters, the model agrees quantitatively with the simulation results for the wall stresses and wall displacements, and qualitatively captures the stress and local volume fractions profiles across the gap through the evolution of the compression.

Wednesday 5:30 Conference Center Lower Level PO5

Flow of biomass undergoing enzymatic hydrolysis

Emilio J. Tozzi[1], Michael J. McCarthy[2], David M. Lavenson[3], Maria Cardona[3], Nardrapee Karuna[4], Tina Jeoh[4], Pernille A. Skovgaard[5], Henning Jorgensen[5], and Robert L. Powell[3]
[1]Aspect Imaging, Davis, CA 95616, United States; [2]Food Science and Tech., Biotechnology & Agricultural Eng., University of California Davis, Davis, CA 95616, United States; [3]Chemical Engineering and Materials Science, University of California, Davis, Davis, CA, CA 95616, United States; [4]Department of Biological & Agricultural Engineering, University of California Davis, Davis, CA 95616, United States; [5]Forestry and Wood Products, University of Copenhagen, Copenhagen, Denmark

The rheological properties of cellulosic biomass suspensions undergoing hydrolysis are influenced by many factors including particle size, shape and concentration. We performed magnetic resonance flow imaging to characterize velocity profiles and rheograms for lignocellulosic and delignified fibers. Depending on the concentration and flow rate many flow phenomena are observed that include turbulence, laminar symmetric and asymmetric velocity profiles and settling. Symmetric, laminar velocity profiles that are well described by generalized Newtonian models only occur at certain ranges of concentration and flow rate. Rheograms obtained during hydrolysis of delignified fibers having different average fiber lengths suggest that crowding numbers computed using length-averaged lengths can be used to predict yield stresses of suspensions where particle aspect ratio undergo rapid changes. In experiments with wheat straw at 5% solids loading the initial velocity profiles were flat, with apparent wall slip. As hydrolysis progressed the profiles changed to a concentric flow with a central plug surrounded by an annular region moving at a non-zero velocity. Later in the hydrolisis the suspensions displayed shear thinning behavior with continuous velocity profiles amenable to obtaining rheograms. Also observed for wheat straw slurries was an increase over time in resistance to flow before any addition of enzymes which is attributed to "swelling" or hydration of the fibers.

Wednesday 5:30 Conference Center Lower Level PO6

Capillary forces in model chocolate suspensions

Susanne Hoffmann, Erin Koos, and Norbert Willenbacher
Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Baden-Württemberg 76131, Germany

Capillary forces can be used to stabilize particle suspensions and precisely tune their rheological behavior. Adding a small amount of an immiscible fluid to the continuous phase of a suspension leads to the formation of a fractal network driven by capillary particle bridging. This occurs even if the secondary fluid wets the particle worse than the bulk fluid. This effect can be used to create food products with distinct texture free of emulsifiers or stabilizing agents.

This poster will present the rheological and thermal behavior of cocoa suspensions in oil. A small amount of water has been added to the suspension to form capillary bridges between the particles. These bridges have been imaged using fluorescence microscopy. The created sample-spanning network induces a change in flow properties and thermal stability. Replacing the water with water / glycerol mixtures or aqueous fructose solutions changes the interfacial and hence the network strength and suspension rheology.

Wednesday 5:30 Conference Center Lower Level PO7

Rheology of particle laden drilling fluid systems

Peter E. Clark
School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078-5020, United States

Drilling fluids are used in the oilfield to clean the hole, carry cuttings, and cool and clean the bit. Horizontal drilling provides a new set of problems in the design and use of drilling fluids. One of the solutions commonly used in the industry involves the addition of small particles into the fluid to lubricate the drill string. This is necessary because the string rests on the bottom of the hole in the horizontal sections. A number of different types of particles are used including glass spheres, hollow glass spheres, and plastic spheres. These materials range in size from 30 microns to over a 1000 microns. Densities are in the range of 0.5 gram/cm^3 to over 2.5 gram/cm^3. The broad range of particle size and density coupled with the flow properties of the base fluid provides interesting measurement challenges. We have used a controlled stress rheometer to study both bentonite and polymer based fluids loaded with spheres of various sizes and densities. Various test fixtures including parallel plates, concentric cylinders, helical rotor and cup, and vane geometries have been used to characterize the slurries.

Wednesday 5:30 Conference Center Lower Level PO8

Rheopectic suspensions with tunable, and even vanishing, yield stress

Guillaume Ovarlez and Philippe Coussot
Laboratoire Navier, Université Paris-Est, Champs sur Marne, France

Materials such as dense suspensions, colloidal gels, concentrated emulsions or foams, are yield stress fluids. Two different classes of yield stress fluids have been recently distinguished: simple yield stress fluids and thixotropic yield stress fluids. For the former there is no significant evolution of structure during flow while for the latter there is a destructuration leading to a decrease of the apparent viscosity followed by a reversible restructuration at rest. Although they are much less often encountered, shear-history-dependent materials of other kind exist, namely rheopectic materials (also called anti-thixotropic materials), the apparent viscosity of which increases during flow. Here we consider suspensions (Carbon black) which have been shown to be rheopectic and focus on the characteristics of their solid-liquid transition. We show that these suspensions behave at first sight as simple yield stress fluids but their rheological behavior is much more subtle. This apparent yielding behavior is associated with a viscosity bifurcation: a series of creep tests at different stress values leads to flows at high shear rates for a stress larger than a critical value (apparent yield stress), but leads to stoppage for a stress lower than this value. However, in contrast with the rheological behavior of thixotropic fluids this apparent yield stress does not at all depend on the time they have been left at rest. This yield stress is tunable: it entirely depends on the previous flow history, which sets up the material in a specific state of structure. Thus these materials can flow steadily for any stress value as long as they have been previously submitted to an appropriate flow history. In addition the critical shear rate separating the flowing region from the static region in steady state also depends on the previous flow history. Finally the spectacular result is that these critical parameters of the fluid can be entirely tuned through a well-chosen flow history.

Wednesday 5:30 Conference Center Lower Level PO9

Rheology of rod-like nanoparticles in liquid crystal polymer solutions

Ana R. Cameron-Soto and Aldo Acevedo
Department of Chemical Engineering, University of Puerto Rico, Mayagüez 00680, Puerto Rico

Liquid crystalline polymers (LCPs) are interesting fluids due to their inherent orientational order and self-organizing properties. Orientation enhances and allows for the control of the mechanical, electrical and thermal properties. Yet, physical properties may be affected by inclusion of particles due to disturbances in the orientation and degree of anisotropy. However, anisotropic particles, such as rodlike nanoparticles, should not significantly affect the phase transition neither the structure of the liquid crystal, due to their geometric similarity with the polymer molecules. In this work, the steady-state viscosity and viscoelastic properties of loaded LCP solutions was determined. The studied systems consist of isocyanate-functionalized multiwalled carbon nanotubes (i-MWCNTs) in poly(n-hexyl isocyanate) (PHIC)/p-xylene, and either carboxylated multiwalled carbon nanotubes (c-MWCNTs) or halloysite nanoclays (HNCs) in hydroxypropyl cellulose (HPC)/acetic acid aqueous solution. The viscoelastic moduli of the PHIC solution was not significantly affected when up to 5 wt% of i-MWCNTs were dispersed using an ultrasonic bath. The steady-state viscosity increased upon addition of 0.5 wt% i-MWCNTs, irrespectively of dispersion method. For HPC solutions, irrespectively of the dispersion quality, the viscosity and viscoelastic properties of the neat matrix are not to be affected by particle loadings of up to 10 wt% for HNCs and 0.5 wt% for c-MWCNTs. A possible interaction between the nanoparticles and the polymer molecules may be improving the dispersion of the nanoparticles. It have been demonstrated that the length of the rod-like nanoparticles is not a critical parameter in the rheological behavior of a LCP. Results suggest that well-dispersed rod-like nanoparticles do not affect the phase transitions (as verified by microscopy) neither the anisotropic structure of semi-rigid LC polymers.

Wednesday 5:30 Conference Center Lower Level PO10

Comparison of Navier-Stokes-Fourier and bivelocity predictions with molecular dynamics simulations for rigid-body rotation of compressible gaseous continua

Shihai Feng, Alan Graham, Alexander M. Mertz, and Antonio Redondo
Los Alamos National Lab, Los Alamos, NM, United States

n this investigation a compressible gaseous continuum (at effectively zero Knudsen number) is contained within the annular region between concentric cylinders undergoing steady rigid-body rotation at the same angular velocity. Each cylinder wall is maintained at the same uniform temperature T_c common to both. The Navier-Stokes-Fourier (NSF) equations predict that the stesdy-state temperature distribution will be isothermal at T_c. However, bivelocity theory predicts a nonisothermal distribution of temperature, with the temperature displaying a minimum near the midpoint of the annular region. These clearly different predictions are compared with the results of large-scale molecular dynamics simulations involving several different molecular species. The resulting temperature distributions are found to be nonisothermal, as predicted by bivelocity theory. We detail the temperature, pressure, and velocity distributions in the annular region and compare them with the theoretical bivelocity predictions.

Wednesday 5:30 Conference Center Lower Level PO11

Self-diffusion and interaction of colloids in liquid crystals via Brownian dynamics simulation

Christian J. Santoni[1] and Ubaldo M. Córdova-Figueroa[2]

[1]Mechanical Engineering, University of Puerto Rico-Mayagüez, Mayaguez, Puerto Rico; [2]Chemical Engineering, University of Puerto Rico-Mayagüez, Mayaguez, Puerto Rico

Colloidal particles in a liquid crystal solvent deform the nearby medium inducing topological defects that strongly depend on their interaction (anchoring) energy. In fact, recent experiments have shown that these defects affect particle diffusivity, the interaction between particles, and bulk properties of the suspension. As the concentration of colloids in the suspension is increased, the colloids interact with each other through the liquid crystal forming aggregates and chain-like structures. For the development of this suspension in useful applications, we must further understand at a particle level the organization of liquid crystal molecules around the colloids and to relate their microstructure with relevant physical properties of the suspension. To pursue this goal, we developed a Brownian dynamics simulation, where it is assumed that the surrounding fluid molecules (liquid crystals) are large enough to be considered as discrete particles of an ellipsoidal shape subject to the Gay-Berne potential. No relative size restriction between the ellipsoids and the colloids is imposed allowing a wide rage of scenarios and longer time scales to consider. First, we corroborate diffusivity results for the case of a single colloidal particle and correlate them to the type of defect created at the particle's surface. Then, we analyze the interaction between a pair of particles for different sizes and potential strengths.

Wednesday 5:30 Conference Center Lower Level PO12

Coarse-grained molecular dynamics simulations of PEGylated lipids and dendrimers

Hwankyu Lee

Chemical Engineering, Dankook University, Yongin 448-701, Republic of Korea

(a) Structure of PEGylated dendrimers: G4 PAMAM dendrimers grafted with poly(ethylene glycol) (PEG) of different sizes (Mw = 550 and 5000) and grafting densities (12-94% of surface terminals) were simulated using the coarse-grained (CG) force fields previously developed and reparametrized in this work. Longer PEG chains with higher grafting density yield PEG-PEG crowding, which stretches dendrimer terminals toward water more strongly, leading to larger size and a dense-shell structure of the dendrimer. Long PEG chains at high grafting densities also penetrate into the dendrimer core, while short ones do not, which might help explain the reduced encapsulation of hydrophobic compounds seen experimentally in dendrimers that are 75%-grafted with long PEG's. This reduced encapsulation for dendrimers with long grafted PEG's has previously been attributed to PEG-induced dendrimer aggregation, but this explanation is not consistent with our previous simulations which showed no aggregation even with long PEG's but is consistent with the new simulations reported here that show PEG penetration into the core of the dendrimer to which the PEG is attached.

(b) Self-assembly of PEGylated lipids: Self-assembly of PEG-grafted lipids at different sizes and concentrations was simulated using the MARTINI CG force field. Mixtures of lipids and PEG-grafted lipids in water self-assembled to liposomes, bicelles, and micelles at different ratios of lipids and PEGylated lipids. Average aggregate sizes decrease with increasing PEGylated-lipid concentration, in qualitative agreement with experiment. PEGylated lipids concentrate at the rims of bicelles, rather than at the planar surfaces; this also agrees with experiment, though the degree of segregation is less than that assumed in previous modeling of the experimental data. The ability of PEGylated lipids to induce the membrane curvature by the bulky headgroup with larger PEG, and thereby modulate the phase behavior and size of lipid assemblies, arises from their relative concentration.

Wednesday 5:30 Conference Center Lower Level PO13

Mesoscopic simulation of entangled polymers via an alternative approach to Dissipative Particle Dynamics

Shaghayegh Khani, Mikio Yamanoi, and Joao M. Maia

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

Dissipative Particle Dynamics (DPD), despite its good potential in simulating soft matter, has some limitations when studying the entangled polymer systems. First limitation which arises from utilizing soft potentials in DPD is associated with unphysical bond crossings. The bond crossings can be avoided by introducing a segmental repulsive potential to the bonds. Another deficiency of DPD in simulating fluids is related to the Schmidt number. In standard DPD the momentum and mass transfer at the same rate and thus this dimensionless number takes a gas-like value (~1) when simulating fluids. In order to overcome this problem a Lowe-Andersen thermostat was used as an alternative method to DPD and the thermostat was found to be more successful in controlling the temperature in equilibrium state (independent from the time step) and over a wide range of shear rates. The ability of the method in capturing the entanglement effect and reproducing the static and dynamic properties of polymer melts and the scaling laws were investigated and the results were compared to the ones from standard DPD. The performance of the method in capturing the main features of the shear flow and reproducing linear and nonlinear viscoelastic properties was also evaluated.

Wednesday 5:30 Conference Center Lower Level PO14

Automated hydrodynamic trap for single molecule polymer dynamics

Christopher A. Brockman and Charles M. Schroeder

Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States

For nearly two decades, fluorescently-labeled double stranded DNA (dsDNA) has been the model system for studying single molecule polymer dynamics in non-equilibrium conditions. Single polymer molecule studies utilizing double stranded DNA (dsDNA) have provided a treasure trove of information regarding polymer dynamics; however, dsDNA is a semi-flexible polymer with markedly different local molecular properties and a large persistence length (l˜53 nm) compared to flexible polymer chains, such as polystyrene (l˜0.7 nm) and ssDNA (l˜0.6 nm). Recently, we developed a biochemical synthesis platform for producing long strands of fluorescently-labeled single stranded DNA (ssDNA). In addition, our lab has also developed a microfluidic-based, automated hydrodynamic trap to confine individual particles in free solution at the stagnation point in planar extensional flow. In this work, we extend the use of the automated hydrodynamic trap to study chain dynamics of both dsDNA and ssDNA in extensional flow. As a proof of principle, we trapped single molecules of dsDNA for up to 10 minutes enabling a host of experiments, including repeated relaxation time measurement an individual molecule and chain behavior for both randomly varying and oscillating strain rates. We then used the automated trap to measure ssDNA relaxation for chains with varying molecular weights and compared the results to our dsDNA measurements to elucidate the differences between relaxation time scaling for "real" and "ideal" chains. Overall, we seek a molecular-based understanding of the non-equilibrium dynamics of flexible polymer chains, which is crucial for control in processing and molecular self-assembly.

Wednesday 5:30 Conference Center Lower Level PO15

Wall slip analysis with FT rheology

Seher Ozkan
Materials Science Group, Global R&D, Ashland Inc., Wayne, NJ 07470, United States

Wall slip behavior and slip velocities of three different microgels of crosslinked poly(acrylic acid), crosslinked methyl vinyl ether/maleic anhydride copolymer, and crosslinked vinyl pyrrolidone/acrylic acid copolymer) were characterized by a modified Mooney method and straight-line marker technique. The slip parameters determined from conventional rheological characterization methods were correlated with a more recent method, Fourier Transform Rheology with Large Amplitude Oscillatory Flow data (LAOS). Other conventional rheological parameters, such as storage and loss modulus from conventional dynamic data, low and high shear rate viscosities, yield stress, consistency index and power law index from a Herschel-Bulkley model with and without suppressing wall slip, were also correlated with the parameters determined from LAOS analysis. Results were statistically analyzed by principle component analysis (PCA) and linear regression analysis. Rheological experiments, without wall slip, revealed that gel strength in the linear viscoelastic region and yield stress of these materials are similar, but exhibit significantly different wall slip and thixotropy behavior in the low shear rate region under wall slip conditions. In particular, the rheological parameters of 1% crosslinked vinyl pyrrolidone/acrylic acid copolymer are significantly affected by wall slip and/or thixotropy related shear banding phenomena. Above the critical shear rate, which corresponds to the yield stress, the materials do not slip and behave as conventional, shear-thinning polymeric fluids. The linear regression analysis of the slip parameters obtained from Mooney analysis and the LAOS data revealed that the even harmonics extracted from the Fourier amplitude spectrum can be used to monitor the slip behavior of the microgels. The linear regression analysis results show a strong correlation between the slip velocity and the relative intensity of the second harmonic (I2/I1, the ratio of the second harmonic to the principle harmonic).

Wednesday 5:30 Conference Center Lower Level PO16

Onset of whipping in the melt blowing process

Changkwon Chung and Satish Kumar
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Melt blowing is a common process for the production of polymer fibers, but its effectiveness can be greatly influenced by the occurrence of fiber whipping. This paper reports the results of a systematic parametric study aimed at elucidating the factors that determine the onset of whipping in the melt blowing process. A quasi-one-dimensional model developed by Yarin and co-workers [J. Appl. Phys. 108 (2010) 034913] is analyzed in detail and extended to consider the influence of different constitutive models. It is found that whipping requires sufficiently large levels of inertia in the fiber and air, as well as a strong inlet perturbation. Strong longitudinal stresses along the jet axis are required too, although elasticity is not necessary. Also essential are a drag force that varies along the fiber length, and an air velocity that decreases in magnitude away from the fiber centerline. Comparison of results from several different constitutive models suggests that melt inertia rather than melt rheology is the more dominant factor in controlling fiber shapes. The results of the present work are expected to be helpful for the development of more quantitatively accurate models of the melt blowing process.

Wednesday 5:30 Conference Center Lower Level PO17

Nanorheology of ultrathin polymer films: Bubble inflation and liquid dewetting

Jinhua Wang and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

There is considerable current interest in the behavior of ultrathin polymer films due to the observation that the glass transition temperature of freely suspended films of polystyrene seems to decrease by over 70 °C when the thickness approaches 10 nm or below. Furthermore, films on supported substrates show much smaller reductions in the glass transition temperature, which leads to the question of whether or not the rigidity of the support influences the dynamics of the ultrathin polymer films. To address this issue, we undertook experiments in which a polymer film is floated onto a liquid substrate, in this case glycerol, and because of the specifics of the polymer-substrate interactions, it dewets. The shrinkage and known surface energies of the systems permit calculation of the creep compliance of the films. While the glassy regime itself cannot be probed, we find that the Rouse-rubbery and terminal flow regimes can be probed. What is observed is that the films dewet at close to the macroscopic glass transition temperature at thicknesses above approximately 25 nm. Below this value one observes a reduction in the glass transition temperature (shift of the creep curves) of approximately 30 °C at 4 nm in thickness, i.e., the behavior is similar to what is observed in films supported on rigid substrates. The conclusion, then, is that the substrate surface interactions with the polymer determine the glass transition temperature reductions while the substrate rigidity is not of fundamental importance. Further work is required to investigate what subtle aspects of the polymer/substrate interactions govern the thin film behavior.

Wednesday 5:30 Conference Center Lower Level PO18

Homogeneous planar elongational flow and elastic instabilities in an optimized-shape cross-slot extensional rheometer

Simon J. Haward[1] and Gareth H. McKinley[2]
[1]FEUP, University of Porto, Porto, Portugal; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

A cross-slot flow geometry, with a shape that has been optimized by numerical simulation of the fluid kinematics, is fabricated using wire electro-discharge machining and subsequently employed to measure the extensional viscosity of a range of dilute and semi-dilute polymer solutions. MicroPIV is used to verify the homogeneity of the kinematics and full-field birefringence microscopy is used to monitor the evolution and growth of macromolecular anisotropy along the stagnation point streamline. We observe the formation of a strong and uniform birefringent strand when the dimensionless flow strength exceeds a critical Weissenberg number, Wi = 0.5. Birefringence and bulk pressure drop measurements in this Optimized Shape Cross-slot Extensional Rheometer (OSCER) provide self-consistent estimates of the planar extensional viscosity of viscoelastic test fluids over a wide range of deformation rates (up to 600 s^{-1}). Measurements with a monodisperse dilute polymer solution are also in close agreement with numerical simulations performed using a finitely extensible non-linear elastic (FENE) dumbbell model. As the imposed extension rate in the OSCER device is increased the homogeneous planar elongational flow ultimately becomes unstable. High-frame rate video-imaging of the birefringence field is used to construct space-time diagrams of the evolution in the flow for seven different viscoelastic test fluids and to construct the first stability diagram for planar extensional flows in cross-slot devices. The mode of instability is found to depend on the elasticity number (El = Wi/Re) of the fluid, with a steady symmetry-breaking purely-elastic bifurcation observed at high El >> 1, and time-dependent three-dimensional inertio-elastic instabilities dominant for El < 1.

Wednesday 5:30 Conference Center Lower Level PO19

The rheological properties of polyacrylonitrile (PAN) solutions in N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO)

Youngho Eom and Byoung Chul Kim
Department of Organic and Nano Engineering, Hanyang University, Seoul, Republic of Korea

Polyacrylonitrile (PAN) has a lot of highly polar nitrile groups, which generate strong intra- or inter-chain polar interactions. Hence, PAN solutions in polar solvents exhibit very complicated physical properties. In this work, the effects of solubility and chemical affinity of polar solvents on the rheological behaviors of PAN solutions were investigated. We selected two solvents, N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), having different polar characters and charge distribution states. PAN/DMSO solutions gave greater intrinsic viscosity and hydrodynamic size than PAN/DMF in the dilute concentration range. In addition, coil size of PAN chains in both solvents were decreased with increasing temperature. In high concentration range, however, increasing temperature resulted in an increase of dynamic viscosity (?') of PAN solutions. Further, PAN/DMF systems gave higher ?' and greater yield stress than PAN/DMSO systems. TEM photographs revealed that PAN/DMSO solutions produced a co-continuous morphology but PAN/DMF solutions gave rise to dispersed morphologies at 30°C.

Wednesday 5:30 Conference Center Lower Level PO20

A simple method for determination of the normal stress differences in polymeric fluids

Meiyu Zhai and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

Normal stress differences in complex fluids are important in the evaluation of nonlinear behavior and their measurement is often challenging. Alcoutlabi et al[1] have evaluated two methods of obtaining these coefficients for polymer fluids. The first method (TFCPPP) uses a combination of parallel plate and cone-plate measurements. The other method uses a pressure plate in cone-plate or parallel plate geometries[2]. They found that the TFCPPP method is prone to error and the pressure plate method is accurate but needs a special sensor to measure the pressure gradient across the sample radius. Alcoutlabi et al1 also suggested that "the strain potential-total force" method, developed for transient experiments[3], might provide a better solution to determine the normal stress differences as it combines both accuracy and simplicity. However this method has not been applied directly to steady state data. In the present work we propose a new method to determine the normal stress differences in steady state flows. Both transient and steady shear measurements were carried out on a parallel plate rheometer using fluids with different entanglement densities. Torque and normal force responses are used to demonstrate the utility of the proposed method, i.e., we show that the first normal stress difference is related to the full history of the shearing stress in the start-up to steady shear experiment. This, then, permits the determination of the second normal stress difference from the total normal thrust information. We find, typical of other more complicated methods, that the second normal stress difference is negative and smaller in magnitude than the first normal stress difference. These results are considered in the context of the Doi-Edwards model.

1. M. Alcoutlabi, S.G. Baek, J.J. Magda, X. Shi, S.A. Hutcheson and G.B. McKenna, Rheol. Acta 48, 191-200 (2009); 2. J.J Magda, J. Lou, S.G. Baek and K.L. DeVries, Polymer 32, 2000-2009 (1991); 3. C. Sui and G. B. McKenna, J. Rheol. 51, 341-365 (2007).

Wednesday 5:30 Conference Center Lower Level PO21

Enhanced charge transport through engineering the network structure of conjugated polymers for photovoltaic applications

Gregory Newbloom[1], Katie Weigandt[2], Jeff Richards[1], Pablo de La Iglesia[1], and Danilo Pozzo[1]
[1]Chemical Engineering, University of Washington, Seattle, WA 98195, United States; [2]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, WA 20899, United States

The sun provides the United States enough annual energy to meet the current power consumption rate 10× over.[1] Organic photovoltaic (OPV) devices with modest efficiencies (> 10%) have the potential to harness this abundant resource in a cost-effective manner. Conjugated polymers, such as poly(3-hexylthiophene) (P3HT), are often utilized in OPV devices. The solubility of conjugated polymers in solution can be tuned to induce self-assembly and gelation at high concentrations. The interconnected network structure formed through gelation is ideal for enhancing the charge transport capabilities of OPV devices. This poster presents our work towards understanding the fundamental gelation mechanism for P3HT using combinations of simultaneous small angle neutron scattering, rheology and dielectric spectroscopy.[2] Furthermore, we present how self-assembly can be tuned to generate unique structures with substantial differences in mechanical and electrical properties.[3] Finally, we present our current successes and future plans for incorporating these promising structures in functional organic photovoltaic devices.[4] References: [1] - Kalowekamo et al., Solar Energy (2009), 83, 1224, [2] - Newbloom, G. M. et al., Soft Matter 2012, 8, 8854-8864, [3] - Newbloom, G. M. et al., Macromolecules 2012, 45, 3452-3462, [4] - Richards, J. J. et al., J. Colloid Interface Sci. 2011, 364, 341-350

Wednesday 5:30 Conference Center Lower Level PO22

Elastic internal yielding of cold drawn polymer glasses well below glass transition temperature

Shiwang Cheng and Shi-Qing Wang
Department of Polymer Science, University of Akron, Akron, OH 44325, United States

This work reports and studies a devitrification phenomenon associated with uniaxial extension of ductile polymer glasses. Our experiments show that cold drawn polymer glasses such as PC and PMMA display a considerable level of tensile stress upon warming up above the storage temperature. It is the intra-chain tension that makes a glassy polymer devitrify well below the glass transition temperature. For polycarbonate, the phenomenon shows up 110 ^{o}C below its glass transition temperature $T_g = 145\ ^{o}$C. This is evidence to support the idea that the mechanical stress in uniaxial extension may be largely intra-chain in origin, i.e., arising from a load bearing chain network.

Wednesday 5:30 Conference Center Lower Level PO23

Slip between polyolefins and extrusion die surfaces

Andrew M. Schmalzer and A. Jeffrey Giacomin
Rheology Research Center and Mechanical Engineering Dept., University of Wisconsin - Madison, Madison, WI 53706, United States

We explore the effect of extrusion die composition and die surface morphology on the slip properties of polyolefins using a sliding plate rheometer. Our experiments consist of five different plate materials, and three different resins. We use steady simple shear to obtain shear stress as a function of shear rate for different gaps, from which we can then identify the slip velocity using the Mooney analysis. We then fit several slip models to our experimental measurements, and find the hyperbolic sine model to be accurate. Our analysis includes characterization of the composition of the sliding plates by energy dispersive spectroscopy (EDS), surface energy measurement by contact angle goniometry, and surface roughness measurement by white light interferometry. We conclude our analysis by adimensionalizing slip, and show using these dimensionless groups how slip occurs.

Wednesday 5:30 Conference Center Lower Level PO24

The effect of isomer on the rheological properties of polyetherimides

Manojkumar Chellamuthu[1], Gurulingamurthy Haralur[2], and Deepak Doraiswamy[3]
[1]Analytical Technology, SABIC, Mt. Vernon, IN 47620, United States; [2]Specialty & High Performance Technology, SABIC, Mt. Vernon, IN 47620, United States; [3]Global Compounding Technology, SABIC, Exton, PA, United States

Poly (etherimide) (PEI) is a well-known high performance resin with applications in markets requiring high temperature resistance, stiffness, and strength. The detailed rheological characterization is critical to define optimum processing conditions. The investigation of the flow behavior of two materials with different positional isomers will be presented in this talk. The main objective of this work is to address the role of entanglement density and segmental relaxation on the shear thinning behavior. A comparison with extensional rheology is also presented. These results will provide guidelines for the interactions between structure, properties and processing behavior

Wednesday 5:30 Conference Center Lower Level PO25

Large-amplitude oscillatory shear of thixotropic viscoelastic constitutive models

Brendan C. Blackwell and Randy H. Ewoldt
Mechanical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States

In this work we explore the use of large-amplitude oscillatory shear (LAOS) as a tool to compare and contrast the behavior of constitutive models that exhibit both thixotropic and viscoelastic phenomena. We demonstrate this use of LAOS by examining the strain controlled LAOS (LAOStrain) response of three closely related constitutive models as a function of four dimensionless parameters: two LAOStrain deformation parameters (the Deborah number and the Wiessenberg number) and two material parameters (the ratio of viscoelastic to thixotropic timescales and the ratio of solvent viscosity to aggregate viscosity). We present these results in a manner that eases the challenges of visualizing a response to four independent parameters. Finally, we address the important differences between strain control and stress control (LAOStrain versus LAOStress) in regards to the same three constitutive models. Through this analysis we show that LAOS characterizes the viscoelastic and thixotropic behavior and provides a useful fingerprint of each constitutive model. These data can be used to inform constitutive model selection and therefore improve the accuracy of flow modeling of thixotropic viscoelastic fluids.

Wednesday 5:30 Conference Center Lower Level PO26

Dielectric relaxation of monodisperse linear PI: Contribution of constraint release

Yumi Matsumiya and Hiroshi Watanabe
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Combination of dielectric and viscoelastic measurements has revealed several interesting features of entangled polyisoprene (PI), for example, success and failure of the dynamic tube dilation (DTD) picture for monodisperse linear and star PI, respectively. For monodisperse linear PI, recent simulations/theoretical modeling suggest that the thermal constraint release (CR) mechanism has no influence on the dielectric relaxation time in the well-entangled regime, which contradicts to previous data. Thus, we have revisited this problem. Specifically, we have made dielectric and viscoelastic measurements for PI/PI blends having the component molecular weights of 43k/1M and 99k/1M and containing 10 vol% of the low-M component (43k or 99k). It turned out that the dielectric relaxation time of those dilute low-M component increases on blending. Thus, the relaxation time of linear PI in the monodisperse system is reduced by the CR mechanism even in the well-entangled regime (up to M/Me = 20). This "ugly" fact, forcing us to consider the "beautiful" simulation/modeling to be insufficient, can be related to the success of the DTD picture for the monodisperse linear systems. The DTD process, being activated by the CR mechanism in those systems, can shorten the tube length to accelerate the dielectric relaxation therein, so that the lack of DTD for the dilute low-M PI chains in the matrix of 1M matrix possibly retards the relaxation of those dilute chains.

Wednesday 5:30 Conference Center Lower Level PO27

Rheology of linear and branched polylactides

Sahar Nouri, Pierre G. Lafleur, and Charles Dubois
Chemical Engineering Department, Ecole Polytechnique de Montréal, Montreal, Quebec H3C 3A7, Canada

Polylactide (PLA) is a thermoplastic polyester that offers desirable characteristics such as good mechanical properties, compostability and production from renewable resources. However, it is also affected by some deficiencies such as brittleness, slow crystallization and poor processability. The low melt strength of linear PLA remains a challenge for applications requiring high melt elasticity such as film blowing process. Reactive modification of linear PLA and direct synthesis of branched polymers can both be used to produce branched PLA. However, the first approach is limited due to the possibility of crosslinking, gel formation and lack of a real control over the final structure, while the second method allows for a great flexibility in designing different molecular architectures. It is thought that branched and hyperbranched PLA could enhance the processability of PLAs blends, particularly with respect to elongational flow. In this work, we prepared star shaped, comb like and hyper-branched PLAs by ring-opening polymerization of lactide with pentaerythritol and triglycerol as multifunctional initiators and glycidol as a cyclic comonomer with hydroxyl group. Rheological properties of branched PLAs were compared to a commercial linear one. In shear mode and LVE conditions, linear PLA showed a well-defined Newtonian plateau over a wide range of angular frequency while for the branched structures the transition from the Newtonian plateau to the power-law region occurred at lower frequencies and they revealed more intensified shear-thinning behavior. Relaxation spectra were calculated, showing that peaks appear at higher relation times for the branched samples. Uniaxial extensional viscosity was measured by an ARES rheometer equipped with a SER universal testing platform. Although the transient elongational viscosity of some branches were lower than the linear ones, a significant strain hardening was only observed for branched polymers.

Wednesday 5:30 Conference Center Lower Level PO28

Adhesive and rheological properties of lightly cross-linked fluorosilicone polymer gels

Nicholas B. Wyatt and Anne M. Grillet
Sandia National Laboratories, Albuquerque, NM 87185, United States

Lightly cross-linked polymer gels are soft, sticky materials with tunable properties making them ideal for use as pressure-sensitive adhesives. Here, the viscoelastic and adhesive properties of fluorosilicone gels of varying equilibrium modulus are examined. The commercially available material manufactured by Dow Corning is a mixture of fluorosilicones that, when heated, undergoes a platinum catalyzed reaction to form a lightly cross-linked gel swollen by long chain fluorosilicone polymers which are not covalently bound into the gel network. In each case, the sol

fraction of the gel is about 50%. The rheology and adhesion properties of the resulting gel can be tuned by varying material parameters such as crosslink density, sol fraction, and polymer molecular weight of the cross-linked polymers or the polymer sol. Adhesive properties such as peak adhesive force, work of adhesion and strain to failure are measured using a typical probe tack test and correlations to the gel rheology are made. Further, adhesive bond failure mechanisms such as bulk cavitation and interfacial cavitation are explored in relation to separation rates and gel material properties.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Wednesday 5:30 Conference Center Lower Level PO29

Effect of supersaturation on the rheological, structural and dielectric properties of conjugated polymer organogels

Pablo de La Iglesia and Danilo Pozzo
Chemical Engineering, University of Washington, Seattle, WA 98195, United States

The control over the gelation of conjugated polymers promises to be an impactful technology in the field of organic photovoltaics and transistors. Organogels of conjugated polymers have structural advantages in these applications due to their nanoscale morphology and because they can increase charge transport efficiency due polymer crystallization. This study demonstrates the possibility of controlling the organogel network structure by tuning the driving force for aggregation so that the properties of the materials can be optimized for a variety of applications. In this study, rheological measurements, small angle neutron scattering (SANS), and impedance spectroscopy are used to characterize the effect of supersaturation on the structure and properties of poly(9,9 di-octylfluorene) (PFO) and poly(3-hexylthiophene) (P3HT) organogels. The mechanical and structural properties of the gels are characterized under different temperatures and solvent conditions. Rheological studies reveal a strong dependence between supersaturation and aggregation kinetics. Fitting of the gelation kinetics suggests a drastic change in the dimensionality of the networks (i.e. fractal dimension) as the driving force for gelation is varied. Neutron scattering experiments also provide insight into the shape and size of the polymer aggregates. The scattering profiles also reveal a dependency between the characteristic size of the networks and the degree of supersaturation. The conductivity is also probed during gelation and there is a substantial increase in the conductivity after gelation, compared to the solution phase, for some systems. There are also significant changes in the conductivity as the driving force for gelation is changed. These results represent a systematic approach towards engineering conjugated polymer organogels for organic electronic applications.

Wednesday 5:30 Conference Center Lower Level PO30

Flavoring effect on the thermal gelation of HPMC physical gels

Carlos A. Pinzon and Aldo Acevedo
Department of Chemical Engineering, University of Puerto Rico, Mayagüez 00680, Puerto Rico

Understanding of the gelation process of pharmaceutically relevant physical gels is necessary to optimize formulations and processes, as well as to discern gelation mechanisms. In this study we evaluate the effect of twelve flavoring agents on the physical gelation temperature of 1wt% Hydroxypropyl Methylcellulose (HPMC) solutions in a water-ethanol mixture. The flavoring agents were organized by its principal functional group, i.e. alcohols, esters, monoterpenes, and aldehydes, and concentrations of up to 0.1 wt% were characterized. Rheological dynamic oscillatory measurements with temperature ramps from 20 to 80 °C were used to determine the gelation temperature, T gel. All measurements were made in triplicate and a variance analysis (ANOVA) for each functional group was performed, to determine the effect of concentration and type of flavoring. Results show that both factors, type of molecule and concentration, have a significant effect on the gelation temperature of the samples. Special cases observed were monoterpenes and ester groups, where no discernible pattern was identified. The Flory-Huggins solubility parameters were used to correlate the effect of different flavors in the gelation temperature of the system. A relationship between the solubility of the flavoring with the solvent and polymer can be correlated to the changes in Tgel of the HPMC solutions.

Wednesday 5:30 Conference Center Lower Level PO31

Steady-state rheology of hydroxypropyl methylcellulose solutions with dispersed drug particle inclusions

Mariel Santiago-Vázquez and Aldo Acevedo
Department of Chemical Engineering, University of Puerto Rico, Mayagüez 00680, Puerto Rico

Physical biopolymer gels are ideal candidates for the drug delivery of solid pharmaceutical drugs. Nevertheless, inclusion of particles may affect the gelation of these systems. In this work, we evaluate the effects of concentration on the viscosity of a model biopolymer-particle system. The studied system consists of aqueous hydroxypropyl methyllcellusose (HPMC) and griseofulvin, a model drug. Loadings of up to 2 wt% were dispersed by ultrasonication in aqueous HPMC solutions at room temperature. The viscosity of the solution was determined at constant temperature (25°C) with a shear rate ramp ranging from 0.01 to 100 s^{-1} in a double gap Couette fixture. A low shear thinning regime was observed followed by a plateau viscosity. The zero-shear rate viscosity and plateau viscosities decreased by up to a 10× factor upon addition of griseofulvin. Nevertheless, it is mostly unaffected by the increase in concentration. The decrease in viscosity is attributed to adsorption of the polymer to the hydrophobic particle surface, which decreases the effective bulk concentration. This is also supported by previous studies of the gel transition of the system.

Wednesday 5:30 Conference Center Lower Level PO32

Modification of tube models for entangled polymers in fast nonlinear flows: Microstructure change by disentanglement and configuration-dependent friction coefficient

Joontaek Park and Nilanjana Banerjee
Chemical and Biochemical Engineering, Missouri University of Science & Technology, Rolla, MO 65409, United States

We modified tube models for entangled monodisperse linear polymers considering entanglement density change as well as configuration-dependent friction coefficient (CDFC), which was proposed by Park et al. [J. Rheol. 56: 1057-1081 (2012)], to study the microstructure change of entangled polymers in fast nonlinear flows. We assumed that the entanglement density of an entangled polymeric liquid decreases during deformation and the resulting disentanglement gives additional relaxation to the entangled structure. We also assumed that the disentanglement behavior, observed in simulations by stochastic tube models, is similar to the actual behavior. Based on the assumptions, an equation for the time evolution of entanglement density was derived from simulation results from a stochastic tube model (PMD model) by Park et al. (2012). The equation was incorporated into a tube model (MLD model) by Mead et al. [Macromolecules 31: 7895-7914 (1998)], which was also modified so that its structural input parameters, which were estimated from an equilibrium polymer structure, should be entanglement density dependent. The modified model can predict the distinguished behaviors of steady elongational viscosity between (thinning) entangled polystyrene melts and (hardening) solutions at strain rates larger than the inverse Rouse time. More discussion on comparison with results from stochastic models will be made to elucidate the effect of the disentanglement and the CDFC on the tube structure change in fast nonlinear flows.

Wednesday 5:30 Conference Center Lower Level PO33

A study on the thermal stabilization of aliphatic polyketone

Seungwon Lee[1], Won-Sik Bae[1], Dong Wook Chae[2], and Byoung Chul Kim[1]
[1]Department of Organic and Nano Engineering, Hanyang University, Seoul 133-791, Republic of Korea; [2]Department of Textile Engineering, Kyungpook National University, Gyeongsangbuk-do 742-711, Republic of Korea

The aliphatic polyketone terpolymer of ethylene, propylene carbon monoxide (EPCO) has excellent mechanical properties and high cost effectiveness. Accordingly, EPCO was considered as one of the best candidates to replace nylon66. However, its thermal degradation through ionic and radical mechanisms during melt processing has been issued. In order to suppress the degradation, an acid scavenger and a radical scavenger were added, calcium hydroxyapatite (CHA) and 2,2'-oxamidobis-[ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (OHP), respectively. According to the theoretical calculation, approximately $4.8*10^{-4}$ mol of acid ion and $8.6*10^{-5}$ mol of radical exist in 60g of EPCO. Consequently, compositions of CHA and OHP, 4/1, 5/1, 6/1, 7/1, and 8/1, were investigated. The total loading level was fixed 0.5 wt% from preliminary experimental results. In time sweep measurements the complex viscosity (?*) was increased with time, indicating that crosslinking by aldol condensation was more dominated during degradation. Particularly, the inflection point of the ?* curve may be defined as dynamic stability time (DST). The composition 7/1 showed the lowest ?* and longest DST which pointed out that it was the most efficient stabilizing composition over the observed compositions. However, in DSC measurements in the static state the composition 4/1 exhibited the noticeable stabilizing effect. This difference of results between dynamic and static states seemed to be result from the fact that the acid-driven degradation might be accelerated by mixing effect under shearing. This result enabled us to establish a processing window of the melt process of EPCO.

Wednesday 5:30 Conference Center Lower Level PO34

The nematic liquid crystalline behavior of poly(2-cyano-p-phenylene terephthalamide) solutions in N-methyl-2-pyrrolidone/calcium chloride

Hu Young Yoon, Youngho Eom, and Byoung Chul Kim
Department Of Organic And Nano Engineering, Hanyang University, Seoul, Republic of Korea

Poly(p-phenylene terephthalamide) (PPTA) is well known to show liquid crystalline behavior and have very strong intermolecular interactions due to the stacking of benzene rings and hydrogen bonding between amide groups which gives rise to high tensile strength and thermal stability. The strong interactions bring about poor solubility to organic solvents. Since the spinning dope has been prepared in fuming sulfuric acid which is harmful to environments. Many studies have been carried out to replace sulfuric acid with an organic solvent by modifying the chemical structure of the polymer. Introducing a cyano group to PPTA proved an effective method. Poly(2-cyano-p-phenylene terephthalamide) (CY-PPTA) was readily soluble in N-methyl-2-pyrrolidone containing calcium chloride (NMP/$CaCl_2$). It is a prerequisite to understand the rheological properties of solutions to design spinning dope. The CY-PPTA solutions in NMP/$CaCl_2$ were rheologically characterized along with polarizing optical microscopy. Dynamic frequency sweep test at 25oC was carried out to investigate the rheological properties and liquid crystalline behavior at concentrations ranging from 2 to 16 wt%. A typical curve of viscosity against concentration for liquid crystalline polymers was obtained. The critical concentration was found to be ca. 3 wt% and the saturated concentration seemed to be ca. 8 wt%. This result correlated well with the results of polarizing optical microscopy in which at 3 wt%, birefringent droplets start to form, followed by textures of liquid crystal domains at 8 wt%. In addition, rheological measurements made us to elucidate the temperature dependence of CY-PPTA, which will support the establishment of the process window.

Wednesday 5:30 Conference Center Lower Level PO35

Importance of solvent quality on the hysteresis in the coil-stretch transition of flexible polymers

Rangarajan Radhakrishnan and Patrick T. Underhill
Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

Direct observations of long flexible polymers like ds-DNA in elongational flow show a coil to stretch transition (CST) and hysteresis in this transition. We examine the solvent effects on the hysteresis of CST for a range of flexible molecules & solvent qualities using Brownian Dynamics simulations. The flow response of a molecule is calculated using a dumbbell model with conformation dependent drag. We employ a newly-developed spring force relation that captures the solvent effects using only a dumbbell. We analyzed two situations of increasing the solvent quality: (1) by increasing the number of Kuhn steps and keeping the solvent quality parameter constant, and, (2) by increasing solvent quality parameter and keeping the number of Kuhn steps constant. In the first case, we found that the width of the hysteresis (ratio of upturn to downturn strain rates) increased with increase in Kuhn steps. In the second case, we found that the width of hysteresis decreased with increase in solvent quality. In particular, we find the largest qualitative change from theta conditions when observing molecules such as ss-DNA in good solvents. These changes in the flow response of molecules with solvent quality are important in understanding the rheology of polymer solutions and in stretching molecules using microfluidic devices.

Wednesday 5:30 Conference Center Lower Level PO36

Phase separation of polymer solutions after exposure to shear and elongational flow

Kyung Hee Oh and Victor Breedveld
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, United States

Shear and elongational deformation in hollow fiber membrane spinning processes affect the membrane performance through the polymer morphology of the membrane. We developed in-situ microfluidic devices to examine the effects of shear and elongation on fiber morphology. Polymer solutions were extruded through straight channels to induce shear flow and contraction channels to create elongational flow. Phase separation video-microscopy and the cross-sectional SEM images of resulting fibers extruded at different rates showed a consistent picture, providing correlations between the fundamental rheological properties of the polymer solutions and fiber morphology. In particular, the occurrence of macrovoids, which are critical membrane defects, was greatly changed under different shear and elongational conditions. At low extrusion speeds, the phase separation process is dominated by mass transfer, resulting in formation of large macrovoids for both shear and elongational flow. At intermediate speed, the morphology depends on the solution composition and thermodynamic properties. At high extrusion rate, the differences between shear and elongation become prominent; we found that shear induces macrovoid formation, while elongation suppresses the evolution of these defects.

Wednesday 5:30 Conference Center Lower Level PO37

Particle tracking velocimetric study of real shear hardening and extreme recoverability in simple shear of branched polystyrene solutions

Gengxin Liu[1], Shiwang Cheng[1], Hyojoon Lee[2], Hongwei Ma[1], Roderic Quirk[1], Taihyun Chang[2], and Shi-Qing Wang[1]
[1]Department of Polymer Science, University of Akron, Akron, OH 44325, United States; [2]Department of Chemistry, Pohang University of Science and Technology, Pohang 790784, Republic of Korea

We observed that in simple shear entangled polymers with long chain branching (LCB) can exhibit a higher transient viscosity than the zero-shear viscosity (shear hardening). LCB resists against a structural breakdown of the entanglement network, postponing the stress overshoot to a shear strain of more than 30 and recoverable strain of 20. Applying particle-tracking velocimetry, we examine whether LCB prevents the entangled polymer solutions from elastic breakup and shear banding.

Wednesday 5:30 Conference Center Lower Level PO38

Anisotropic thermal transport in polymer networks subjected to uniaxial elongation

David Nieto Simavilla, David C. Venerus, and Jay D. Schieber
Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL, United States

Deformation during processing of polymeric materials induces large stresses. These are coupled with large temperature gradients due to the low thermal conductivity characteristic of these materials. Over the last 15 years our research group has investigated the relationship between anisotropic thermal transport and the stresses developed during deformation. Using Forced Rayleigh Light Scattering(FRS), a linear relationship between anisotropy in thermal diffusivity and stress, known as the Stress-Thermal Rule(STR), has been found to be valid. We report recent measurements of anisotropic thermal diffusivity, birefringence and stress in a Polyisoprene (PI) network system subjected to uniaxial elongation. These results showed that the STR holds even at stress levels where the well-known Stress-Optic Rule fails. This suggest that birefringence and thermal diffusivity scale with different moments of the orientation in the network segments. Further research testing different materials is necessary to understand the molecular principles governing anisotropy in the thermal properties. A novel experimental technique, based on Infrared(IR)-imaging, is presented as a complementary method to the previously used FRS. IR-imaging opens the possibilities for a broader range of materials to be studied. We present results comparing both techniques in a Polybutadiene (PBD) network system.

Wednesday 5:30 Conference Center Lower Level PO39

Understanding pressure sensitive adhesive performance from rheological testing

Bharath Rajaram and Gregory W. Kamykowski
US-West, TA Instruments, Schaumburg, IL 60173, United States

Relating the strength and tackiness of pressure sensitive adhesives (PSA) to their performance poses a significant hurdle in the product development and determining the end-use applications of these materials. Rheological testing presents an excellent avenue for investigating PSA behavior on account of their inherently viscoelastic characteristics. Here, the material's adhesion strength and its ability to hold surfaces together are linked with its elastic component while the flowability of the adhesive is characterized by its viscous component. In this study, we present results from rheological characterization of PSAs using a multitude of frequency sweeps and creep tests performed over a wide range of temperatures. Through the use of Time-Temperature Superposition (TTS) transformation, we quantify the material properties over several decades on the time scale, from its response to instantaneous loads to behavior over extremely long time periods. We conclude by highlighting results from tack-peel off studies and discuss the relevance of rheological testing for PSA characterization.

Wednesday 5:30 Conference Center Lower Level PO40

Measurement of hydrodynamic resistance due to purely elastic instabilities in curvilinear microchannels

Deepak E. Solomon and Siva A. Vanapalli
Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

Purely elastic instabilities can develop when polymeric fluids flow through curvilinear channels.Although several studies investigated flow kinematics in this geometry a clear understanding of evolution of flow resistance with Weissenberg (Wi) number remains unanswered.

The measurement of hydrodynamic resistance in such devices caused by purely elastic instabilities can be challenging because of the difficulty to integrate pressure or flow rate sensors. However, recent works have shown that by employing a fluidic comparator it is possible to determine flow resistance. We use a similar fluidic comparator connected to a curvilinear channel downstream to measure change in resistance as a function of flowrate. As a first step we investigated the limits of operation of the fluidic comparator to measure flow resistance due to polyethylene oxide Boger fluids. The results from the microfluidic comparator were independently assessed using particle image velocimetry (PIV). We found that above a critical Wi (Wic) flow instabilities developed in the comparator region. The flow field was found to vary both temporally and spatially. The flow profile above Wic deviates significantly from laminar flow indicating that the range of flow resistance that can be measured as a function Wi using the microfluidic comparator is limited.

To overcome the limitation of the microfluidic comparator technique, we propose a new method to measure the mean flow resistance due to purely elastic instabilities. We use a long capillary tube attached to the outlet of the curvilinear channel. The resistance of the tube is ~1% of the total resistance in the device. This capillary allows us to quantify average flow rate by measuring the velocity of the progressing fluidic slug, enabling us to calculate the flow resistance of the polymeric fluid. This technique thus enables measurement hydrodynamic resistance caused by purely elastic instabilities in a broader range compared to the microfluidic comparator.

Wednesday 5:30 Conference Center Lower Level PO41

A somewhat exaggerated examination of the Cox-Merz “rule”

Montgomery Shaw
Institute of Materials Science, U-3136, University of Connecticut, Storrs, CT 06269-3136, United States

The linear viscoelastic function $|\eta^*|(\omega)$ is often accepted (and named) as "the viscosity" by researchers; and, indeed, the approximation known as Cox-Merz rule equating $|\eta^*|(\omega)$ with the steady shear viscosity at a shear rate equal to ω can be very precise for less-complex solutions and melts [e.g., Shara, V. and G. H. McKinley, *Rheo. Acta*, **51**, 487-495 (2012)]. Molecular theory justifying the rule is sparse [e.g., Mead, D., *Rheo. Acta*, **50**, 837-866 (2011)]. With this in mind, the acceptance of the null hypothesis for a simple linear polymer poly(dimethyl siloxane) was examined. To accomplish this, a block design was applied using a melt of a poly(dimethyl siloxane) in a cone-and-plate geometry. Importantly, the block excluded reloading error by running sequential steady and dynamic determinations in the region between the end of the Newtonian plateau (about 1 s^{-1}) and the start of unstable flow (about 5 s^{-1}). Tested factors included run sequence (dynamic-then-steady vs. steady-then-dynamic) and gas content, in addition to rate.

Wednesday 5:30 Conference Center Lower Level PO42

Relationship between shear rate, morphology and properties of EPCO/polyester-based TPE blends

Hyunmin Hwang, Jeong Sik Bae, Youngho Eom, and Byoung Chul Kim
Department of Organic and Nano Engineering, Hanyang University, Seoul, Republic of Korea

Polyketone terpolymer (EPCO) was blended with polyester-based thermoplastic elastomer (HY) to enhance the impact strength. EPCO and HY were melt-mixed in the composition of 9:1, 8:2, 7:3 and 6:4. It is well known that dispersion state and size of domain affect the mechanical properties of the blend system. According to the Taylor's prediction, the breakup of domains would occur more readily as the magnitude of viscosity of each polymer gets closer. The dynamic viscosity (?') of polymeric material changes by shear rate. The rheological method was adopted for deeper understanding of the relationship between shear rate and morphology. The ratio of ?' of EPCO to HY got closer to 1 at higher shear rate. The samples were prepared at different mixing speeds of 10, 40 and 80 rpm for 6, 5 and 4 min, respectively. It was confirmed by scanning electron microscope that HY existed as dispersed domains in EPCO matrix at the composition of 9:1 and 8:2. In the composition of 7:3

and 6:4, however, HY domain formed co-continuous phase. The composition of 8:2, PH8/2, was chosen for further investigation since it showed more significant difference in domain morphology. The domain size and distribution of PH8/2 decreased as the mixing speed increased. Additional shear was given to PH8/2s prepared at 10 and 80 rpm for 3 min to evaluate the morphological stability of HY domains. The experiment was carried out at two frequencies, 1 and 100 rad/s. The spherical HY domains turned into more and more ellipsoidal ones at higher frequency. The size and distribution of HY domains are also analyzed. The impact strength of PH8/2 increased with increasing mixing speed as expected.

Wednesday 5:30 Conference Center Lower Level PO43

Solventless fabrication of polymer-ionic liquid composites

Robert J. Frank-Finney and Malancha Gupta
Chemical Engineering, University of Southern California, Los Angeles, CA, United States

Polymer-ionic liquid composites have attracted significant research interest due to their potential applications in fuel cells and electrochemical devices since they combine the conductivity of ionic liquids with the mechanical properties of polymers. We have developed a solventless method for fabricating thin film polymer-ionic liquid composites by introducing ionic liquids into a vapor phase polymerization process. By varying the reactor conditions such as substrate temperature, pressure, and deposition time, we can modify the amount and the molecular weight of the polymer being formed. We characterized the composites using dynamic mechanical analysis to determine the conditions that give a solid structure with the largest ionic liquid composition.

Wednesday 5:30 Conference Center Lower Level PO44

Investigation of rheological behavior and thermal conductivity of thermoplastic elastomers based on PP/EPDM by adding nano-ZnO particles

Toktam Behrouz[1], Fatemeh Goharpey[2], Hossein Nazockdast[2], Mohammad Reza Kalaee[1], and Farhad Soltani[3]
[1]Department of Polymer Engineering, Islamic Azad University, Tehran South Branch, Tehran, Iran; [2]Department of Polymer Engineering, Amirkabir University of Technology, Tehran, Iran; [3]Department of Material Research and Engineering, Supplying Automotive Parts Company - SAPCO, Tehran, Iran

Attempt were made to study the rheology and thermal conductivity of thermoplastic elastomer (TPE) nanocomposites by using Polypropylene (PP)/Ethylene-Propylene-Diene-Monomer (EPDM) composites and the ratio of 70 to 30 (w/w %) respectively, with different percentages of Zinc-Oxide nanoparticles (nano-ZnO) containing 1, 3, 5 and 7wt% along with 10wt% of Ethylene-Propylene-Copolymer (EPC) as a compatibilizer which was used to promote the interfacial interactions between the components and relative partitioning of nano-ZnO particles in polymer phases. The samples were prepared via melt mixing in a laboratory internal mixer at 180oC and rotor speed of 60 rpm. Rheological behaviors of prepared TPE nanocomposites revealed that with increasing of nano-ZnO content and frequency concurrently, complex viscosities (?*) and loss factor (tand) were decreased, whereas storage modulus (G') and loss modulus (G") of PP/EPDM composties were increased which these variations were observed at middle and high frequencies. It was found that nanoparticles may be located within interfaces or embedded in EPDM droplets and form the sandbags. Also results showed that melt viscosity decreased due to the agglomeration of nanoparticles when nano-ZnO concentration reached more than 5wt% in the composites. Furthermore, when compatibilizer was incorporated into the composites, the deformation characteristics of the droplet (and interfaces) were affected by the copolymer. Moreover, slip at polymer-polymer interfaces was lowered due to the additional friction provided by the copolymers. Thermal conductivity of the composites filled with nano-ZnO was also measured. It was found that thermal conductivity increased with increasing of temperature from 25^oC to 90^oC. It should be noticed that thermal conductivity depends on nanoparticles concentration, and it increases linearly with the filler loading.

Wednesday 5:30 Conference Center Lower Level PO45

Linear viscoelastic and dielectric behavior of oligomeric sulfonated styrene

Quan Chen and Ralph H. Colby
Department of Materials Science and Engineering, The Pennsylvania State University, State College, PA 16802, United States

Linear viscoelastic modulus (by Weiss and coworkers: Macromolecules 45, 481 (2012); J. Rheo. 53, 191 (2009)) on three sets of ionomers, obtained through sulfonation of oligomeric styrene at low ionic content, i.e., ionic groups per chain N_{ionic} = 0.95, 1.82, and 2.50, were analyzed on the basis of a sticky-Rouse model. Oligomeric styrene with M = 4000g/mol ensures that the ionomers are free from entanglement effects and accordingly enables an exclusive test on the dynamic role of ionic groups. For each set of ionomers, the terminal relaxation is increasingly delayed with a reduction of counterion size. This result is in accordance with a expectation that the lifetime of ion association increases with ion interaction energy. The amplitude of modulus, on the other hand, exhibits complex behavior: the ionomers having N_{ionic} = 0.95 exhibit dim plateau of amplitude about two orders lower than vkT, with v being the chain density. The plateau becomes clear with amplitude approaching vkT on increasing N_{ionic} to 2.50. This result strongly suggests that the fraction of delayed chains changes significantly when N_{ionic} becomes slightly higher than one. Detailed analysis shows that this change is related to the different roles of ionomer chains having different N_{ionic}: the chains having N_{ionic} = 0 and 1 behave as diluent and dangling ends, respectively, in a network where ionic clusters serve as reversible crosslinks, and chains having N_{ionic} = 2 are composed of either loop or bridge strands, connecting two distinct or identical ionic cluster (s), respectively. The amplitude of the plateau is strongly related to the number fraction of chains containing bridged strands, which is further correlated to a relative dimension of ionomer chain and cluster-cluster distance measured from small angle X-ray scattering. A sticky Rouse model incorporating this number fraction describes the linear viscoelastic modulus of the ionomer samples.

Wednesday 5:30 Conference Center Lower Level PO46

Creep dynamics of non-entangled miscible polymer blends and block copolymers

Quan Chen
Department of Materials Science and Engineering, The Pennsylvania State University, State College, PA 16802, United States

The bead-spring model, as a fundamental model of polymer physics, has been widely utilized so far for polymer chains of various topological structures under the strain-controlled conditions. Nevertheless, the full analysis of conformational dynamics of these polymer chains during the creep (stress-controlled) process has not been given until recently by Watanabe and coworkers (2004). In this study, this analysis is extended to disordered block copolymers and miscible polymer blends for which effect of frictional distribution/heterogeneity manifests. Due to the requirement of constant stress, different components exhibit correlated anisotropic change before the steady state is achieved. Furthermore, this change contains two stages with a growth of the orientational correlation among the segments. Namely, the first segmental stage where the anisotropic change reflects the intrinsic mobility of segments, and the second global stage where the anisotropy approaches the steady state defined with respect to specific position of a given chain. In a special case that the anisotropic change for segments is opposite during the two stages, a reverse of anisotropic change can be clearly observed.

Wednesday 5:30 Conference Center Lower Level PO47

Osmotic effect on polymer dynamics in block copolymer nanodomains

Hiroshi Watanabe and Yumi Matsumiya
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Nanodomain morphology of block copolymers is determined by contradicting thermodynamic requirements of randomizing the block conformation, reducing contacts of chemically different segments, and uniformly filling each nanodomain with the block segments therein. In particular, the osmotic requirement of uniform domain-filling is very strong in bulk copolymer systems and affects the polymer dynamics in the nanodomain. This effect was dielectrically investigated for styrene (S)-isoprene (I) block copolymers having the type-A dipole along the I block. Dielectric tests were made at $T \ll T_g(PS)$ for blends of SIS triblock copolymers and homo-I chains, the latter being mixed in the spherical domains formed by the I blocks to probe the effect of the osmotic requirement therein, as well as for neat SI diblock copolymers. In the SIS blends at low T, the ends of the I blocks were fixed to the glassy S matrix and the I block motion was dielectrically inert. The probe I chains mixed with such I blocks exhibited broadened/retarded dielectric relaxation attributable to the osmotic requirement. Magnitude of this broadening/retardation was found to be insensitive to the probe I molecular weight, which suggests that the probe dynamics is governed by the osmotic requirement and the spatial confinement in the domain has just a secondary effect. For the neat SI copolymers forming spherical (Sph), cylindrical (Cyl), and lamellar (La) I domains, the dielectric relaxation was found to be broader in the order of Sph > Cyl > La. This result suggests that the effect of the osmotic requirement on the polymer dynamics is stronger in this order possibly because of the domain dimensionality (a higher dimensionality helps the block to move without violating the osmotic requirement).

Wednesday 5:30 Conference Center Lower Level PO48

The use of the linear amplitude sweep test and large amplitude oscillatory shear testing to characterize asphalt binder

Gregory W. Kamykowski and Bharath Rajaram
US-West, TA Instruments, Schaumburg, IL 60173, United States

Rotational rheometry has established itself as an indispensable method for characterizing asphalt binders. Several tests have become established and are used by asphalt suppliers and state Departments of Transportation to ensure the quality of asphalt used for paving roads. These include Original Binder, Rolled Thin Film Oven, Pressure Aged Vessel, and, more recently, Multiple Stress Creep & Recovery testing. In efforts to extend the predictions of pavement longevity and get more information from rotational rheometry, additional test methods are being investigated. One of these is the Linear Amplitude Sweep (LAS) test, whereby time sweeps are performed at strains that are increased incrementally, up to 30% strain. Data are analyzed according to the Viscoelastic Continuum Damage (VECD) Model. Another test that is gaining more attention in current rheology research is the Large Amplitude Oscillatory Shear (LAOS) test. These two test methods have been used to characterize asphalt samples, and results will be presented to show the utility of both test methods .

Wednesday 5:30 Conference Center Lower Level PO49

Transient and steady-state shear banding in aging soft glassy materials

Jeffrey Martin and Thomas Hu
Unilever Research & Development, Trumbull, CT 06611, United States

Transient and steady-state shear banding in a Laponite suspension were studied by particle imaging velocimetry in Couette and cone and plate flow geometries on samples with varying age. The time evolution of the velocity profile and shear stress was measured simultaneously as a fixed shear rate was imposed on the sample. By varying the aging time of the rejuvenated samples, we examined the effect of the stress overshoot on the shear banding behavior. Transient banding only occurred for aged samples that showed a stress overshoot. However, steady-state banding occurred when the imposed shear rate was below a critical value, even in the absence of a stress overshoot or transient banding. These results were consistent for independently prepared samples with vastly different overall ages, and in different flow geometries with varying intrinsic stress gradients. Different mechanisms for transient and steady-state shear banding will be discussed.

Wednesday 5:30 Conference Center Lower Level PO50

Complex flows of soft glassy fluids: Simple shear, extensional and porous media flows

Arijit Sarkar and Donald L. Koch
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

The soft glassy rheology (SGR) model describes the behavior of many fluids near or within a glassy state and features a broad spectrum relaxation times and relaxation rates that are enhanced by strain. Most studies of such fluids have considered only simple shear flows. We have developed an SGR model for complex flows exhibiting a variety of local linear flows and applied it to the complex stochastically varying flow of a fluid through an isotropic fixed bed of fibers. The tensorial stress in the model is related to a vector which represents the stretch experienced by a fluid element before it hops or relaxes. An anisotropic hopping rate allows the model to capture a range of relative strengths of extensional and shear response. We show that the successive straining of a fluid element as it passes through a fixed bed leads to large stresses as has been previously predicted and observed for polymer solutions in fixed beds. In an extensional flow or flow in a fixed bed, the stress in the SGR model exhibits a rapid increase at moderate strain rates and then grows at a slower, logarithmic rate at high strain rates. The slower rate of growth of the strain at high strain rate results from the strain enhanced relaxation rate.

Wednesday 5:30 Conference Center Lower Level PO51

Apparent viscosity of bulk metallic glass in confined size

Zhen Shao[1], Manesh Gopinadhan[1], Sundeep Mukherjee[2], Yanhui Liu[2], Golden Kumar[3], Jan Schroers[2], and Chinedum O. Osuji[1]
[1]Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, United States; [2]Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06511, United States; [3]Mechanical Engineering, Texas Tech University, Lubbock, CT 79409, United States

Liquid flows in confined spaces present interesting contrasts compared to flows on macroscopic length scales because of the breakdown of Navier-Stokes modeling in the former case. Experiments performed on sub-nanometer thin films of non-polar liquids, typically within ten molecular diameters, routinely show an increase in viscous resistance relative to flows in the bulk. The sluggish crystallization kinetics in bulk metallic glass (BMG) formation has enabled us to measure the viscosity over the entire temperature range from T_g (glass transition temperature) to T_L (melting temperature). Thus far, the viscosity measurement of BMG is limited to large metallic samples on micro-scales. Here we present a method to explore the size dependence of the viscosity of BMG on nano-scales. BMG samples were melt-pressed into nanoporous ceramic molds using a controlled loading profile at a temperature above T_g and below T_X (crystallization temperature). The length of BMG rods formed in the molds was measured by SEM and used to calculate the apparent viscosity of the BMG during the melt-pressing operation. The size of pores was varied to estimate the dependence of the BMG viscosity on confinement. Strikingly, we observe that the apparent viscosity increases with confinement, with a roughly exponential decay below 100 nm, which is in line with non-polar solvents. We speculate that the increase of viscosity may be caused by restriction of cooperative motion as the confinement is approaching the size of cooperatively rearranging regions.

Wednesday 5:30 Conference Center Lower Level PO52

Passive microrheology: Non-intrusive measurement of the emulsions viscoelastic properties

Christelle Tisserand[1], Guillermo Smart[2], Mathias Fleury[1], Roland Ramsch[1], and Gérard Meunier[1]
[1]Formulaction, L'Union 31240, France; [2]Formulaction Inc, Miami, FL 33330, United States

This work presents a new technique of the passive microrheology for the study of the microstructure properties of soft materials like emulsions. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between 10-1 and 105 seconds. Different parameters can be measured or obtained directly from the Mean Square Displacement (MSD) curve like a fluidity index, an elasticity factor, a viscosity factor, a relaxation time, a MSD slope. This technique allows to monitor the evolution of the microstructure, the restructuration after shearing, the variation of the viscoelastic properties versus temperature, pH, the physical stability of emulsion or suspension... This work focuses on the measurement of viscoelastic properties evolution of emulsions to follow their stability. The results will show the advantages of using a non intrusive method to detect nascent destabilisation of the microstructure before rheology or visual method. This paper presents also characterization of low fat emulsions.

Wednesday 5:30 Conference Center Lower Level PO53

Passive microrheology for the determination of the gel point

Guillermo Smart[1], Christelle Tisserand[2], Mathias Fleury[2], and Gérard Meunier[2]
[1]Formulaction Inc, Miami, FL 33330, United States; [2]Formulaction, L'Union 31240, France

This work presents a new technique of the passive microrheology for the study of the microstructure properties of soft materials. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between 10-3 and 105 seconds. Different parameters can be measured or obtained directly from the Mean Square Displacement (MSD) curve like a fluidity index, an elasticity Index, a Solid Liquid Balance, a Macroscopic Viscosity Index, a relaxation time, a MSD slope... Also when the particles move only thanks to the Brownian motion, the Generalised Stokes Einstein Relation given by Mason and Weitz can be applied to calculate the visco-elastic moduli G' and G" over a large frequency range. This technique allows to monitor the evolution of the microstructure, the variation of the viscoelastic properties versus temperature, pH, le gel point.... This work focuses on viscoelastic properties evolution and will show application examples and advantages of using a non intrusive method for: - Gelation process of food products in order to measure the speed of the gelation, le gel point and the final strength of the network (mesh size) - Methylcellose viscoelastic properties evolution versus temperature - Carraghenan networks formation and comparison of their viscoelastic properties versus concentration.

Wednesday 5:30 Conference Center Lower Level PO54

Microflows of ionic liquids

Carson T. Riche, Noah Malmstadt, and Malancha Gupta
Chemical Engineering, University of Southern California, Los Angeles, CA, United States

We study the multi-phase flow and emulsification of ionic liquids within microchannels. Ionic liquids are low-melting organic salts that have inherently high viscosities and complex interfacial properties. Break-up of the ionic liquid phase was aided by modifying the surface chemistry of the microchannels using a vapor phase polymerization process. The effects of flow rate, surface chemistry, and viscosity are evaluated.

Wednesday 5:30 Conference Center Lower Level PO55

Flow induced torus-like micellar structures in surfactants solution

Joshua J. Cardiel[1], Alice Dohnalkova[2], Lige Tonggu[3], Liguo Wang[3], Ya Zhao[1], and Amy Q. Shen[1]
[1]Mechanical Engineering, University of Washington, Seattle, WA, United States; [2]Environmental Molecular Sciences Laboratory,EMLS, Pacific Northwest National Laboratory, PNNL, Richland, WA 98015, United States; [3]University of Washington, Seattle, WA, United States

We observe torus-like micellar bundles from transmission-electron microscopy (TEM), created from a semi-dilute wormlike micellar solution by passing the solution in a microfluidic device. The aqueous micellar solution consists of the cationic surfactant cetyltrimethyl ammonium bromide (CTAB, [CTAB=50 mM]) and sodium salicylate (NaSal, [NaSal=16mM]). The formation of torus-like micelles is due to the combination of a pre-straining process in the precursor solution, and micro-spatial confinement in a series of micropost arrays. We report the elastic properties (bending energy, spontaneous curvature and saddle-splay constant) of the torus-like micelles as well as their free energy. Understanding the formation and elastic properties of the torus-like micelles brings new pathways to design and develop nanomaterials with novel morphologies for different technological applications.

Wednesday 5:30 Conference Center Lower Level PO56

Measuring viscosity of water using a dynamic shear rheometer: Issues and limitations

Madhu Namani
TA Instruments, New Castle, DE 19720, United States

From time to time one might be asked to measure the viscosity of water as a standard verification sample on a dynamic shear rheometer, but water as a test material is just not a good material for a rotational rheometer. The high surface tension can make the sample appear to be non-Newtonian, and if you add some surfactant to break the surface tension you can easily introduce shear thinning behavior, one also need to be concerned about evaporation that can also make the sample appear non Newtonian. also at high shear rates secondary flows dominate because of fluid inertia which causes an apparent increase in viscosity.

Wednesday 5:30 Conference Center Lower Level PO57

Viscoelasticity and shear-induced structure of transient nanoemulsion organohydrogels formed by polymer-surfactant complexation

Juntae Kim, Casey A. Hebebrand, Elke Peirsegaele, and Matthew E. Helgeson
Chemical Engineering, UC Santa Barbara, Santa Barbara, CA 93117, United States

Controlling the rheology of nanoemulsions is essential for a wide range of applications, including pharmaceuticals, foods, and consumer products. Here, we explore the use of polymer-surfactant complexation as a broad means to control the rheological properties of nanoemulsions. Specifically, we have discovered that polymer-surfactant interactions cause thermoreversible viscoelasticity at low temperature in nanoemulsions, which is distinct from emulsion-free polymer-surfactant mixtures. Interestingly, these gels exhibit Maxwell-like viscoelasticity that follows time-temperature superposition (TTS) over a wide temperature range - the first time such behavior has been observed in emulsions. Small angle neutron scattering (SANS) shows that the low-temperature nanoemulsion gels exhibit well-dispersed droplet microstructure that is insensitive to temperature, confirming that the gel-like viscoelasticity arises entirely from the dynamics of the system. We thus hypothesize that low-temperature gelation arises from a temporary polymer network mediated by polymer-surfactant interactions at the droplet interface. To test this hypothesis, we use TTS to probe the relation of viscoelastic properties and material parameters and compare them with temporary network theory. The results show that the viscoelasticity is critically linked to the stoichiometry of polymer and surfactant, which reflects the thermodynamics of complexation in surfactant-polymer solutions. These nanoemulsion gels also exhibits characteristics of extreme shear thinning and shear banding at sufficiently low temperature. Rheo-SANS measurements indicate that shear-induced structure similar to aggregating polymer-colloid mixtures is responsible for this behavior, despite the lack of suspension instability. Overall, our studies demonstrate polymer-surfactant complexation as a highly generic mechanism to control both the linear and non-linear rheology of nanoemulsions, which could be exploited to design new materials with dynamically controlled rheology.

Wednesday 5:30 Conference Center Lower Level PO58

A shear cell for the direct visualization of constant-stress deformation in soft materials

Hubert K. Chan and Ali Mohraz
Chemical Engineering and Materials Science, University Of California, Irvine, Irvine, CA 92697, United States

The application of external stresses to a viscoelastic material can induce complex rheological responses such as creep, shear-induced strengthening, and delayed yielding. Understanding the underlying physics of these phenomena requires the ability to characterize how the material's microstructure evolves during the deformation. Here, we introduce a custom-built, stress-controlled shear cell coupled to a fast-scanning confocal microscope for direct visualization of constant-stress shear deformation in soft materials and complex fluids. The torque generator is a cylindrical Taylor-Couette system with a Newtonian fluid between a rotating inner bob and a free-to-move outer cup. A spindle / cone assembly coaxially coupled to the cup transfers the torque exerted by the fluid to the sample of interest in a cone-and-plate geometry. We model and experimentally demonstrate the performance of our device in both steady state and transient experiments with different viscoelastic materials. Our apparatus can conduct unidirectional constant-stress experiments as accurately as most commercial rheometers, with the capability to directly visualize the flow field. Further, our step-stress experiments on viscoelastic materials are devoid of creep-ringing, which is an advantageous aspect of the viscous coupling between the torque generation mechanism and the viscoelastic sample. We specifically demonstrate this aspect of our shear cell both theoretically and experimentally with a rubbery, crosslinked polymer well approximated as a Kelvin-Voigt fluid.

Wednesday 5:30 Conference Center Lower Level PO59

Modeling gel breakdown in oilfield downhole fluids

Jason Maxey, Dale Jamison, and Sandeep Kulkarni
Halliburton, Houston, TX, United States

Formation of a gel structure is essential for good drilling fluid performance, providing for proper hole cleaning and for suspension of weight materials and cuttings. However, the formation of a microstructure can result in pressure spikes when the gel structure is broken down, such as during pump initiation and tripping pipe. These spikes can be severe and limiting in operations where a narrow window between the fracture pressure of the formation and the hydraulic pressure of the fluid exists, such as in managed pressure drilling (MPD). There is a general understanding as to how the breakdown and resulting over-pressure are influenced by mechanical (annular size, pump speeds) and chemical (hydrophilic and organophilic clay interactions, emulsion droplets interaction, colloidal/fines loading) controls. The future success of critical operations such as MPD depends on a better understanding of how the gel structure breakdown occurs and modeling which allows incorporation into existing well design programs. This paper presents a new model for evaluation of gel breakdown in a variety of drilling fluids. This model allows for the recognition of mechanical effects observed in the breakdown, effects of the startup conditions (shear rate, acceleration), and for potential modeling of multiple modes of microstructural bond breakage by independent parameters. Comparison of the breakdown parameters included in this model clearly illustrates differences between mud types. The effects of the breakdown parameters on hydraulic pressures predicted with the inclusion of this model are also presented.

Wednesday 5:30 Conference Center Lower Level PO60

Structure and dynamics of cylindrical micelles and micelle-nanoparticle complexes from molecular dynamics simulations

Ashish V. Sangwai[1], Abhinanden Sambasivam[2], and Radhakrishna Sureshkumar[2]
[1]Intel Corporation, Hillsboro, OR, United States; [2]Syracuse University, Syracuse, NY, United States

Non-equilibrium Molecular Dynamics (MD) simulations that span microseconds in time scale are performed to study the dynamics of cationic cylindrical micelles in shear flow in presence of explicit solvent and electrostatic interactions. Transition from a diffusive to a flow-aligned regime occurs when the shear rate S ~ inverse of the angular relaxation time τ with the micelle tumbling period ~ $S^{0.68}$ and the width of the Gaussian orientation distribution function $S^{-0.31}$, consistent with mesoscopic theories. Simulations suggest a linear energy-micelle extension relationship and predict micelle rupture when $S\tau >> 1$. Further, binary interactions of flow-aligned micelles resulting in micelle fusion are also observed. Such fusion events could help explain shear-induced structure formation and shear thickening observed in cationic micelle solutions. MD simulations are also performed to explore the molecular mechanisms underlying the self-assembly of nanoparticles with cylindrical micelles. Interaction of cylindrical micelles with surfactant-clad nanoparticles results in the formation of stable junctions primarily though the opening up of the end cap of the micelle. The energetics of the bridging process and the effect of flow shear on their stability will be discussed.

References: Sangwai and Sureshkumar, Langmuir, 27(11), 6628-6638 (2011); 28(2), 1127-1135 (2012).

Support from the National Science Foundation (Grant CBET-1049454) is gratefully acknowledged.

Wednesday 5:30 Conference Center Lower Level PO61

Capillary break-up, gelation and extensional rheology of hydrophobically modified cellulose ether solutions

Vivek Sharma[1], Simon J. Haward[2], Asa Soderlund[3], Phil Threlfall-Holmes[4], and Gareth H. McKinley[5]
[1]Chemical Engineering, University of Illinois Chicago, Chicago, IL, United States; [2]FEUP, University of Porto, Porto, Portugal; [3]AkzoNobel Functional Chemicals, Hamnvägen, Sweden; [4]AkzoNobel Research, Development and Innovation, Felling, United Kingdom; [5]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Associative polymer solutions are used extensively in the formulations of functional soft materials like inks, paints, food, nasal sprays, cosmetics, insecticides, fertilizers and bio-assays to control the rheology and processing behavior of multi-component complex fluids. These complex dispersions are processed and used over a broad range of shear rates (1-1E6 s^{-1}) and extensional rates (1-1E5 s^{-1}), and their non-Newtonian behavior displayed under processing conditions is often not measurable in the conventional rheometric measurements. In this talk, we use the example of cellulose ether - ethyl-hydroxyethyl-cellulose (EHEC) - and its hydrophobically modified analog (HMEHEC) to illustrate the influence of hydrophobic stickers on the linear and nonlinear rheology of their aqueous solutions. We show that a constitutive model based on fractional calculus can be used to characterize the physical gelation in HMEHEC solutions, and we use microfluidic rheometry to extend viscosity measurements to high shear rates (1E3-1E6 s^{-1}). The transient extensional viscosity response of the associative polymer solutions dictates the complex pinch-off dynamics during jetting and spraying, where inertial, viscous and elastic effects moderate capillary break-up of cylindrical fluid elements into droplets. We compare the responses of EHEC and HMEHEC solutions to extensional deformations during capillary break-up using (a) capillary break-up extensional rheometer (CABER) and (b) Rayleigh Ohnesorge Jetting Extensional Rheometer (ROJER), an imaging-based technique capable of attaining high extension rates that has been developed as a part of this study. Furthermore, we measure extensional viscosity using excess pressure drop and flow induced birefringence in the vicinity of a stagnation point in a cross-slot extensional rheometer. This study highlights a number of complimentary techniques that are critical for the design and characterization of functional soft materials used in complex processing operations such as jetting and spraying.

Wednesday 5:30 Conference Center Lower Level PO62

High pressure rheology of fracturing fluids and gels

James P. Eickhoff[1], Gina G. Paroline[2], and Patrick Heyer[3]
[1]Anton Paar USA, Ashland, VA 23005, United States; [2]Anton Paar USA, Houston, TX 77032, United States; [3]Anton Paar Germany, Ostfildern, Germany

Hydraulic fracturing has long been utilized in oil and gas production and has become increasingly vital in recent years. The goal of this technique is to increase the porosity of rock layers by fracturing under a high hydraulic pressure. An important component of this process is the fracturing fluid. Development of specialized fracturing fluid systems in research and development has been heavily emphasized to provide better performance and reduced environmental impact. This research describes rheological measurements of fracturing fluids under varying pressure up to 1000 bar and temperatures up to 125°C using a rotational rheometer. At lower shear rates, the data obtained from the pressure cell setup is compared with a standard cup/bob setup to confirm comparability.

Wednesday 5:30 Conference Center Lower Level PO64

Electrorheological characterization of a starch in oil suspension

Aadil Elmoumni and Aloyse J. Franck
Product Management, TA Instruments - Waters LLC, New Castle, DE 19720, United States

Electrorheological fluids are suspensions of extremely fine non-conducting particles in an electrically insulating fluid, which show dramatic and reversible rheological changes when the electric field is applied. These changes in apparent viscosity can be up to five decades in magnitude and the suspensions can go from the consistency of a liquid to that of a solid, and back, with response times on the order of milliseconds. Various modes of deformation underlying a range of voltage profiles, including step, ramp, sinusoidal, triangular, and pulse, were performed on the suspension. Experimental setup and results of these experiments will be shown.

Wednesday 5:30 Conference Center Lower Level PO65

Dielectric-rheology simultaneous analysis

Minglong Yao
TA instruments, New Castle, DE 19720, United States

Newly developed dielectric accessory can be equipped with DHR, ARES-G2 and RSA-G2 rheometers, and dielectric-rheology simultaneous measurements and synchronized data sampling can be easily carried out through rheometer operation software. The software offers various types of operation modes which allow the system to perform almost any combination test of dielectric and rheology. This poster will brief the technology, the unique features and the interesting applications data.

Wednesday 5:30 Conference Center Lower Level PO66

Dynamical equations for the contact line of a sessile drop

Eliot Fried[1] and Michel Jabbour[2]
[1]Mechanical Engineering, McGill University, Montreal, Quebec H3A 0C3, Canada; [2]Mathematics, University of Kentucky, Lexington, KY 40506, United States

The equations that govern, away from equilibrium and accounting for dissipation, the evolution of the contact line of an evaporating or condensing sessile drop on a rigid, planar substrate are derived. Aside from the normal and tangential components of the standard (Newtonian) force balance, these include a configurational force balance. At equilibrium, the normal component of the standard force balance reduces to the modified Young equation first mentioned by Gibbs. The remaining balances are purely dissipative and hence are vacuous in equilibrium. A complete description of contact-line dynamics generally involves all three equations. The theory is embedded in a thermodynamical framework that ensures consistency of all constitutive relations with the second law. In the simplest case, these involve six contact-line viscosities. When viscous coupling is neglected, only three viscosities remain. One is associated with stretching of the fluid along the contact line. The remaining two are related to dissipation that accompanies mass transfer between liquid and vapor phases during evaporation or condensation.

Wednesday 5:30 Conference Center Lower Level PO67

Statistical-mechanical derivation of the Canham–Helfrich free-energy density

Eliot Fried[1] and Brian Seguin[2]
[1]Mechanical Engineering, McGill University, Montreal, Quebec H3A 0C3, Canada; [2]McGill University, Montreal, Canada

The Canham-Helfrich free-energy density for a lipid bilayer has drawn considerable attention. Aside from the mean and Gaussian curvatures, this free-energy density involves a spontaneous mean-curvature that encompasses information regarding the preferred, natural shape of the lipid bilayer. We use a straightforward statistical-mechanical argument to derive the Canham-Helfrich free-energy density. Our derivation (i) provides a justification for the common assertion that spontaneous curvature originates primarily from asymmetry between the leaflets comprising a bilayer and (ii) furnishes expressions for the splay and saddle-splay moduli in terms of derivatives of the underlying potential.

Wednesday 5:30 Conference Center Lower Level PO68

Out of phase modulation of Taylor-Couette flow with viscoelastic fluid

Mehdi Riahi[1], Said Aniss[1], Mohamed Ouazzani Touhami[1], and Salaheddine Skali Lami[2]
[1]Laboratory of Mechanics, University Hassan II, Casablanca, Morocco; [2]Institut National Polytechnique de Lorraine, Laboratoire d'Energetique, Mécanique Théorique et Appliquée, Nancy, France

The hydrodynamic instability of a pulsed flow in a viscoelastic fluid confined in a Taylor-Couette system is investigated. Both cylinders are subject to an out-of-phase modulation of rotation having the same amplitude and frequency. We focus attention on the linear stability analysis in the case of a linear Maxwell model and on the effect of the Deborah number and frequency number on the critical values of the Taylor and wave numbers. The linear stability analysis has been solved using the Floquet theory and a technique of converting a boundary value problem to an initial value problem. We show that in the limit of low frequency, the Deborah number has no effect on the stability of the basic state which tends to a stable configuration corresponding to steady circular Couette flow. When the frequency number increases, the basic flow tends to a stable state and the Deborah number has a destabilizing effect more pronounced in the high frequency limit. Furthermore, by increasing the Deborah number, the critical values of the Taylor and wave numbers tend to constant values and vary independently of the frequency number. These numerical results are in good agreement with the asymptotic solutions obtained in the limit of high and low frequencies

Wednesday 5:30 Conference Center Lower Level PO69

Rheological characterization of monoclonal antibody solutions by multiple particle tracking microrheology

Hui Tung Lam and Eric M. Furst
Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Monoclonal antibodies (mAbs) have emerged as a popular class of protein therapeutics that target oncologic and immunologic diseases. The most conventional route of delivery for protein drugs has been intravenous administration in low concentrations. However, mAb therapies require frequent and chronic administration, and the subcutaneous administration is the more appealing route because of its ease of storage and opportunity for patient self-administration. This requires formulations with high concentrations of mAbs, which increases viscosity and may lead to protein destabilization. High viscosity also leads to challenges in production and processing. Thus, identifying formulation conditions that mitigate solution viscosity is critical in the early development of high concentration biotherapies. Passive microrheology has emerged as a powerful method to study scarce therapeutic materials. It obviates the challenges of large amount of sample needed and the associated cost during the early stages of drug development, and offers distinct advantages of small sample size and short acquisition time over macrorheology. In the present work, we study the applicability of multiple particle tracking microrheology in mAb solutions, and compare the results of microrheology and macrorheology. The effect of surface chemistry on probe stability will also be examined.

Wednesday 5:30 Conference Center Lower Level PO70

Deformation of mAb clusters at high concentration and shear rates

Rosalynn Taing[1], Jacob Luoma[1], Ankit Patel[1], Fred Lim[2], and Isidro E. Zarraga[1]
[1]Late Stage Pharmaceutical Development, Genentech, South San Francisco, CA 94080, United States; [2]Pharmaceutical Processing & Technology Development, Genentech, South San Francisco, CA 94080, United States

The high shear rheological behavior of two concentrated monoclonal antibody (mAb) solutions (mAb1, mAb2) was examined using a rotary rheometer to determine viscosity, shear stress and normal stresses. The viscosity results show at high concentrations, mAb 1 has much higher viscosities than mAb2. Additionally, for the high viscosity mAb1 solution shear thinning or viscosity lowering occurs at sufficiently high shear rates (relevant to needle expulsion) providing evidence of mAb clustering. Indeed, viscosity vs. shear stress plots reveal a yielding phenomenon, i.e. past a critical shear stress the mAb cluster is disrupted. This mAb cluster disruption is reversible in that the original viscosity is quickly recovered when the shear rate is ramped back down to lower levels. Additionally, a significant positive first normal stress difference (N1), which measures the structural anisotropy, for high viscosity mAb solutions was observed. The N1 starts to become measurable at the onset of shear thinning, consistent with a cluster structure becoming increasingly anisotropic (via deformation or disruption) as shear rate is increased.

Wednesday 5:30 Conference Center Lower Level PO71

Impact of external flow on the dynamic properties of microorganisms near surfaces

Sandeep Chilukuri, Cynthia H. Collins, and Patrick T. Underhill
Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

The behavior of polymers and colloids in flows between surfaces has been of interest for a long time, especially with recent developments in microfluidics. The increased usage of microfluidics in the areas of microbial behavior and cellular biophysics motivates us to investigate the response of microorganisms in narrow flow channels. Swimming organisms have been extensively studied, in part because of their relevance in the medical field and also in the development of artificial microswimmers with applications in sensing and drug delivery. Swimming microorganisms are often found in confined spaces or on surfaces, where attachment to surfaces and biofilm formation can have detrimental effects, ranging from infection to biofouling and corrosion. The active (propulsive) motion of the organisms will change their behavior from that of a passive colloidal suspension. In the absence of external flow, surface accumulation of microorganisms observed in experiments has been compared with theories that include (1) hydrodynamic interactions (HI) between the cells and surfaces, (2) surface mediated collisions, and (3) rotational Brownian motion. In our computer simulations, we include all three effects, and investigate the role of HI with the surfaces. The HI is included in the simulation by modeling the organisms as force dipoles. We use two simple flows, a uniform shear (Couette) and a parabolic (Poiseuille) flow. The results of our simulations illustrate the importance of hydrodynamic interactions with walls and specific flow conditions on the steady-state density distribution, orientation distributions and mean-squared displacement of microorganisms between two surfaces. These observations are of relevance where surface accumulation and upstream migration enable growth and adaptation

Wednesday 5:30 Conference Center Lower Level PO72

Mechanical response of a circulating tumor cell in a narrow microchannel

Zeina S. Khan[1], Nabiollah Kamyabi[1], Souad Sennoune[2], Raul Martinez-Zaguilan[2], and Siva A. Vanapalli[1]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]Health Sciences Center, Texas Tech University, Lubbock, TX, United States

An important step in cancer metastasis is the hydrodynamic transport of the so-called circulating tumor cells (CTCs) through blood microvessels. In vivo imaging studies in animal models show episodes of confinement and trapping of tumor cells at microvessel bifurcations, suggesting that these hydrodynamic phenomena are important processes regulating CTC dissemination. Our goal is to use microfluidics to understand the interplay between tumor cell rheology, confinement and fluid forces that may help to identify physical factors determining CTC transport.

We use leukemia cells as model CTCs and mimic the in vivo situation by investigating their motion in a confined microchannel. We also integrate a microfluidic manometer to measure time variations in the blockage pressure during tumor cell motion. By analyzing the high-speed movies, variations in blockage pressure, cell shape, cell velocity, and cell entry time into the microchannel are simultaneously quantified. We find that the blockage pressure is more sensitive to the driving parameters and cell size than the cell shape under confinement. Comparisons of the cell response to flow through a confined channel to simple model systems reveals a framework to characterize the rheological properties of a CTC under confined shear flow.

Wednesday 5:30 Conference Center Lower Level PO73

Nanoporous scaffold with enzyme encapsulation during flow-induced gelation

Ya Zhao[1], Joshua J. Cardiel[1], Jong-Hoon Kim[2], Jae-Hyun Chung[2], and Amy Q. Shen[2]
[1]Mechanical Engineering, University of Washington, Seattle, WA, United States; [2]University of Washington, Seattle, WA 98195, United States

One important area of biosensor research is the immobilization of enzymes with retained or enhanced activities and lifetimes as it is critical to enhance biosensor performance. The enzyme immobilization method introduced here is based on our recent work of forming stable nanoporous scaffolds with proper hydrodynamic conditions and spatial confinement from a wormlike micellar solution. We mix the enzyme (glucose oxidize, GOx) in a wormlike micellar solution containing nonionic surfactants (25%wt of Tween 80 and the concentration of ML at a weight ratio of 0.09) before they pass through a series of micropost arrays. The spatial confinement, high strain rates (~100000 1/s), and high strain (~10000) induced an irreversible gelation, forming a nanoporous scaffold which serves as a host matrix with immobilized enzyme GOx. Our new approach used microfluidic devices to facilitate the single-throughput, in-situ process to immobilize enzymes in a nanoporous scaffold that can retain the enzymes' native stabilities and reactivities. This nanoporous scaffold provides the favorable host matrix that isolates the enzyme molecules, protecting them from self-aggregation and leaching, while providing a similar local aqueous microenvironment as in biological media. The glucose sensor designed by this nanoporous scaffold shows high sensitivity, stability, and selectivity

Wednesday 5:30 Conference Center Lower Level PO74

A microfluidic study of nanoparticles in simulated blood flows: Understanding the effect of margination

Erik Carboni[1], Grant Bouchillon[2], Leslie Shor[1], Suzy Torti[3], and Anson Ma[1]
[1]Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT, United States; [2]Department of Civil and Environmental Engineering, University of Connecticut, Storrs, CT, United States; [3]University of Connecticut Health Center, Farmington, CT, United States

There has been a growing interest in using nanoparticles as drug delivery vehicles, especially for cancer treatment [Nat. Rev. Cancer, 5(3): 161 (2005); MRS Bulletin, 37: 828 (2012)]. Nanoparticles of different sizes and shapes have been produced from a variety of materials and the surface chemistry of these nanoparticles can be further tailored to evade the immune system and/or facilitate their selective attachment at the targeted sites. However, little is known about the rheology of nanoparticles in blood flow, which must be understood if the nanoparticles are to be administered intravenously. Further, Decuzzi et al. [Ann. Biomed. Eng., 33(2): 179 (2005)] proposed theoretically that the interactions between the blood vessel walls and nanoparticles can lead to a "margination" phenomenon wherein the nanoparticles trend toward the periphery of blood vessels. The implication is a higher chance for the nanoparticles to diffuse into the tumor through the leaky vasculature typically found near tumor sites. We examine this important hypothesis by studying the flow dynamics of 100 nm polystyrene spheres in microfluidic devices mimicking blood vessel bifurcations.

This work is supported by grant W81XWH-10-1-0434 from the Department of Defense and the NSF EAGER award (#1250661).

Wednesday 5:30 Conference Center Lower Level PO75

Ewoldt fingerprints for large amplitude oscillatory shear flow analysis: Both kinds

Chuanchom Aumnate[1] and A. Jeffrey Giacomin[2]
[1]Mechanical Engineering Department, University of Wisconsin-Madison, Madison, WI 53706-1572, United States; [2]Rheology Research Center and Mechanical Engineering Dept., University of Wisconsin - Madison, Madison, WI 53706, United States

We analyze responses to LAOS with dimensionless loops of shear stress and of the normal stress differences versus shear rate over a two-dimensional Pipkin diagram, We/De versus De. We call these interesting and informative grids Ewoldt fingerprints of the first kind (EF1K) [1]. We then replace the ordinate with just We, keeping De on the abscissa, and we then call these Ewoldt fingerprints of the second kind (EF2K). We use these fingerprints to investigate the viscoelastic behavior of molten polyethylene in large amplitude oscillatory shear flow (LAOS) by solving the dimensionless differential form of the corotational Maxwell model numerically. We use MAPLE version 15.00 (MaplesoftTM, Waterloo, Ontario, Canada) to solve the initial-value problems numerically for the differential equations using the Runge-Kutta method [2]. We compare our finite difference solutions with a recent approximate analytical solution [3] which was obtained by integrating the corotational Maxwell model using the Goddard-Miller inversion [4].

Wednesday 5:30 Conference Center Lower Level PO76

The need to monitor the edge is part of the “folklore” of rheometry: Effects of over- and underfilling in rotational rheometry

Naveen K. Reddy, Ruth Cardinaels, and Christian Clasen
CIT, KU Leuven, Heverlee, Belgium

The first part of the above title, which is a quote of Denn and coworkers[1], stresses the importance of the shape of the sample edge in measurements of the rheological properties using rotational rheometry. Requirements on the sample boundaries and corresponding procedures for sample trimming can be found in most basic rheology textbooks. Nevertheless, the effects of over-and underfilling of the sample are too often neglected or correct filling may not always be feasible. For instance, when measuring slip on a superhydrophobic material, the sample will always be either over-or underfilled due to contact angles >150°. Samples that are extremely sensitive to degradation may be inserted in a closed oven (without trimming) or overfilled to avoid exposure to the environment. Hence, quantification of the contributions of over- and underfilling to the rheological parameters would allow researchers to assess when they can be neglected and which corrections should be taken into account when over- or underfilling is unavoidable. In the present work, the effects of sample over- (up to 100%) and underfilling (up to 60%) on the rheological properties measured in rotational rheometry are presented. A variety of standard samples, covering a range of viscosities, both with and without viscoelasticity and shear thinning, are used. Experimental results are obtained by systematically varying the amount of over- and underfilling by changing the gap height for a given sample volume. The errors due to over- and underfilling vary based on sample type and measuring geometry. The largest errors occur for measuring geometries with a small radius and/or large measuring height (for parallel plates). For Newtonian samples, measurement errors of up to around 20% can occur for parallel plates with a gap spacing of 1 mm. For non-Newtonian samples, errors are larger. The effects of underfilling are even more devastating. These effects are qualitatively captured using numerical simulations. [1] D.S.Kalika et al., J.Rheol., 33,1059(1989)

Author Index

Paper Index

Plenary Lectures and Award Presentation

Monday, February 11 *8:30 AM, C102-C104*	**Rheological consequences of localization** Charles F. Zukoski *Department of Chemical and Biological Engineering, University at Buffalo*
Tuesday, February 12 *Bingham Lecture* *8:30 AM, C102-C104*	**Linear viscoelasticity of associating ionomers** Ralph H. Colby *Materials Science and Engineering, Penn State University*
Wednesday, February 13 *8:30 AM, C102-C104*	**Drag reduction and the dynamics of turbulence in simple and complex fluids** Michael D. Graham *Chemical and Biological Engineering, University of Wisconsin-Madison*
Thursday, February 14 *Metzner Award Presentation* *8:00 AM, C106*	**New directions in single polymer dynamics: Molecular rheology, hybrid biomaterials, and microfluidic trapping** Charles M. Schroeder *Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign*

Social Program

Sunday, February 10	**Welcoming Reception**	
	6:30 PM – 8:30 PM	Conference Center Lower Level
	Hosted by TA Instruments	
Tuesday, February 12	**Society Business Meeting**	
	12:05 PM	C106, Conference Center
	Awards Reception	
	7:00 PM – 8:00 PM	Athenaeum, Caltech
	Sponsored by a generous contribution from Xpansion Instruments	
	Awards Banquet	
	8:00 PM	Athenaeum, Caltech
Wednesday, Febraury 13	**Poster Session Reception**	
	5:30 PM – 7:30 PM	Conference Center Lower Level
	Sponsored by a generous contribution from Anton-Paar USA	

The Society gratefully acknowledges the generous support of
Anton-Paar USA, TA Instruments, and Xpansion Instruments.