THE SOCIETY OF RHEOLOGY

81ST ANNUAL MEETING
PROGRAM AND ABSTRACTS

Monona Terrace
Madison, Wisconsin
October 18 - 22, 2009

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Meeting Schedule

Monday, October 19, 2009

8:30	N. J. Wagner (PL1)				
9:20	Coffee				
9:45	SC1	SA1	MR1	BR1	MS1
10:10	SC2	SA2	MR2	BR2	MS2
10:35	SC3	SA3	MR3	BR3	MS3
11:00	SC4	SA4	MR4	BR4	MS4
11:25	SC5	SA5	MR5	BR5	MS5
11:50	Society Luncheon at NOON				
1:55	SC6	SA6	MR6	BR6	MS6
2:20	SC7	SA7	MR7	BR7	MS7
2:45	SC8	SA8	MR8	BR8	MS8
3:10	SC9	SA9	MR9	BR9	MS9
3:35	SC10	SA10	MR10	BR10	MS10
4:00	Coffee				
4:25	SC11	SA11	MR11	BR11	MS11
4:50	SC12	SA12	MR12	BR12	MS12
5:15	SC13	SA13	MR13	BR13	MS13
5:40	SC14	SA14	MR14	BR14	MS14
6:05	SC15	SA15		BR15	MS15
6:30	End				
7:00	Society Reception				

Tuesday, October 20, 2009

8:30	G. B. McKenna (PL2)				
9:20	Coffee				
9:45	SC16	SM1	MR16	BR16	MS16
10:10	SC17	SM2	MR17	BR17	MS17
10:35	SC18	SM3	MR18	BR18	MS18
11:00	SC19	SM4	MR19	BR19	MS19
11:25	SC20	SM5	MR20	BR20	MS20
11:50	Lunch				
1:30	SC21	SM6	EB1	GG1	VS1
1:55	SC22	SM7	EB2	GG2	VS2
2:20	SC23	SM8	EB3	GG3	VS3
2:45	SC24	SM9	EB4	GG4	VS4
3:10	SC25	SM10	EB5	GG5	VS5
3:35	Coffee				
4:00	SC26	SM11	EB6	GG6	VS6
4:25	SC27	SM12	EB7	GG7	VS7
4:50	SC28	SM13	EB8	GG8	VS8
5:15	SC29	SM14	EB9	GG9	VS9
5:40	SC30	SM15	EB10	GG10	VS10
6:05	End				
6:10	Society Business Meeting				
7:00	Awards Reception				
8:00	Awards Banquet				

Wednesday, October 21, 2009

8:30	A. K. Sood (PL3)				
9:20	Coffee				
9:45	SC31	SM16	EB11	GG11	FM1
10:10	SC32	SM17	EB12	GG12	FM2
10:35	SC33	SM18	EB13	GG13	FM3
11:00	SC34	SM19	EB14	GG14	FM4
11:25	SC35	SM20	EB15	GG15	FM5
11:50	Lunch				
1:30	SC36	SM21	EB16	GG16	FM6
1:55	SC37	SM22	EB17	GG17	FM7
2:20	SC38	SM23	EB18	GG18	FM8
2:45	SC39	SM24	EB19	GG19	FM9
3:10	SC40	SM25	EB20	GG20	FM10
3:35	Coffee				
4:00	IC1	SM26	EB21	GG21	FM11
4:25	IC2	SM27	EB22	GG22	FM12
4:50	IC3	SM28	EB23	GG23	FM13
5:15	IC4	SM29	EB24	GG24	FM14
5:40	IC5	SM30	EB25	GG25	FM15
6:05	End				
6:10	Poster Session & Reception				

Thursday, October 22, 2009

7:45	SC41	SM31	IC6	GG26	FM16
8:10	SC42	SM32	IC7	GG27	FM17
8:35	SC43	SM33	IC8	GG28	FM18
9:00	SC44	SM34	IC9	GG29	FM19
9:25	SC45	SM35	IC10	GG30	FM20
9:50	Coffee				
10:10	SC46	SM36	IC11	GG31	
10:35	SC47	SM37	IC12	GG32	
11:00	SC48	SM38	IC13	GG33	
11:25	SC49	SM39	IC14	GG34	
11:50	SC50	SM40	IC15	GG35	
12:15	End				

Session Codes

BR = Biorheology and Rheology in Biological Systems
EB = Emulsions, Blends and Multiphase Systems
FM = Non-Newtonian Fluid Mechanics and Stability
GG = Gels, Glasses and Jammed Systems
IC = Industrial and Complex Systems Rheology
MR = Microrheometry and Microfluidics
MS = Molecular Modeling and Simulation in Rheology
PL = Plenary Lectures
SA = Self-Assembled Systems and Interfacial Rheology
SC = Suspensions and Colloids
SM = Polymer Solutions and Melts
VS = Viscoplasticity and Soft Solids

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Lecture Hall PL1

Microstructure and rheology relationships for concentrated colloidal dispersions: Shear thickening fluids and their applications

Norman J. Wagner

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Measurements of the microstructure commensurate with the viscosity and normal stress differences in shearing colloidal suspensions provides an understanding of how to control the viscosity, shear thinning, and shear thickening rheological behavior typical of concentrated dispersions. In this presentation, I will review some of the experimental methods and key results concerning the micromechanics of colloidal suspension rheology. In particular, colloidal and nanoparticle dispersions can exhibit shear thickening, which is an active area of research with consequences in the materials and chemical industries, as well as an opportunity to engineer novel energy adsorbing materials. A fundamental understanding of shear thickening has been achieved through a combination of model system synthesis, rheological, rheo-optical and rheo-small angle neutron scattering (SANS) measurements, as well as simulation and theory. In particular, the shear-induced self-organization of "hydroclusters" (transient colloid concentration fluctuations) as predicted by Stokesian Dynamics simulations are measured and connected to the suspension rheology. The onset of shear thickening is demonstrated to be understood as a balance of convective, colloidal and hydrodynamic forces and their associated timescales. The limits of shear thickening behavior are also explored at extreme shear rates and stresses, where particle material properties come into play. Although many applications of concentrated suspensions are hindered by shear thickening behavior, novel materials have been developed around shear thickening fluids (STFs). Ballistic, stab and impact resistant flexible composite materials are synthesized from colloidal & nanoparticle shear thickening fluids for applications as protective materials. The rheological investigations and micromechanical modeling serve as a framework for the rational design of STF-based materials to meet specific performance requirements not easily achieved with more conventional materials, as will be discussed.

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Monday 9:45 Lecture Hall SC1

Hydrodynamic interactions between particles in viscoelastic liquids: Trajectory analysis

Jan Vermant[1], Frank Snijkers[1], Rossana Pasquino[2], and Nino Grizzuti[2]

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Particles in viscoleastic fluids find applications in consumer care products, particle filled polymers and nanocomposites. Viscoelasticity in the suspending medium will affect particle motions and hydrodynamic interactions-, which in turn will have effects on structure formation and rheology of the suspensions. In the present work, we investigated experimentally the effects of fluid rheology on the motion of particles, with an emphasis on fluid rheology effect on the hydrodynamic interactions. To evaluate the effect of variations in rheological properties of the suspending media, fluids have been selected which highlight specic constitutive features. These include a reference Newtonian fluid, a constant viscosity, high elasticity Boger fluid, a single relaxation time wormlike micellar surfactant solution and a broad spectrum shear-thinning elastic polymer solution. Particles were suspended in these fluids and a counterrotating device was used to analyze the particle trajectories. Whereas the trajectories are reversible and symmetric for Newtonian fluids, this symmetry gets broken for viscoleastic liquids in a manner which depends on the fluid characteristics. The implications of these results for for structure (necklace) formation and the overall suspension rheology will be discussed.

Monday 10:10 Lecture Hall SC2

Buckling transition in wall-bounded hydrodynamic crystals

Jerzy Blawzdziewicz[1] and Eligiusz Wajnryb[2]

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Complex structural transitions occur in hydrodynamically driven quasi-2D systems of microspheres confined in a microchannel. In our recent investigations we have observed order-disorder transitions, fingering instabilities, and development of dislocations and disclinations in a particle lattice. In this talk we analyze novel structural transformations that occur in periodic square arrays of microspheres, resulting in a new hexagonal order with a large number of mobile defects.

We explain the transition in terms of a buckling instability producing vertical displacements of particle rows. Our simulations predict that at the early stages of the evolution the particle lattice is stabilized by random transverse particle displacements that prevent coherent movement of particle rows. We also discuss implications of this novel stabilizing mechanism for systems such as compressed membranes undergoing thermal fluctuations.

Monday 10:35 Lecture Hall SC3

Numerical simulation of concentrated suspensions of non-colloidal particles in Couette flow

Kyongmin Yeo and Martin R. Maxey
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Fully three-dimensional numerical simulations of concentrated suspensions of O(1000) particles in a Couette flow at zero Reynolds number are performed with the goal of determining the wall effects on concentrated suspensions of non-colloidal particles. The simulations are based on the force-coupling method (FCM), using the lubrication correction scheme in Yeo & Maxey (2009). The scheme for the lubrication force is tested against previous boundary collocation and Stokesian Dynamics results. The simulations are performed for 0.2 < phi < 0.4 and $10 < L_y/a < 30$, where phi denotes the volume fraction and L_y and a are, respectively, the channel width and the particle radius. It is shown that the suspensions can be divided into two region; the wall region where the structured particle-layering is dominant and the core region in which the suspension field is quasi-homogeneous. The width of the wall region is a function of phi and not sensitive to L_y/a, once L_y/a is larger than a threshold. Rheological properties in each regions are investigated. In the core region, the ratio of the normal stress differences is $N_2/N_1 \sim 1$ while $N_2/N_1 > 1$ in the wall region. The particle stresses are compared with previous rheological models.

Monday 11:00 Lecture Hall SC4

Performance of mesoscale modeling methods for predicting rheological properties of charged polystyrene/water suspensions

Peter R. Schunk[1], Jeremy B. Lechman[1], Gary S. Grest[1], Steve J. Plimpton[1], Matt K. Petersen[1], Richard Jendrejack[2], Pieter in't Veld[3], Horst Weiss[3], Chris Stoltz[4], David Heine[5], Jonathan L. Higdon[6], and Amit Kumar[6]
[1]Sandia National Laboratories, Albuquerque, NM, NM 87185, United States; [2]3M Corporation, St. Paul, MN 55144, United States; [3]BASF Corporation, Ludwigshafen, Germany; [4]Procter and Gamble Co., West Chester, OH, United States; [5]Corning, Inc., Corning, NY, United States; [6]Chemical and Biomolecular Engineering, University of Illinois, Urbana, IL 61801, United States

In this presentation we examine the accuracy and performance of a suite of discrete-element-modeling approaches to predicting equilibrium and dynamic rheological properties of 950 nm polystyrene suspensions. What distinguishes each approach presented is the methodology of handling the solvent hydrodynamics. Specifically, we compare stochastic rotation dynamics (SRD), fast lubrication dynamics (FLD), dissipative particle dynamics (DPD), and the Galerkin/finite element method of solvent hydrodynamics against each other and against experimental data. Quantities examined are equilibrium structure properties (e.g. pair-distribution function), equilibrium dynamic properties (e.g. short - and long-time diffusivities), and dynamic response (e.g. steady shear and dynamic relaxation). In all approaches we deploy the DLVO potential for colloid-colloid interactions. Comparisons are made over a range of volume fractions and salt concentrations.

Monday 11:25 Lecture Hall SC5

Low-order statistical properties of suspensions based on an algebraic closure model for the fourth-order orientation moment

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Non-spherical particles dispersed in a fluid have a tendency to align in shear flows because of particle-fluid drag. This phenomenon is opposed by rotary diffusion. At high concentrations and in the absence of hydrodynamic couples, self-alignment occurs because excluded volume forces prevent the return-to-isotropy of anisotropic states by rotary Brownian motion. The balance between microhydrodynamic and diffusive torques at the microscale has a direct impact on the rheological properties of particulate suspensions and liquid crystalline polymers at the continuum scale. Over the past sixty years, important characteristics of the microstructure associated with the foregoing alignment phenomenon have been quantified in terms of the low-order moments of the orientation density function governed by the rotary Smoluchowski equation. In the low-order statistical theory presented in this paper, an algebraic preclosure equation that relates the fourth-order orientation moment to the second-order orientation moment is used to develop a realizable closure. The preclosure equation preserves the six-fold symmetry and contraction properties of the original orientation tetradic operator. In the presence of a simple homogeneous shear field, the new theory predicts that all two-dimensional and three-dimensional anisotropic states relax to either a steady state (isotropic or anisotropic) or an anisotropic periodic state, depending on the specific characteristics of the suspension and the characteristic time scale associated with the simple homogeneous shear field. The microstructure and the rheological characteristics predicted for rigid-rod fluids by the realizable closure model agree with previous theoretical and experimental results. The coexistence of stable anisotropic states predicted by the theory may provide an explanation of why micro defects occur during the processing of some structured fluids.

Symposium SA
Self-Assembled Systems and Interfacial Rheology

Organizers: Sascha Hilgenfeldt and Lynn Walker

Monday 9:45 Meeting Rooms KLOP SA1

An investigation of the collective behavior of colloidal particles trapped at a fluid-fluid interface

Shenghan Yan, Eric S. Shaqfeh, and Gerald G. Fuller
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It is now well known that charged colloidal particles form an effective two-dimensional suspension at a fluidic interface. Although microscopic images and rheological measurements have been obtained in abundance,the underlying physics behind the collective behaviour of such systems is not fully understood. In the case of charged, neutrally buoyant colloidal particles at a fluidic interface, capillary attraction arises from the meniscus deformation, which is predominantly due to the mismatch of dielectric constants between the aqueous phase and the non-polar phase. On the other hand, aggregation is prevented by the long range Coulombic repulsion through the non-polar phase as proposed by Aveyard and coworkers. With these interaction potentials present, Monte Carlo simulation and Brownian dynamics simulation were performed, assuming pair-wise interactions with all physical constants of the system calculated for latex particles trapped at a water-decane interface. Microscopic images of such a system were recorded concurrently, serving as an internal verification of the numerical simulation. Furthermore, the pair distribution function in the radial direction and the angular order parameter, were extracted from the equilibrium configuration of the Monte Carlo simulation as well as real-time microscopic images to investigate the phase transition behaviour. We obtain qualitative agreement between the experimental observations and the simulations showing a two-dimensional phase transition from a disordered liquid phase to an ordered solid phase as the surface coverage of the particles increases. The numerical and the experimental methodologies can be readily extended to other two-dimensional colloidal suspensions, such as systems with non-spherical particles and different interfacial properties.

Monday 10:10 Meeting Rooms KLOP SA2

Apparent microrheology of oil-water interfaces by particle tracking

Chih-yuan Wu[1] and Lenore L. Dai[2]
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We investigate the dynamics of charged microparticles at polydimethylsiloxane (oil) - water interfaces using Pickering emulsions as an experimental template. The mobility of the charged particles depends largely on the viscoelastic properties of the oil phase and the wettability of the solid particles. More importantly, we have explored the potential of developing one-particle microrheology and two-particle microrheology at liquid-liquid interfaces. The complex, loss, and storage moduli of oil-water interfaces as a function of frequency measured from microrheology are compared with those of bulk oils measured from a conventional rheometer and developed bulk microrheology. The nature of the tracer particles plays an important role in one-particle microrheology at liquid-liquid interfaces, especially when the oil phase is viscoelastic. Finally, the difference between the results of one- and two-particle microrheology is compared.

Monday 10:35 Meeting Rooms KLOP SA3

Experimental rheological measurements at liquid-gas interfaces

Timothy P. Koehler, Melissa A. Yaklin, Carlton F. Brooks, Ray O. Cote, Anne M. Grillet, and Lisa A. Mondy
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The stability and dynamics of foams and emulsions are strongly influenced by interfacial rheology because of their large relative surface area. Several experimental techniques were employed to characterize the rheology at liquid-gas interfaces with an emphasis on the non-Newtonian behavior of surfactant-laden interfaces. An interfacial stress rheometer (ISR) was used to measure the steady and dynamic rheology by applying an external magnetic field to actuate a magnetic needle suspended at the interface. Micro-interfacial rheology (MIR) was also performed using optical tweezers to manipulate suspended microparticle probes at the interface to investigate the steady and dynamic rheology. Additionally, a surface dilatational rheometer (SDR) was developed and used to periodically oscillate the volume of a pendant drop. Applying the Young-Laplace equation to the drop shape, a time-dependent surface tension can be calculated and used to determine the effective dilatational viscosity of an interface. Using the ISR, SDR, and MIR, a wide range of sensitivity in surface forces (fN to nN) were explored as each experimental method has different sensitivities.

Monday 11:00 Meeting Rooms KLOP SA4

The measurement of surface rheological and surface adhesive properties using nanoparticle embedment and interfacial force microscopy

Stephen A. Hutcheson and Gregory B. McKenna
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In previous work, we determined the actual rheological behavior at the surface of a polystyrene film (1), a phase separated copolymer (2) and a commercially available polydimethylsiloxane (PDMS) rubber (3) at the nanometer scale by applying a viscoelastic contact mechanics model to experimental data. The objective of the current research is to build off this analysis and use nanosphere embedment experiments to probe the nanorheological behavior of the PDMS surfaces in the solid rubbery state with different particle diameters and chemistries. In this work, we use an atomic force microscope (AFM) to measure the embedment depth as nanoparticles are pulled into the surface by the thermodynamic work of adhesion. The results show that silica probes of different sizes (500 nm and 300 nm) give different results for the surface adhesion properties, although still within the range calculated using literature sources. Preliminary results from Interfacial Force Microscopy (IFM) are also compared with this technique. The addition of carbon-black filler into the PDMS is also studied. The results show embedment depths are affected, and an increase in modulus at these sub-micron scales is seen.

REFERENCES
1. S. A. Hutcheson and G. B. McKenna, Phys. Rev. Lett., 94, 076103 (2005); Phys. Rev. Lett., 94, 189902 (2005).
2. S. A. Hutcheson and G. B. McKenna, ANTEC 2007, Proceedings of the 65th Annual Technical Conference, Society of Plastics Engineers, Cincinnati (2007).
3. "The Measurement of Surface Rheological and Surface Adhesive Properties using Nanosphere Embedment," S. A. Hutcheson and G. B. McKenna, APS March Meeting 2008, American Physical Society, New Orleans, LA (2008).

Monday 11:25 Meeting Rooms KLOP SA5

Double wall ring geometry to measure interfacial rheological properties

Aloyse J. Franck[1], Steven Vandebril[2], and Jan Vermant[2]
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The interfacial shear rheology of thin liquid layers composed of particles, surfactants and macromolecules has been subject of many investigations during the last decade. The rheological characterization of these 2D structures is motivated by their intensive use in a variety of industries, ranging from enhanced oil recovery, food technology as well as biomedical applications. The most used devices measuring interfacial properties that can be attached to a commercial rheometer are the Du Noüy ring, disc or bi-cone geometry. These measuring devices on commercial devices are robust in usage, but have their limitations. The Du Noüy ring is only suitable for purely viscous interfaces, and even the more as an indexer. The bi-cone and disc geometries can be used for viscous and viscoelastic interfaces, but the sensitivity is limited because these device intrinsically posses a large area in contact with the bulk fluids, relative to the perimeter in contact with the interface to be measured. In this presentation a new double-wall ring geometry to be used with a standard rotational rheometer is introduced. It has the advantages of a good intrinsic sensitivity due to a small area in contact with the bulk phase and well defined flow fields that enable bulk and surface contributions to be separated. Yet, combined with a sensitive rheometer, it has a very large dynamic measurement range. The double-wall ring geometry has a square edged cross-section and is used with a temperature controlled bottom circular channel arrangement to contain the fluid. Results on model interfaces show that the new geometry is able to measure viscous as well as visco-elastic interfaces in both continuous shear and oscillatory experiments. The measured results are also corrected for the subphase drag by an iterative procedure based on the analysis of the subphase velocity profile.

Symposium MR
Microrheometry and Microfluidics

Organizers: Daniel Blair and Amy Shen

Monday 9:45 Hall of Ideas G MR1

Formation of supramolecular hydrogel microspheres via microfluidics

Amy Shen[1], Yajiang Yang[2], and Wanyu Chen[2]
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Supramolecular hydrogels have attracted increasing interest in recent years due to their fascinating physical and morphological properties and their potential applications in drug delivery, oil recovery, and tissue engineering. Supramolecular hydrogel microspheres are hydrogel particles formed by the self-assembly of hydrogelators in water, through noncovalent interactions. In comparison with the traditional bulk format of the supramolecular hydrogels, hydrogel microspheres provide faster responses to external stimuli. In this paper, we provide a novel strategy to prepare supramolecular hydrogel microspheres with diameters ranging from 15 to 105 microns by using microfluidics. Optical and scanning electron microscopy (SEM) demonstrate that compact entanglement round cage-like aggregates of hydrogelator were formed within the supramolecular hydrogel microsphere, in contrast to loose and less compact aggregates within bulk hydrogel. Thermal analysis (DSC) indicates that supramolecular hydrogel microspheres are more thermally stable and can immobilize more water molecules, owing to compact entangled three-dimensional network structures. This observation is of particular importance for potential drug delivery, bioseparation, and biosensor applications, as it allows unstable biomolecules to be encapsulated inside the hydrogel microspheres.

Monday 10:10 Hall of Ideas G MR2

Microfluidic device incorporating closed loop feedback control for uniform and tunable production of micro-droplets and emulsions

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Micro- and nanofluidics are both finding increasing use in the growing toolbox of nanotechnology; for the production of nanoparticles, and as micro-reactors for carefully controlled chemical reactions. These laboratories-on-a-chip hold vast potential for industrial application, however, only the most simple are truly starting to emerge as commercially viable, particularly in the area of droplet formation and emulsion creation. In order to automate droplet production with a desired size and dispersity, we have designed a microfluidic-based technology utilizing elementary microchannel geometries in combination with a closed loop feedback system to control the continuous and dispersed phase flow rates. Both the device geometry and control system have been optimized to allow for the production of a tunable emulsion. By utilizing discrete linear control theory, the device is able to produce the desired results with little to no prior knowledge of the fluid material properties to be used in either phase. We will present our results from initial development using a flow-focusing microfluidic geometry for droplet formation, computer-tethered syringe pumps to individually control the continuous and dispersed phase flow rates, a high-speed camera, and a controller and driver system for the optical measurements and pumps, respectively. We will show the efficacy of this technique for Newtonian and viscoelastic liquids, with and without the presence of surfactants. It can be envisioned that through careful control optimization, such a system can be developed to a point that will allow the production of "designer" emulsions with droplets eventually reaching the nanoscale.

Monday 10:35 Hall of Ideas G MR3

Microscale shear flow of focal conic defects in layered liquids

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Intermolecular interactions in liquid crystals and concentrated surfactant solutions lead to unique microstructures including lamellae, in which parallel layers are incompressible but bend easily. In such systems, planar layers are easily destabilized via external fields and nearby surfaces to produce topological defects of the order of tens of microns in size. These microscopic defects play a leading role in the flow behavior of such materials, and therefore impact numerous industrial applications including optoelectronic devices and displays and the processing of coatings, adhesives, and biomaterials to encapsulate drugs. To examine the interaction between such microscale defects and flow, we have developed a shear cell to impose a linear Couette flow in a microscale thin gap, while allowing for real time microscopic visualization. We use the shear cell to visualize the dynamics of defect formation in initially defect-free samples of a common small-molecule thermotropic liquid crystal, 8CB. We observe that the formation of focal conic defects, a specific topological defect typically found in thermotropic smectic liquid crystals, is triggered by edge effects and occurs in a series of phases, marked by distinct changes in the birefringence intensity. The defects are seen to annihilate partially or completely on reverse shear. The effect of shear rate and strain amplitude on defect formation and annihilation is studied.

Monday 11:00 Hall of Ideas G MR4

Confinement effects on the self-assembly of organogels

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1,3:2,4-di-p-methylbenzylidene sorbitol (MDBS) is a small organic molecule that is capable of inducing self-assembly in a wide variety of organic solvents and of forming organogels. In this paper, we present a novel approach to tune the network architectures of organogels by utilizing geometric confinement while varying the gelator concentration. Self-assembly of MDBS in propylene carbonate (PC) is investigated in a series of microchannels with widths varying from 20 um to 80 um and the gelator concentration varying from 2%wt to 7%wt. We demonstrate by optical microscopy, and scanning electron microscopy (SEM) that a transition from fibrillar structure to sheaflike spherulite structure occurs when (a) the channel width is increased for fixed gelator concentrations; (b) gelator concentration is increased for fixed channel widths. A phase diagram is built based on these observations. The thermal properties of the organogel is measured by differential scanning calorimetry (DSC) to verify the structural difference obtained under confined and unconfined conditions and the structure stability. Our results provide a novel strategy to control the topological structure of self-assembled systems and to modify their thermal properties via geometric confinement.

Monday 11:25 Hall of Ideas G MR5

Design of a microfluidic device for droplet capture

Swastika S. Bithi and Siva A. Vanapalli
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

We investigate the behavior of a train of droplets in a microfluidic loop containing a narrow constriction. Depending upon the hydrodynamic resistance of the network and the hydrodynamic resistance of individual droplets we observe capture and break-up of droplets that we classify into four different behaviors: 1) no-capture, no-break-up, 2) no-capture, break-up, 3) capture, break-up and, 4) capture, no-break-up. We present a phase diagram that identifies the optimal conditions for storing nanoliter-scale droplets on a microfluidic device. We will discuss these observations in the context of capillarity and hydrodynamic resistive droplet interactions.

Symposium BR
Biorheology and Rheology in Biological Systems

Organizers: Prosenjit Bagchi and Michael R. King

Monday 9:45 Meeting Rooms MNQR BR1

Oriented matrices of collagen for directed cellular growth

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The most prevalent protein found in the human body is collagen, which subsides mainly in connective tissues (tendons) and load bearing tissues such as bone and teeth. A collagen molecule itself is a rod-like molecule of about 300 nm in length and 1.5 nm in diameter. The molecular structure consists of three polypeptide strands wound in a left-handed triple helix. The rod-like molecule can self-assemble and transition from an isotropic phase into a highly oriented liquid crystal. The distinct liquid crystalline structures can be observed in many natural tissues such as bone, tendon, and human dermis. This research focuses on the production of a biocompatible substrate that can dictate cellular level control but also have similar mechanical properties of the natural tissues, such as tensile strength and flexibility. We have been able to manipulate the self-assembly of collagen molecules into various architectures using different flow processing techniques. The hydrodynamic forces orient the collagen molecules parallel to the flow direction prior to fiber formation, resulting in oriented gels of collagen. These oriented structures have demonstrated effective contact guidance of adult human fibroblasts where the cell bodies polarize their cytoskeleton along the direction of the fibers. In addition, the collagen matrices can retain their orientation while the surface is modified for different chemical or structural properties, adding versatility to these oriented structures of collagen. Chemical attachment of molecules, such as growth factors, onto the collagen substrates can attract the growth of cells along the oriented structures. The oriented collagen gels may also undergo crosslinking treatments to enhance their structural properties. A scaffold or substrate that has the ability to encourage attachment and proliferation of cells is an important step for the progression of finding compatible tissue replacements and biomimetic materials.

Monday 10:10 Meeting Rooms MNQR BR2

Rheological behavior of modified poly(2-hydroxyethyl methacrylate) [pHEMA]/normal human fibroblast [NHF] composite substrates: Applications for percutaneous medical implants

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Percutaneous implants are a family of medical devices that penetrate the skin, commonly failing from epidermal regression (marsupialization) that leads to the removal of the device and the suspension of treatment. Contributing to this problem is the mechanical discontinuity at the skin/device interface that initiates stress concentrations and chronic micro-trauma that hampers the formation of an optimal seal. To further the understanding of the in situ mechanics our group quantified the mechanical behavior of human skin under isothermal (37oC) low-magnitude shear loads over physiologically relevant frequencies (0.01-12Hz @ 0.1% strain), utilizing a stress-controlled rheometer. This analysis also included creep characterization. This data was a design criteria for the development of a novel, poly(2-hydroxyethly methacrylate)[pHEMA]-based solution to epidermal regression around percutaneous medical devices. Motivated chiefly by the mechanical interactions between the host tissue and the medical device, we developed a cell-based, co-culture in vitro assay to examine the change in shear-based mechanical behavior of a novel pHEMA-based substrate when presented with human fibroblasts [HFs], the dominant cell type in the human dermis, over a physiologically relevant frequency range. The study provided information about both the biological interaction (cellular infiltration) between the substrate and the ECM producing HFs and also the change in G' and G" values over the given frequency range as a consequence of those interactions. Any solution to epidermal regression must address the host immune-response but this approach offers an important glimpse into the mechanical behavior of the post-implantation substrate. The rheological characterization of pHEMA/NHF+ECM composite facilitated the design of the current pHEMA-based substrate currently under investigation in an on-going animal study aimed at advancing a solution to epidermal regression in percutaneous medical devices

Monday 10:35 Meeting Rooms MNQR BR3

Combined use of a rotational rheometer and Piezo-Rotary-Vibrator (PRV) to characterize soft biomaterials at sonic frequencies

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Piezoelectric technology was combined with a traditional rotational rheometer for sonic frequency measurements of soft biomaterials. A range of materials, well suited for vibratory body organs (the voice, the skin, or the ear), were evaluated. They included a micronized dermal dispersion (Cymetra), hydrogels including carbomers and hyaluronic acid-derived materials, and high molecular weight hyaluronate. Each sample was loaded onto the same parallel plates for both low and high frequency measurement 0.1 - 2000 Hz. One motor is enabled at a time. The torsional Gemini rheometer measures viscoelastic properties at 0.1 - 100 Hz while the lower Piezo-Rotary Vibrator (PRV) is locked (Malvern Instruments, Worcestershire, UK). Prior to 1 - 2000 Hz measures, the upper torsional motor is locked and the PRV is unlocked and engaged for rheologic measurement. The PRV is an enclosed six spoke system. A Lock-In amplifier excites three of the spokes with minimal voltage and the other three spokes detect angular deflection. Low and high frequency data overlapped well in the mid-frequency range, validating PRV measures for weak dispersions and gels. Rheologic implications for physiologic function of the biomaterials and additional functionality of the rheometer for the purpose of regenerative medicine are discussed.

Monday 11:00 Meeting Rooms MNQR BR4

Building gels with cells: Associating biopolymers mediating self-assembly of new tissues

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Here, we demonstrate that a hydrophobically-modified derivative of chitosan (hm-chitosan) is able mediate the self-assembly of cells into 3 dimensional solid gel networks. By reacting 6% of available primary amines along the chitosan backbone with C-12 aldehydes, we create associating biopolymers which are able form gel networks upon mixing with human umbilical vein endothelial cells (HUVECs). The working hypothesis is that by insertion of the hydrophobes along the chitosan backbone into hydrophobic cell membranes, the biopolymer is able to act as a bridge between neighboring cells; the cells act as the crosslinking points within the network. The HUVECs are used as model cells in this study as they are an essential component of new tissues and their size (15-20 microns) is representative of many important soft tissue cells. By adding two liquid solutions, (1) 0.5 wt% hm-chitosan and (2) 135,000 cells/ml of HUVECs, we form a solid gel which holds its weight upon vial inversion. In previous experiments, we have shown that hm-chitosan is capable of forming gels with vesicles (~100 nm). We characterized the mechanical properties of these gels by means of dynamic rheology. In the present study, these associating biopolymer networks are mechanically characterized with much bigger entities acting as the crosslinks. Dynamic rheology of the 0.5 wt. % hm-chitosan - 135,000 cell/ml HUVEC mixture showed that the sample possessed an elastic modulus (2.5 Pa) that was greater than the viscous modulus over a practical range of shear frequencies, and became independent of shear frequency, ω, as ω approaches 0 , characterizing the sample as an elastic gel. For the unmodified chitosan sample, rheology characteristic of a gel is not observed upon mixing with HUVECs. Lastly, we can reverse gelation of the hm-chitosan/HUVEC mixtures by the addition of a-cyclodextrin.

Monday 11:25 Meeting Rooms MNQR BR5

Structure and mechanics of dense fibrin gels from neutron scattering and non-linear rheology

Danilo C. Pozzo[1], Kathleen Weigandt[2], and Lionel Porcar[3]
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Fibrin self assembles into a nanofibrous network that is the primary structural component of a blood clot. Defining relationships between the formation conditions, structure, and mechanical behavior of fibrin networks is crucial to the understanding and treatment of various clotting pathologies. In this study, the structural and rheological properties of coarse fibrin gels formed in D2O solutions are investigated over a wide concentration range using neutron scattering and rheology. Scattering allowed us to expand the concentration range beyond that of any previous studies and to also include protein concentrations relevant to the composition of fully formed blood clots (> 20 mg/mL). SANS and USANS is used to seamlessly characterize the structural features of fibrin clots over length scales ranging from one nanometer to several micrometers. SANS and USANS also allow us to characterize the structure of strained fibrin networks in-situ. Fibrin, like many other biopolymers, is known for its unique strain dependent mechanical properties. The rheological properties of the fibrin clots, are also found to be highly concentration dependent. Using shear-SANS and rheo-SANS, the magnitude and existence of new strain stiffening and softening regimes is related to the fiber deformation in the network.

Symposium MS
Molecular Modeling and Simulation in Rheology

Organizers: Rajesh Khare and Nicos Martys

Monday 9:45 Hall of Ideas J MS1

Dynamic Monte Carlo simulations of lattice polymers subjected to shearing flows

Sachin Shanbhag
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For polymers subjected to a simple shear flow, the flow field is nonconservative and a flow potential cannot be synthesized easily, because the energy difference between any two points depends on the path taken. Following the idea of Xu et al. (1997) we partition the flow field into conservative (elongational) and non-conservative (rotational) components, and build a pseudo-potential based on the conservative component, and apply it to polymer melt system. We are able to describe several key features in the non-linear flow regime. A new transition probability scheme is proposed to expand the regime of applicability of the original model to faster flows.

Reference: G. Xu, J. Ding, and Y. Yang. J. Chem. Phys., 107(10):4070-4084, 1997.

Monday 10:10 Hall of Ideas J MS2

Dynamic Monte Carlo simulation of melt rheology

John R. Dorgan
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Dynamic Monte Carlo (DMC) simulation of polymers has been developed as a technique for studying polymers under flow conditions. Preliminary results are in excellent agreement with well-established experimental facts; a shear thinning viscosity is obtained, the first normal stress difference increases with shear rate, and the first normal stress coefficient decreases with shear rate. Importantly, the zero shear viscosity exhibits a transition and scales appropriately with molecular weight. Because of the terrific efficiency of the simulation technique, new and novel phenomena not previously observable in simulations can be studied in exquisite detail; the results generated shed insight into novel confinement effects that are being exploited in emerging areas of nanotechnology.

Monday 10:35 Hall of Ideas J MS3

A comparison of Brownian dynamics and lattice-Boltzmann simulations of dilute polymer solutions

Rahul Kekre, Jason E. Butler, and Anthony Ladd
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We compare the results of lattice-Boltzmann and Brownian dynamics simulations of a single flexible polymer in isolation and in confinement. We use identical potential parameters for the polymer model and correct for differences between the periodic boundaries used in the lattice-Boltzmann simulations and the unbounded domains used in the Brownian dynamics simulations. The dynamic properties of the isolated polymer molecule, including diffusivity and Rouse relaxation time, resulting from the two types of calculations agree within 2%. The LB results depend on the ratio of grid spacing to polymer size and converge to the values obtained from the BD simulation as the resolution increases; the results are insensitive to the temperature and fluid viscosity. Additional comparisons are made between calculations of the concentration profile for the polymer model in bounded regions with rectilinear flows. These results are also in numerical agreement for this more complex calculation.

Monday 11:00 Hall of Ideas J MS4

Effects of fluctuating hydrodynamic interactions on the dynamics of confined polymer solutions: Grooved channels and pore-translocation rates

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We present results of simulations of solutions of flexible polymers molecules during flow. A self-consistent coarse-grained Langevin description of the polymer dynamics is adopted in which hydrodynamic effects are included through a Green's function formalism. The $O(N)$ General Geometry Ewald-like Method is used to calculate the confined Stokeslet and concentrations in the range from ultra-dilute to semi-dilute (near the overlap concentration). For flowing polymer solutions in a grooved channel, the groove is almost completely depleted of polymer chains at high Weissenberg number in the dilute limit, but at finite concentration this depletion effect is dramatically reduced. Only upon inclusion of hydrodynamic interactions can these phenomena be properly captured. The rate constant for flow-induced translocation of polymer molecules through a square channel has been calculated using the Forward Flux Sampling method. The rate constant is affected by the walls and the confinement provided hydrodynamic interactions are taken into account. Such interactions lead to a decrease of the rate constant due to the decrease in particle mobility near rigid walls, and an increase due to the increase of the diffusion coefficient of hydrodynamically interacting polymer molecules.

Monday 11:25 Hall of Ideas J MS5

Reverse Poiseuille flow - the virtual rheometer

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Reverse Poiseuille flow (RPF) is demonstrated to be an accurate and convenient virtual rheometer for the acquisition of steady shear-rate rheological properties (non-Newtonian viscosity and normal stresses) of simulated fluids. The flow is generated from two Poiseuille flows driven by uniform body forces in opposite directions in the left and right halves of a computational domain. The RPF rheometer was tested on fluid systems of undiluted bead-spring chain models and their solutions using Dissipative Particle Dynamics (DPD). Periodic boundary conditions in RPF ensure the velocity to be zero on the walls without density fluctuations. Hence the calculated material functions are bulk properties. For isothermal solutions the material functions satisfy the principle of time-concentration superposition, and for undiluted chains temperature dependence is reconciled by the principle of time-temperature superposition. In overlapping shear-rate regimes properties calculated in plane Couette flow with Lees-Edwards periodic BC (LEC) were found to be in excellent agreement with RPF results. The RPF arrangement is generally more efficient and spans a greater range of shear rates than its Couette counterpart.

Monday Afternoon

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Monday 1:55 Lecture Hall SC6

Controlling the rheology of biomass

Joseph R. Samaniuk[1], Charles T. Scott[2], Thatcher W. Root[1], and Daniel J. Klingenberg[1]
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Rising demand for liquid fuel and increasing focus on global warming have created a need for fuel from renewable resources. The National Renewable Energy Laboratory (NREL) has proposed a process for converting lignocellulosic biomass to liquid fuel. The process has tremendous promise but its economics are inhibitory. NREL's process calls for roughly 10 wt% biomass. The costs associated with heating and pumping 90 wt% water slurries can be dramatically reduced by increasing the solids fraction. NREL's plans call for an increase in solids content from 10 to 40 wt% resulting in a 4-fold decrease in heating cost and a 6-fold decrease in the water requirement.

Processing concentrated biomass leads to a number of difficulties. Concentrated biomass is a Bingham fluid with a yield stress that increases rapidly with solids concentration, which makes transporting the slurry difficult if not impossible. In addition, the mass transfer required to mix enzymes and reagents into the slurry is severely inhibited. Experimentally characterizing the rheology of biomass is also challenging, as these materials exhibit large normal stresses, fracture and ejection from certain geometries. Understanding and controlling the rheology of biomass is critical for the success of high solids biomass processing.

In this presentation, we describe the use of rheological modifiers to control the rheology of biomass. By using high molecular weight water-soluble polymers, we can significantly reduce the yield stress of wood fiber and corn stover slurries. Using only a few wt% (based on dry solid) of these modifiers, yield stresses can be reduced several-fold, permitting flow at high concentrations. We will describe the effects of properties of the rheological modifiers (e.g., type and molecular weight) on rheological behavior, show evidence of the microscopic mechanisms producing the observed behavior, and examine the effects of the modifiers on the downstream biomass processing.

Monday 2:20 Lecture Hall SC7

Effect of fiber properties on the rheology of cellulosic suspensions visualized using magnetic resonance imaging

Emilio J. Tozzi[1], Michael J. McCarthy[2], Sharon P. Shoemaker[2], David Lavenson[1], and Robert L. Powell[1]
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Efficient processing of fibrous biomass requires adequate rheological characterization of fiber suspensions. Most published data on biomass rheology has been obtained using rotational rheometers and interpreted through generalized-Newtonian models. Due to the large size of fibrous biomass particles, settling, entanglements and migration occur. These phenomena cause difficulties in rheological studies made with rotational rheometers and analyzed using generalized-Newtonian models. Direct imaging of velocity profiles provides a way of characterizing flow in the presence of such non-idealities. We used magnetic resonance imaging to measure velocity profiles of cellulosic fiber suspensions flowing in an horizontal tube. Pressure drop and video images were simultaneously recorded. We observed a strong influence of fiber length, concentrations and flow rates on velocity profiles and pressure drops. At low flow rates and low concentrations vertically asymmetric velocity profiles were observed due to settling. At increased concentrations, entanglement of longer fibers was detected as solid-like regions moving with uniform velocity. Disruption of fiber entanglements at higher flow rates was observed in some cases. Advantages and challenges of using MRI for rheological characterization of biomass suspensions having various particle sizes are discussed.

Monday 2:45 Lecture Hall SC8

The effect of particle morphology on the maximum packing fraction and rheology of biomass slurries

Clare J. Dibble and Jonathan J. Stickel
National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401, United States

Biochemical conversion of ligno-cellulosic biomass to ethanol provides a renewable transportation fuel that can help reduce the use of non-renewable fossil fuels. However, designing an economical biochemical conversion process requires an understanding of the flow behavior of slurries of non-edible plant matter. Concentrated suspensions of dilute acid pretreated corn stover (PCS) were previously found to have a significant yield stress that decreases as enzymes break down cellulose into soluble sugars [Roche et al., Biotechnol. Bioeng. DOI 10.1002/bit.22381 (2009)]. Additionally, particle size and aspect ratio distributions of the PCS vary as a function of pretreatment severity and extent of enzymatic hydrolysis. In this work, we use these slurries with different particle morphologies to examine subtleties in the relationships between particle characteristics, particle volume fraction, and yield stress. Differences in distributions of area weighted particle diameter and aspect ratio lead to different yield stresses at the same volume fraction. The primary relationship between yield stress and volume fraction was modeled using the Wildemuth-Williams model [Wildemuth and Williams, Rheol. Acta. 24, 75-91 (1985)]. Variation in the best-fit model parameters with particle morphology shows that both size and shape information, along with the volume fraction, must be incorporated to properly capture the rheological behavior of polydisperse, non-spherical particulate suspensions.

Monday 3:10 Lecture Hall SC9

Bacterial cellulose, a natural choice for fiber network formation

Marco Caggioni, Seth E. Lindberg, and Patrick T. Spicer
Complex Fluid Microstructures, Procter & Gamble, West Chester, OH 45069, United States

Suspension and stabilization of solid particles in complex fluid microstructures is often a requirement for consumer products such as shampoos, conditioners and detergents. This task poses many challenges as optical transparency and negligible impact on product viscosity are required in addition to preventing particle sedimentation. In naturally selected complex fluids, such as cell cytoskeletons, a combination of fiber networks provides structure and plasticity. Cytoskeleton microstructures ensure the stability of suspended colloidal structures while preserving the possibility of flow. Inspired by nature, we design a fiber network to stabilize consumer products using Bacterial Cellulose (BC), a naturally occurring nano-fiber, secreted by the vinegar bacterium *Acetobacter Xilinum* [1]. The high aspect ratio of bacterial cellulose fibers allows the formation of colloidal gels at very low polymer concentration. The stability of the colloidal gel in very different solvent conditions is surprising and qualifies BC as an ideal material for producing yield stress materials. We propose BC structured fluids as a powerful suspending medium as well as a model system to study yield stress material properties.

[1] M. Tabuchi, NATURE BIOTECHNOLOGY 25, 389 (2007).

Monday 3:35 Lecture Hall SC10

Ultrasonic rheometry of pulp suspensions

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Pulp suspensions are opaque, inhomogeneous, non-Newtonian fluids and their rheological characterization is a complex task. It requires careful interpretation of the experimental data and it is commonly accompanied by large uncertainty of the measured parameters. To understand the rheology of pulp suspensions at a fundamental level, ultrasonic pulses are used to measure velocity profiles in pulp suspensions sheared in a vane-in-a-large cup rheometer. The rheological properties of pulp suspensions are then obtained using the velocity profiles that are fitted with predictions from viscous constitutive equations. In one case a Herschel-Bulkley model seems to adequate predict their viscous behaviour. These results (constants of the Herschel-Bulkley model including the yield stress) are compared with those obtained from macroscopic measurements in a conventional controlled-stress rheometer using a vane geometry and found to compare reasonably well. Experiments with model carbopol solutions are also performed to validate the experimental protocol and procedure.

Monday 4:25 Lecture Hall SC11

Rheology of polymer nanocomposites in the "nanoparticle limit"

Jonathan E. Seppala and Michael E. Mackay
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In the nanoparticle limit the radius of gyration of a suspending polymer is larger than both the radius of the dispersed nanoparticle and the interparticle half-gap. For linear, monodisperse polystyrene we previously found that a variety of dispersed nanoparticles reduce the melt viscosity of entangled polymers, swell polymer chains, and increase the tensile modulus in the glassy state in this limit. Continuing this work for polydisperse polymers, particularly for bidisperse blends, demonstrates that one component could be in the nanoparticle limit while the other would not be. Here we show that in many cases both must in the nanoparticle limit for a viscosity reduction to occur, although this is not a strict conclusion. Details will be discussed in the oral presentation.

Monday 4:50 Lecture Hall SC12

Aging of polystyrene melts filled with graphene layers: Rheology and dielectric spectroscopy

Hyunwoo Kim and Christopher W. Macosko
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We studied aging kinetics of polystyrene (PS) melts containing functionalized graphene sheets (FGS) using in-situ rheological and dielectric measurements. After large-amplitude shearing, temporal changes in elasticity and dielectric properties were monitored. Real and imaginary parts of complex shear modulus G* and dielectric permittivity ε* grew logarithmically with annealing time,~ t^a. Increases in elasticity and DC conductivity indicated restoration of stress-resisting and charge-conducting networks. Especially, samples near the particle percolation threshold displayed a drastic transition from insulator to conductor. Analogous physical aging was reported for aqueous suspensions of Laponite (Bonn, D., S. Tanase, B. Abou, H. Tanaka and J. Meunier Phys. Rev. Lett. 89, 015701 (2002)) and polymer melts filled with layered silicates (Ren, J., B. F. Casanueva, C. A. Mitchell and R. Krishnamoorti Macromolecules 36, 4188 (2003)). These changes are interpreted within the framework of aging soft colloidal glasses (Bonn, D., H. Kellay, H. Tanaka, G. Wegdam and J. Meunier Langmuir 15, 7534 (1999)). Effects of temperature, test strain, frequency, matrix molecular weight, viscosity, particle shape and concentration on micro-structural evolution of graphene networks will be also reported.

Monday 5:15 Lecture Hall SC13

Physical gelation and ripening dynamics of a model colloid

H. Henning Winter[1], Xiaoliang Wang[2], Gi Xue[2], and Pingchuan Sun[3]
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There is a large class of physical gels that slowly develop a structure of increasing connectivity. Most of the structural development occurs in the solid state after having passed through an early liquid-to-solid transition. Such physical gels are often called "soft glasses" because of their slow out-of-equilibrium dynamics. Here we examine the ripening of an out-of-equilibrium model colloidal solid that consists of clay particles that swell and exfoliate into randomly oriented clay sheets through the action of end-functionalized ("sticky") polymer molecules. The nano-composite gel serves as model material in search of regular patterns in the non-equilibrium dynamics in the approach of a stable final state close to equilibrium. Surprisingly, there exists a simple pattern in the time-resolved viscoelasticity: the product of equilibrium modulus and longest relaxation time, Ge(tr)·max(tr), remains constant throughout the ripening process. Parameter is the duration of the isothermal ripening process ("ripening time", tr). The product Ge·max has the dimension of a viscosity but belongs to the solid state of the gel. As a consequence of Ge·max =constant, a single scaling relation with two power law regions, a fast ripening process (~ tr-2) followed by slow ripening (~ tr-1/2), defines the state of ripening, e.g. the time necessary to reach equilibrium. Experiments on a wider group of physical gels is in progress with the objective of confirming or rejecting universality of the novel findings. The experimental protocol includes time-resolved rheometry (Rheol Acta 33:385-397, 1994) and rescaling of data (Rheol Acta 45:331-338, 2006).

Acknowledgment: NSF support through CBET-0651888.

Monday 5:40 Lecture Hall SC14

Time strain superposition in nanoparticle organic hybrids

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We report frequency-dependent shear rheology of dense suspensions of hairy nanoparticles. These materials mimic soft glass materials in many ways , including a yield stress, slow dynamics and divergence of the viscosity. We find that measurements performed over a limited range of frequencies and varying shear strains can be superposed onto a master curve that spans more than 22 decades in frequency. SGR model predicts consistent result with experimental data only at strains lower than yield strain. For larger strains, the strain-dependent horizontal shift factor is Surprisingly fit well by the empirical WLF equation for amorphous polymers, with temperature replaced by strain.

Monday 6:05 Lecture Hall SC15

Transient shear and extensional rheology and nanostructure of polymer nanocomposites

Christopher Kagarise[1], Monon Mahboob[2], Koki Miyazono[1], Kurt W. Koelling[1], and Stephen E. Bechtel[2]
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We have studied the rheological behavior of melt phase polystyrene (PS)/carbon nanofiber (CNF) composites under transient shear and extensional flows. Composite samples were made that contained CNF concentrations of 0, 2, 5 and 10 wt% in order to determine the effects of nanoparticle concentration on the rheological response to flow. A new method was developed to directly measure the three-dimensional nanostructure of the CNFs in the samples using transmission electron microscopy. This method allowed us to track the evolution of CNF orientation that occurred as a result of an applied shear or extensional flow and to draw conclusions about the effects of strain rate and flow type on the degree of orientation that occurs during processing. In addition to experimental measurements of nanocomposite rheological behavior a constitutive model was used to predict the rheology and nanostructure development during shear and extensional flows. The model includes parameters that account for properties such as the rheology of the polymer matrix; nanoparticle shape, concentration, and orientation; particle-particle interactions and polymer-particle interactions. The model predictions have been validated through comparison with experimental measurements of shear and extensional viscosities and nanofiber orientation.

Symposium SA
Self-Assembled Systems and Interfacial Rheology

Organizers: Sascha Hilgenfeldt and Lynn Walker

Monday 1:55 Meeting Rooms KLOP SA6

Flow of wormlike micellar solutions through rectilinear and hyperbolic converging channels

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We examine the inhomogeneous response of the VCM model (Vasquez, Cook and McKinley (2006)) in pressure-driven flow through a channel. The VCM model, a microstructural network model, was developed to describe concentrated solutions of wormlike micelles and incorporates breakage of the micelles and non-local effects arising from coupling between the stress and the microstructure. The resulting model comprises of a set of coupled partial differential equations, which incorporate the breakage and reforming of two micellar species (a long species 'A' and a shorter species 'B') in addition to reptative and Rousian stress-relaxation mechanisms. We first examine pressure-driven flow in straight channels with rectangular cross-sections. Above a critical pressure drop, the velocity profile predicted by the VCM model deviates from the regular parabolic profile expected for a constant viscosity fluid and exhibits shear-banding events near the channel walls. This shear-banding is analogous to that expected in circular Taylor-Couette flow (Zhou et al, 2008) and similar transitions have been observed experimentally in microfluidic channel flow experiments (Nghe et al (2008), Masselon et al (2008) and Marín-Santibáñez et al (2009)). Secondly, we consider pressure-driven flow of the model in a micofluidic device with hyperbolic converging/diverging walls. The hyperbolic planar contraction is of special interest due to the dominant contribution of extensional flow along the centerline and the proposed use of such flows as microfluidic extensional rheometers. The model predictions are compared with point-wise birefringence measurements of the evolution in the local microstructural orientation for CTAB and CPyCl-based micellar solutions.

Monday 2:20 Meeting Rooms KLOP SA7

Study of the rheological behavior of telechelic micellar solutions

Florian J. Stadler and Christian Bailly

Unité de Physique et de Chimie des Hauts Polymères, Université catholique de Louvain, Louvain-la-Neuve, Belgium

Micelles formed in ethanol from a poly(styrene)-b-poly(*tert*-butylacrylate) diblock copolymer bearing a ligand at the extremity of the coronal block were further assembled by using different divalent metal ions. These materials form a temporary network at rather low concentrations (strong gelation already at 12%). The gel point is indeed lowered by a factor 2 in comparison to micelles without the ligand at their periphery, indicating a strong influence of the metal-ligand bridges on the gelation.

The strength of the network can be varied by the choice of ion. While the absence of ion or the addition of Zn^{2+} does not lead to the formation of a network, the use of Ni^{2+} and Fe^{2+} leads to a strong network characterized by a rubbery behavior. Increasing the concentration only slightly will lead to a dramatic increase in the elasticity at small deformation amplitudes, characterizing a rubbery network.

This network can be reversibly destroyed by high shear, forming again after cessation of the strong shear forces. The reforming of the network occurs on three time scales, with the original properties mostly recovering after 1 min but the final perfection of the network requires more than one hour. Depending on the shear amplitude a rubbery, gel-like, or viscoelastic behavior was found to dominate. At deformation amplitudes around 100% a peak in G' is found, indicating a stretch of the supramolecular linkers, whose breaking around γ_0=300% is characterized by a peak in G". At higher deformation the network breaks down mostly but some part is retained because the viscosity of the highly sheared network is still higher than that of the micelles without interactions.

This system reveals very interesting rheological behavior based on supramolecular interaction, which can lead to gelation, if proper metal ions are used for reversible cross-linking. The recovery of the structure indicates significant potential for self-healing applications.

Monday 2:45 Meeting Rooms KLOP SA8

A pH induced transition from rigid nanorods to a semiflexible string-of-spheres in a polyelectrolyte-surfactant aggregate system

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A water-soluble system of polyelectrolyte-surfactant aggregates shows a reversible pH induced structural transformation. Both structural states are stable with time and the two states have been characterized both macroscopically and microscopically. Using small-angle neutron scattering, dynamic light scattering, and nuclear magnetic resonance, we show that the local structure and cross section of the aggregates do not change but significant changes in aggregate flexibility and hydrodynamic diameter are observed. The form factor at low pH resembles one of a closely-spaced string of spheres while the structure at neutral pH is that of a rigid rod. Rheology is used to probe the macroscopic structure and we see a transformation from a low viscosity fluid at neutral pH to a viscoelastic fluid at low pH. The low pH state exhibits strong temperature dependence which is not observed at higher pH. The temperature dependence of rheological behavior and the large activation energy of this system indication hydrogen bonding; this information is used to propose a simple structural model for the two different states of the aggregates.

Monday 3:10 Meeting Rooms KLOP SA9

Non-aqueous photorheological fluids by self-assembly of simple, commercially available molecules

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Fluids having light-tunable rheological properties (i.e., "photorheological" or PR fluids) may find use in a variety of applications, such as in sensors and microfluidic devices. However, current formulations of these fluids often require synthesis of complex organic molecules by elaborate procedures, which limits their widespread use. Our lab has been developing new classes of PR fluids based on organic molecules that are readily available and quite inexpensive. Since no new synthesis is required, these systems could prove to be more attractive for a variety of applications. We recently reported two formulations of aqueous PR fluids that exhibit dramatic rheological changes upon UV irradiation (JACS 2007, 129, 1553 and Soft Matter 2009, 5, 797). Here, we report the design of non-aqueous fluids that can show either an increase or a decrease in viscosity upon irradiation with light. These fluids are based on simple, inexpensive molecules rather than complex photo-surfactants. The concept behind the light responsiveness of these fluids lies in controlling the ability of molecules to assemble into cylindrical chains or fibrils. This is coupled with the fact that certain molecules undergo changes in their geometry in response to light (photo-isomerizations). We will describe ways to control both the magnitude of the photorheological effect as well as its timescale in these fluids. Results from rheological, spectroscopic, analytical and scattering techniques will be presented.

Monday 3:35 Meeting Rooms KLOP SA10

Oriented monolayers of single-walled carbon nanotubes using interfacial flow processing

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Anisotropic single-walled carbon nanotubes (SWNT) possess electrical properties attractive to the fabrication of microelectronic devices. In this study, conjugated polymer coated SWNTs are aligned at the air/water interface with the use of a Langmuir trough and the orientation is observed with linear dichroism. The aligned SWNTs are then transferred to a substrate and the morphology observed using an electron microscope. Transitions from gaseous to liquid-expanded then to liquid-condensed phases of SWNTs are observed during compression of the monolayers, and SWNTs are aligned perpendicular to the Langmuir trough barrier direction when compressed to the liquid-condensed phase. At high compression rates, the flow induced anisotropy is more stable due to increased relaxation times of the SWNTs. The Langmuir trough method is successful in achieving SWNT anisotropy and the long orientational relaxation times of the nanotubes allow convenient transfer onto solid substrates. The UV-Vis spectra of the deposited anisotropic films and their conductivities are also reported.

Monday 4:25 Meeting Rooms KLOP SA11

Self-assembled networks of collagen-inspired polypeptides with precisely defined functionality

Jasper Van der Gucht[1], Paulina Skrzeszewska[1], Frits De Wolf[2], and Martien A. Cohen Stuart[1]
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We study transient networks formed by monodisperse telechelic polypeptides with collagen-like end blocks and a random coil-like middle block. These artificial proteins are created using recombinant DNA techniques. Upon cooling, the end blocks associate reversibly into triple helices, leading to gels with well-defined, trifunctional crosslinks. The well-defined topology of the gels allows us to describe both the linear rheology and the gelation kinetics in a quantitative manner with an analytical model that requires no adjustable parameters, and accounts for the molecular structure of the gel, and the presence of loops and dangling ends. The non-linear rheology of these gels is characterized by a remarkable "post-shear stiffening".

Monday 4:50 Meeting Rooms KLOP SA12

Confinement enhanced self-assembly of lipid vesicles into oriented lipid tubules

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Vesicle self-assembly offers means to construct micro structures from nano-sized building blocks. However, current vesicle self-assembly processes produce non-oriented structures that vary in shape and size. We show here that, when confined between two glass surfaces, lipid vesicles rapidly assemble into oriented tubules that can grow to be long as 13~mm under ambient conditions without externally supplied flow, temperature control, or catalyzing agents. Tubule membrane and its internal aqueous content can be manipulated by controlling the vesicle's lipid composition and aqueous entrapment. This self-assembly process opens up new pathways for generating complicated and flexible architectures for use in bio-compatible molecular and supramolecular engineering. We demonstrate these possibilities by generating encapsulated siRNA tubules, inter-digitated branching tubules, and polymerized solid tubules in a single-throughput self-assembly process.

Monday 5:15 Meeting Rooms KLOP SA13

Direct measurement of polymer-polymer interfacial slip

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Polymeric liquids often exhibit slip at either liquid-solid or liquid-liquid interfaces. Such slip phenomena have important roles in physical properties of blends, polymer processing, and properties of final products. While many studies have been focused on liquid-solid interfacial slip, slip at polymer-polymer interfaces remains less understood. To study polymer-polymer interfacial slip we used sliding plate rheometer to control interfacial area and to reach high shear stresses. The polymer pair, polyethylene and fluoropolymer, was chosen because they are highly immiscible (interaction parameter = 0.1), and fluoropolymers are used commercially to increase productivity by promoting interfacial slip. The viscosity and storage modulus of each neat polymer are similar. A simple bilayer was constructed and slip velocity was measured directly by imaging the relative displacement between marks on the interface of each polymer. These results compared well with interfacial slip velocity from the difference between the average viscosity of each polymer assuming no slip and the nominal viscosity of the bilayer. We observed that there are two slopes in the log plot of slip velocity vs. stress: 6.2 up to 55 kPa and 1.8 at higher stresses. We discuss our results with respect to the theory of Brochard-Wyart and de Gennes [C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre l'Univers, 317, 13-17 (1993)] which predicts slopes of infinity and one.

Monday 5:40 Meeting Rooms KLOP SA14

Convective deposition of binary suspensions

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We investigate the coupling between the suspension properties and the deposition process during convective deposition of aqueous binary suspensions of colloidal microspheres and nanoparticles. The microsphere monolayer structures formed from this rapid and scalable process have use in a variety of optical, chemical, and biochemical sensing applications. Under ideal conditions, co-deposition of two monosized species creates long range order of the larger species embedded within the nanoparticles when the size ratio of particles is sufficiently large. However, when altering the volume fractions of the two species, instabilities arise that lead to modulation of surface morphology and localized order. At the highest concentration of nanoparticles, the larger species is destabilized via depletion interactions that also strongly interfere with the deposition process through agglomeration and altering the particle-substrate affinity. Direct measurements of deposition are visualized via high speed confocal laser scanning microscopy to generate local dynamic information regarding the deposition as well as the long range structure of assembled microsphere coatings.

Monday 6:05 Meeting Rooms KLOP SA15

Can salts influence self-assembly in oil? Gelation of lecithin organosols by multivalent cations

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It is well known that lecithin, an uncharged zwitterionic lipid, can self-assemble into spherical "reverse" micelles in organic solvents. We have explored the effects of adding inorganic salts to lecithin organosols. Salts are insoluble in organic solvents, and therefore the effects of salts on reverse self-assembly have rarely been studied. Our studies show, however, that in the presence of lecithin, salts can dissolve in organic solvents. More interestingly, salts of multivalent cations like calcium (Ca^{2+}), magnesium (Mg^{2+}) and lanthanum (La^{3+}) greatly increase the viscosity of lecithin organosols and eventually lead to the formation of organogels. Based on data from small-angle neutron scattering (SANS), we believe that gelation is due to a transformation from spherical micelles to cylindrical fibrils. A two component organogelator such as lecithin/Ca^{2+} could find application in the gelling of fuels, especially due to its negligible cost. Gelled fuels have numerous advantages in comparison to liquid fuels, including performance, safety, storage and transport. Also, these gelators could be useful in the containment of oil spills.

Symposium MR
Microrheometry and Microfluidics

Organizers: Daniel Blair and Amy Shen

Monday 1:55 Hall of Ideas G MR6

Flow birefringence measurements of shear-banding wormlike micellar solutions under high rate deformations

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The study of the flow of viscoelastic fluids at the microscale, offers the ability to achieve high deformation rates (10^4-10^5 s^{-1}), which can be difficult to access with conventional rheometers [1]. These small length and time scales are representative of complex flows in ink jet printers and lab on a chip experiments. In the present experiments, we couple micro particle image velocimetry (µ-PIV) measurements with measurements of flow-induced birefringence (FIB), to probe the local dynamics of micellar solutions under extensional and shear deformations. We describe a birefringence microscopy system, which is capable of making time-resolved full-field measurements of the local extinction angle and retardance in a microfluidic device, allowing for high-resolution tracking of the local microstructural evolution in a micellar solution undergoing strong deformation. From our µ-PIV measurements we can evaluate the local kinematics of the micellar solution (e.g. the formation of shear bands), and from our measurements of FIB we can determine the consequences of such transitions on the molecular orientation and stress field in the fluid.

First, we demonstrate our ability to measure FIB of a wormlike micellar solution flowing through a prototypical microfluidic geometry. Then we build on recent work in our group [2], to observe the state of stress and local kinematics in more complicated geometries, e.g. hyperbolic converging channels and T-shaped microchannels. These measurements can be used to explore the performance of specific constitutive models, for example the VCM model, in predicting the evolution of the stress and kinematics in shearing and extensional flow fields.

[1] Pipe, C. J., et al. (2008). Rheologica Acta 47(5-6): 621-642.
[2] Soulages J., et al. Proceedings of the XVth International Congress on Rheology, Monterey, California, AIP Conf. Proc., 2008, 1027:973-975.

Monday 2:20 Hall of Ideas G MR7

High-throughput microrheology of biocompatible hydrogelators

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Biocompatible hydrogels have become essential in therapeutic applications such as controlled release, wound healing and tissue engineering. Understanding the gel compositions and gelation kinetics over a large and increasingly complex parameter space of composition and molecular properties facilitates hydrogel engineering, but requires rheological measurements of a large number of samples. To enable such measurements, we use a combination of rapid sample preparation with microfluidics and microrheological characterization of the resulting material rheology. Facile preparation and parallel equilibration of many samples results in a high-throughput method for screening a large parameter space while minimizing material requirements. We demonstrate this approach using a covalently cross-linked multi-functional hydrogel system, consisting of maleimide-functionalized high molecular weight heparin (HMWH) cross-linked by bis-thiol poly(ethylene glycol) (PEG). Heparin has the ability to sequester and stabilize proteins, including growth factors. Multiple particle tracking microrheology is used to measure the material properties of the hydrogel system. 219 unique compositions are measured as a function of total polymer concentration, heparin maleimide functionality and PEG cross-linker molecular weight. Each sample is characterized as a sol or gel, resulting in a "gelation envelope" in the composition space. Furthermore, we show that, although Flory-Stockmayer theory is in reasonable agreement with the gelation envelopes, empirical libraries are useful when the gelation is complicated by steric effects or intramolecular looping. Overall, our approach conserves both material and time, and leads to critical insight into assembly mechanisms and mechanics of biomaterial hydrogelators, which can then be used for further materials development and optimization in therapeutic applications.

Monday 2:45 Hall of Ideas G MR8

The stiffening of ultrathin polymer films in the rubbery regime – the relative contributions of bending, membrane stress and surface tension

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Using a nano-bubble inflation technique [1], the absolute creep compliance of nanometer thin polymer films has been determined. The results have shown that at thicknesses below approximately 100nm the rubbery plateau creep compliance decreases with decreasing film thickness and scales as approximately the square of the film thickness. At low inflation pressures, and hence small deformations, the behavior is dominated by the bending stiffness. At higher pressure and larger deformations the material is under membrane conditions and the behavior is dominated by the biaxial stiffness of the films. In addition, the film is subject to surface tension effects, which may become more significant as the film thickness is decreased. To resolve the relative contribution of membrane stresses, bending stresses and surface tension to the measured compliance values data have been measured as a function of applied pressure. These data have been analyzed to determine the relative contribution to the response from these three modes. The results suggest that at sufficiently large deformations the bending contribution is small while the surface tension contribution varies depending on loading conditions, film thickness etc. However neither contribution is sufficient to account for the observed stiffening in the rubbery regime.

[1] O'Connell P.A. and McKenna G.B. Rheological measurements of the thermoviscoelastic response of ultrathin polymer films. Science. 307, 1760-1763 (2005)

Monday 3:10 Hall of Ideas G MR9

Nanoscale viscosity measurements using magnetic nanoparticles

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Magnetic nanoparticles with diameters of up to 20 nm typically consist of single crystalline domains with an embedded magnetic moment. So-called thermally blocked magnetic nanoparticles behave as nanoscale permanent magnets which respond to imposed magnetic fields by aligning their magnetic moment through rigid body rotation of the particle. Such response is retarded by the viscous drag of the surrounding medium, thus it is possible that nano-scale rheological information may be obtained through the response of magnetic nanoparticles to magnetic fields. We will illustrate this possibility through a combination of the underlying theory and experimental demonstrations of: (1) comparisons of gelation temperatures obtained through nano- and macro-scale viscosity measurements; (2) quantitative comparisons of the temperature dependent nano- and macro-scale viscosity of mineral oils; and (3) quantitative comparisons between the nano- and macro-scale viscosity for linear poly(ethylene glycol) as a function of molecular weight.

Monday 3:35 Hall of Ideas G MR10

Anomalous diffusion of tracers in polymeric liquids

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We present data on different size particles in mucus, mucus simulants and benchmark polymer liquids. The data exhibits anomalous diffusion, with sub-diffusive power law behavior of mean-squared-displacement on intermediate timescales. We then present Generalized Langevin Equations (GLEs) with a family of memory kernels that generalizes the Rouse and Zimm memory spectrum. The GLEs are solved in the zero mass limit in closed form, showing the ability to tune any sub-diffusive power law behavior of MSD and to select the window of sub-diffusive behavior. The effect of neglecting mass is then analyzed numerically and with asymptotic analysis. With these tools, a protocol emerges to detect and model sub-diffusive behavior of tracers in a wide range of polymeric liquids.

Monday 4:25 Hall of Ideas G MR11

Effect of nanoconfinement on the coil-stretch transition of DNA molecules

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Controlled stretching of DNA molecules is critical for single molecule genomic and polymer physics studies. To date, most devices have relied on hydrodynamic flows to stretch DNA in an unconfined environment. In contrast, we employ electric field gradients to electrophoretically deform DNA. The purely elongational nature of electric field allows us to use very thin nanofluidic channels and thus explore how nanoconfinement can affect stretching. Here we experimentally study DNA stretching dynamics in a nano-slit cross-slot device. We measure three steady-state quantities at varying strain rates: the average extension, the magnitude of extension fluctuations, and the average orientation of the DNA molecules in the electric field. By comparison with the unconfined case, we show that the presence of the nanoconfinement results in a highly-modified coil-stretch transition of the DNA. We develop a model to demonstrate that these experimental observations are directly related to the fact that the confinement alters the conformational energy landscape of the DNA molecules.

Monday 4:50 Hall of Ideas G MR12

The dynamics of tethered DNA in shear: Cyclic dynamics and processing for molecular wire scaffolds

Eric S. Shaqfeh, Chris Lueth, and Guihua Yu
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In this work, we use a combination of theoretical predictions and ?-phage DNA single molecule fluorescence microscopy to study the behavior of polymers tethered to surfaces. Brownian dynamics simulations of a number of coarse-grained polymer models - dynamic and equilibrium Kratky-Porod chains as well as bead-spring chains - were completed and compared with analytical and experimental results. Experiments of tethered ?-phage DNA in shear flow are presented for the first time in the flow-gradient plane. Extension behavior was shown to agree well with bead spring simulations, but deviations were discovered for weak flows in the extensional fluctuations, mean distance from the wall, and orientation angle. Cyclic dynamics - where the polymer continuously diffuses away from the wall, subsequently undergoes stretch in the flow direction, is then "entropically pulled back" towards the wall, and finally recoils - were observed and quantified through cross correlations and power spectral densities. Again, quantitative agreement was observed between experiments and bead spring simulations, both of which demonstrate a fundamental frequency of cyclic dynamics which scales sublinearly with Weissenberg number. The onset of cyclic dynamics was found to occur at Wi = 4 and the power in the cycle was found to decline with increasing Wi to the point where it was almost immeasureable at Wi = 300. Finally, the flow dynamics and its effect on various processing steps associated with using tethered DNA as scaffolds for molecule wires will be presented including flow effects on enzymatic cleavage through the use of restriction enzymes.

Monday 5:15 Hall of Ideas G MR13

Feasibility study of a deformability-activated cell sorting microfluidic platform

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Deformable particles are theoretically found to experience additional lateral forces in Poiseuille flow that will act in superposition with inertial lift forces to create modified lateral equilibrium positions. Here we report, for the first time, progress on using inertial focusing in combination with deformability induced migration for high throughput cell separation. Experiments with polydisperse solid PDMS particles with varied effective Young's moduli and viscous oil droplets were conducted separately to isolate dominant contributions from elastic and viscous properties on particles' lateral migration. In addition, inertial focusing of live cells was examined to determine whether they behaved similar to viscous or elastic particles. The inertial focusing equilibrium position (Xeq) of elastic solid particles with various Young's moduli was found to solely depend on particle size while that of viscous oil droplets was observed to shift significantly toward the center of microfluidic channel, suggesting a dominant viscous effect. Moreover, Xeq for HeLa cells followed a comparable trend to that of viscous droplets while that for RBCs was found to be between purely viscous and elastic particles. Furthermore, the transverse diameter of RBCs was found to decrease as the flow speed increases while that of HeLa cells increases under the same circumstances, providing further cell separating modes. Viscoelasatic differences, along with size differences in lateral equilibrium position have the potential to enable high-throughput sorting of cancer cells from normal cells in blood.

Monday 5:40 Hall of Ideas G MR14

Evidence of strong anomalous diffusion in living cells

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We present experimental evidence of *strong anomalous diffusion*; that describes super-diffusive motion resulting from two mechanisms. The scaling exponents $\lambda(q)$ of the moment order q of the time-dependent displacements $<|r(t+\tau)-r(t)|>^q\sim\tau^{\lambda(q)}$ is used as an indication of strong anomalous diffusion; where non-linearity and other characteristics of the scaling exponents are typically expected. Intracellular transport exhibits a range of modes-of-motion from sub-diffusion and diffusion to super-diffusion; the motion of embedded particles is in general a combination of those modes and results from a combination of thermally and actively induced motion, due to ATP-related processes in the cell, e.g. molecular-motor induced transport. In our work, we have tracked the real-time motion of synthetic probes internalized in living, human, breast-cancer cells, using particles of two sizes and two different surface chemistries.

We have found that the scaling exponents for the intracellular probe motion are not linear with q, and that $\lambda(2)>1$, thus satisfying the conditions for strong anomalous diffusion. Moreover, under all test conditions evaluated here, the scaling exponents exhibited a piecewise linear functional form, with two different slopes. That has never before been observed experimentally, to the best of our knowledge. The presence of two linear fits is indicative of two mechanisms of motion; at low moments and high moments, diffusion and active transport are more dominant, respectively. At low moments ($q<2$), slopes were similar for all experimental conditions, while at ($q>2$), fits depended on bead size and surface chemistry. The critical moment of transition was also probe size dependent. This analysis approach can be used to elucidate underlying transport mechanisms in the cell.

Symposium BR
Biorheology and Rheology in Biological Systems

Organizers: Prosenjit Bagchi and Michael R. King

Monday 1:55 Meeting Rooms MNQR BR6

Surface tension driven pumping for cell based assays

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We have developed a surface tension driven approach to pumping fluids through microchannels. The method is based on pressure differences between different sized droplets as predicted by the Young-LaPlace equation such that if two drops of different size are connected via a fluid-filled tube, the smaller drop will shrink while the larger one grows. The method has proved to be a broad enabler of microfluidic cell-based assays providing the functionality of microfluidics without the typically associated internal or external mechanical pumps and valves. We have used this method as the basis of a number of cell-based assays to enable cancer biology research. Importantly, the approach is compatible with existing automated liquid dispensing equipment and endpoint detection (e.g. plate readers). Further, we have used the method for both 2D (a monolayer of cells on a surface) and 3D (cells dispersed in a matrix) cell culture models. Laminar flow allows for the compartmentalization of cells to study paracrine signaling (e.g. between epithelial and stromal cells). Additionally, control of process parameters allows one to easily create both aligned and random extra cellular matrix compositions. In summary, the approach allows one to take a "screening" approach to exploring the role of the cellular microenvironment on cell behavior - such a screening approach has not been practical with canonical cell culture vessels and methods.

Monday 2:20 Meeting Rooms MNQR BR7

Neutrophil motion, adhesion and activation in an in vitro micropipette model of a lung capillary

David Tees[1], Young Eun Choi[1], Prithu Sundd[2], and Douglas J. Goetz[3]
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Leukocyte sequestration in lung capillaries is a key step in the inflammatory response to lung infection. P-selectin and ICAM-1 have well defined roles in leukocyte adhesion in systemic venules but their role in pulmonary capillaries is still unclear. Here, a novel in vitro Micropipette Cell Adhesion Assay (MCAA) used P-selectin, ICAM-1 or BSA coated capillary-sized glass microvessels as an in vitro model for a pulmonary capillary. Leukocytes were aspirated into adhesion molecule-coated micropipettes of varying diameters. Cell velocities and activation times were determined under pressures representative of lung capillaries. Neutrophil velocities in MCAA were significantly lower on P-selectin than BSA and decreased with increasing P-selectin concentration. Pre-treating P-selectin-coated microvessels with an anti-P-selectin mAb resulted in a increase in velocity. ICAM-1 expressed alone or with P-selectin, does not mediate adhesion of unstimulated neutrophils in pulmonary capillary geometry. These results demonstrate that P-selectin at low density mediates leukocyte adhesion in the pulmonary capillary geometry. The effect of micropipette size on activation time in the presence of these adhesion molecules will also be described.

This work was supported by grant BES-0547165 from the National Science Foundation.

Monday 2:45 Meeting Rooms MNQR BR8

Particle size and the efficacy of vascular–targeted drug carriers: Role of hemorheology and hemodynamics

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Localized delivery of therapeutics offers the possibility of increased drug effectiveness while minimizing side effects often associated with systemic drug administration. Existing literature have focused mainly on identifying target epitopes and the degradation/drug release characteristics of a wide range of drug-carrier formulations. Absent in the literature, are work focused on the potential roles of particle size on the ability of vascular-targeted drug carriers to interact with the vessels - an important consideration that will control the effectiveness of drug targeting regardless of the targeted disease or delivered therapeutic. Nanometer to submicron-sized spherical particles are widely proposed for use in vascular drug delivery, yet very little evidence has been presented in the literature as to their optimal use for vascular-targeted drug delivery. This paper focuses on elucidating the effect of particle size along with blood rheology/flow dynamics on the efficiency of drug carrier interaction with inflamed endothelium in vitro. Our data shows that the binding efficiency of particles to inflamed endothelium from blood flow increase with increasing particle size at low and intermediate shear stresses for particle sizes from 100nm up to 10 micron. Furthermore, nano-sized particles show minimal binding when compared to larger-sized spheres in horizontal (anti-gravity) and vertical channels on the order of medium arteries. Finally, we find that conditions promoting red blood cell (RBC) deformation rather than aggregation enhanced particle adhesion to wall.

Monday 3:10 Meeting Rooms MNQR BR9

A numerical simulation study of rheology and dynamics of healthy red blood cells and parasitized by Plasmodium falciparum

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The main characteristics of the malaria disease are progressing changes in red blood cell (RBC) mechanical properties and rheology, and its cytoadhesion to the vascular endothelium. Malaria-infected RBCs become considerably stiff compared to healthy ones, and may bind to the vascular endothelium of arterioles and venules. This leads to a significant reduction of blood flow, and eventual vessel obstruction. We present a coarse-grained RBC model which incorporates realistic RBC properties and rheology. Rheological measurements characterized by time-dependent complex modulus are extracted from the membrane thermal fluctuations for healthy RBC and parasitized by Plasmodium falciparum. The dynamics of RBCs in shear flow in combination with a cell adhesion at later stages of the parasite development will be explored.

Monday 3:35 Meeting Rooms MNQR BR10

Quantitative models of monocyte-endothelial cell interactions in atherosclerosis

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Atherosclerosis is a progressive disorder of medium- to large-size arteries characterized by hardening and narrowing of the vessels due to formation and calcification of atheromatous plaques on the inside of the vessel walls. It is established that this disorder develops near vessel bifurcations and curvatures (where separation and reversal of blood flow occur) as a result of oxidative damage to vascular endothelium caused by oxidized low-density lipoproteins (oxLDL). Such endothelial dysfunction leads to increased adhesion of monocytes to endothelial cells and accumulation of monocytes/macrophages in the intimal layer of the arterial wall. In this talk, we present three-dimensional computational models of monocyte-endothelium interactions that take into account 1) monocyte viscoelasticity, 2) complex flow conditions existing at atherosclerosis-prone sites, and 3) chemokine-stimulated and multiple-receptor-mediated cell adhesion kinetics. We also discuss our in vitro experiments on oxLDL-induced adhesion of monocytic cell line THP-1 to HUVEC in a micro-fluidic flow chamber. Through comparison of in vitro and computational studies, we show that firm adhesion of monocytes to endothelial cells is very sensitive to monocyte rheological properties and flow conditions to which endothelial cells and monocytes are exposed.

Monday 4:25 Meeting Rooms MNQR BR11

Rheological and tribological investigation of protein interactions in synovial fluid

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Hyaluronic acid (HA) and the plasma proteins, albumin and γ-globulins, are the most abundant macromolecules in synovial fluid, the fluid that lubricates freely moving (synovial) joints. In previous studies, bovine synovial fluid, a synovial fluid model (SFM) and albumin in phosphate buffered saline (PBS) were observed to be rheopectic-viscosity increases over time under constant shear. Additionally, steady shear experiments, where the shear rate was increased from low to high, and then decreased from high to low, showed hysteresis in only protein containing solutions, whereas samples of HA in PBS behaved as a "typical" polyelectrolyte in solution. Both the observed rheopexy and hysteresis are indicative of structure building in solution, and is most likely caused by protein aggregation in the fluid. The external protein modification through the application of a low shear rate causes a slight unfolding of albumin in solution creating many opportunities for protein molecules to reorder themselves, resulting in the formation of a network within the fluid. The network effectively acts as a structure, which restricts the free motion of the longer HA chains, causing the observed rheopexy in the SFM. Additionally, the relationship between the rheology and tribology of the SFM was studied through a series of nanoscratch tests using a Hysitron nanoindenter. The nanoindenter has the ability to measure both normal and lateral forces simultaneously, which gives an indication of the lubricity of the solution. The coefficient of friction values for solutions of varying protein and HA concentrations, and varying molecular weights of HA were determined by dividing the lateral force by the normal force. The tribological studies show that the lubricity of the joint is enhanced only at the protein concentration found in healthy synovial joints. Finally, the HA component of the synovial fluid model was replaced with anionic and neutral polymers in order to examine the role of HA in synovial fluid.

Monday 4:50 Meeting Rooms MNQR BR12

Particle-tracking in breast-cancer cells and model microenvironment under electric fields

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Direct-current (DC) low-intensity electric-fields (LIEF) has been suggested as a novel method for treating various types of cancer, both *in vivo* and *in vitro*. *In vitro* studies have focused on cancer cells alone, while the influence of LIEFs on the entire cancer microenvironment is not well-understood. We suggest that death and stress responses of treated cells will be apparent through intracellular mechanics. Thus, we combine particle tracking with cell biology approaches, to elucidate cell responses and their timescales. We track motion of fluorescent sub-micron particles internalized into the cells, to evaluate changes in the internal structural density and local rheology of the cells following DC-LIEF treatment. We use a simplified model for the *in vivo* tumor microenvironment: co-cultured human, epithelial, breast cancer cells and fibroblasts from a breast-tumor adjacent site. In that system, we evaluate the immediate- and longer-term effects of DC-LIEF treatments on cell local-mechanics and viability in our co-culture, breast-cancer model system.

We evaluate changes in viability and intracellular mechanics of cancer cells cultured alone and within the model-microenvironment. When treated separately, the cancer cells exhibit vast death and morphological changes, while the fibroblasts continue to grow with minimal death. The cancer cells round-up following treatment, concurrently exhibiting reduced particle motion, and spread out again within a few hours, indicating a possible transient, intracellular structural change. Conversely, the fibroblasts do not exhibit any apparent morphological changes right after the treatment; however particle motion becomes more super-diffusive up to an hour after the treatment, likely indicating active remodeling inside those cells. Interestingly, those changes are delayed or not observed altogether in the co-cultured cancer cells or fibroblasts, respectively.

Monday 5:15 Meeting Rooms MNQR BR13

Characterization of tendon and ligament viscoelasticity

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Tendons and ligaments serve to stabilize and allow free motion of the musculoskeletal system. Though similar in morphology, they play very different roles in the body. Therefore, the examination of the properties of both tendon and ligament is crucial to the understanding of biomechanics. This study inspected the viscoelastic behaviors of porcine digital flexor tendons and medial collateral ligaments at physiological strains (up to 6% strain) and found stark differences between the two.

Stress relaxation curves were strain-dependent and followed a power law behavior (in time) in both tendon and ligament. In the tendon, stress relaxation occurred at a faster rate at high strains than at low strains. Conversely, stress relaxation occurred at a slower rate at high strains (6%) than at low strains in the ligament. In both tendon and ligament, recovery following the removal of load progressed at a slower speed than relaxation.

Stress relaxation behavior can be characterized by a number of viscoelastic models; many models can fit the curve of a single relaxation, but few can accurately predict future loading and unloading patterns. A three-step model approach was used in this study to test the accuracy of viscoelastic models to fit the behavior of tendon and ligament in step loading and unloading conditions. Interestingly, a model based on Schapery's nonlinear viscoelastic constitutive equation was able to fit the loading and unloading behavior of both the tendon and ligament, even though their trends in stress relaxation were opposite.

Reference: Schapery, RA. On the Characterization of Nonlinear Viscoelastic Materials. Polymer Engineering and Science 9: 295-310 (1969).

Monday 5:40 Meeting Rooms MNQR BR14

The dilute rheology of swimming suspensions: A simple kinetic model

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A simple kinetic model is presented for the shear rheology of a dilute suspension of particles swimming at low Reynolds number. If interparticle hydrodynamic interactions are neglected, the configuration of the suspension is characterized by the particle orientation distribution, which satisfies a Fokker-Planck equation including the effects of the external shear flow, rotary diffusion, and particle tumbling. The orientation distribution then determines the leading-order term in the particle extra stress in the suspension, which can be evaluated based on the classic theory of Hinch and Leal [J. Fluid. Mech. 52(4):683-712 (1972)], and involves an additional contribution arising from the permanent force dipole exerted by the particles as they propel themselves through the fluid. Numerical solutions of the steady-state Fokker-Planck equation were obtained using a spectral method, and results are reported for the shear viscosity and normal stress differences in terms of flow strength, rotary diffusivity, and correlation time for tumbling. It is found that the rheology is characterized by much stronger normal stress differences than for passive suspensions, and that tail-actuated swimmers result in a strong decrease in the effective shear viscosity of the fluid.

Monday 6:05 Meeting Rooms MNQR BR15

Dynamic simulation of semiflexible filaments with hydrodynamic interaction

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In this study we use dynamic simulation to explore the effect of hydrodynamic interaction on the Brownian fluctuations of a semiflexible filament. In a semiflexible filament, the entropic-driven bending fluctuations are resisted by the filament's elastic stiffness, and the Worm Model is commonly used to describe it. The Worm Model assumes a uniform friction coefficient at every point on the filament. However Lagamarsino et al. (2005) showed that most of the friction drag occurs at the filament ends. This increases the tendency of the filament to bend even when under a uniform driving force. The non-uniform drag is due to hydrodynamic screening- the solvent flow induced by the filament ends reduces the relative velocity and therefore drag experienced by the filament center. The phenomenon gets even complicated when Brownian forces are included, as the solvent flows set up by the bending fluctuations alter the drag experienced along the filament. Dynamic simulation offers a way to explore the effect of hydrodynamic interaction on the dynamics of a semiflexible filament. We describe a string-of-rods approach to modeling a semiflexible filament. The filament is treated as a string of continuously bending rods, and the large-strain Euler bending equations is solved on each rod simultaneously. It has the advantages of being computationally cheaper and of preserving filament inextensibility. We also describe how hydrodynamic interaction within/between filaments can be captured by an implicit version of the Methods of Reflection. The technique is equivalent to capturing infinite reflections of solvent flow between neighboring particles. We incorporate an averaged version of this technique into the string-of-rods approach to simulate the Brownian dynamics of a semiflexible filament. We show how hydrodynamic interaction affects the bending profiles of a freely-fluctuating and laterally-confined semiflexible filament.

Symposium MS
Molecular Modeling and Simulation in Rheology

Organizers: Rajesh Khare and Nicos Martys

Monday 1:55 Hall of Ideas J MS6

What is measured by passive microbead rheology?

Jay D. Schieber and Ekaterina Pilyugina

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It is often claimed that the relaxation and storage moduli of a viscoelastic medium can be measured by following the trajectory of a small bead subject to Brownian motion. In the pioneering manuscript that introduced the idea [T.Mason and D.Weitz, Physical Review Letters 74,1250(1995)], this equivalence between the autocorrelation function and G* was assumed. Later work claimed that a correspondence could be proven, but to our knowledge, the proof has never been shown. We use here an analytic solution of the forces on a sphere undergoing arbitrary

displacement combined with the fluctuation-dissipation theorem to derive what is actually measured in the microbead rheology experiment. We find that a convolution of G* is indeed measured in the followed autocorrelation function. However, under certain restrictions the autocorrelation function is a direct measurement of the relaxation modulus. We examine experimental data published in the literature and are unable to find any data where the restrictions do not hold. Nonetheless, the results suggest that the technique could also be used at higher frequencies, if proper analysis is made of the data.

Monday 2:20 Hall of Ideas J MS7

Rheology, microstructure and migration in colloidal suspensions

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The goal of this work is to demonstrate that suspended, spherical colloidal particles can be effectively modelled as single dissipative particle dynamics (DPD) particles provided the conservative repulsive force is appropriately chosen. The suspension model is further improved with a new formulation of which augments standard DPD with non-central dissipative shear forces between particles while preserving angular momentum. We have investigated the rheology, microstructure and shear-induced migration of a monodisperse suspension of colloidal particles undergoing plane shear flows (Couette and Poiseuille) with the proposed new formulation. To achieve a well-dispersed suspension, we chose exponential conservative forces for the colloid-colloid and colloid-solvent interactions, but kept the conventional linear force for the solvent-solvent interactions. Since the effective size of DPD particles is determined by their conservative repulsions their sizes can be adjusted to differentiate between colloid and solvent particles, in the ratio of about 4-to-1 in this work. Our simulations yield relative viscosity vs. volume fraction curves in good agreement with both experimental data and empirical correlations. The shear-dependent viscosity and the first and second normal stress were also studied in both Couette and Poiseuille flows. It was found that with increasing shear rates the suspension becomes shear-thinning within the limit of attainable Peclet numbers. Consistent with experimental observations, our simulations near the close packing volume-fraction (64%) at low shear rates, demonstrated the transition to flow-induced string-like structures of colloidal particles simultaneously with the transition to a non-linear Couette velocity profile. After a sufficient increase of the shear rate the ordered structure melted into disorder with restoration of the linear velocity profile. In Poiseuille flow migration effects compare well with experiments and other numerical simulations.

Monday 2:45 Hall of Ideas J MS8

Molecular scale rheometry

Shihai Feng[1], Alan L. Graham[1], Bruce Murch[2], and Antonio Redondo[3]
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In this investigation we explore the use of large-scale molecular simulations to explore nanoscale rheology of liquids. In these numerical experiments, molecular liquids are subjected to simple shear flow and pressure-driven flow. We also consider a falling-ball rheometer. Temporal and spatial averaging is used to calculate both the momentum transport and the boundary conditions. Particular care is taken with the conservation equations to insure that that coarse graining of the molecular dynamics properly represents the molecular-scale transport phenomena. With appropriate averaging, we find that the continuum limits hold to extremely small relative spatial scales of the flow fields. In very confined geometries the discrete nature of the systems is apparent and the continuum approximation breaks down.

Monday 3:10 Hall of Ideas J MS9

Active nanorheology: Calculation of viscoelastic properties of complex materials using molecular dynamics simulations

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In recent years, microrheology, which involves tracking the motion of microscale probes in the matrix, has emerged as a new technique for the determination of the viscoelastic properties of complex materials. The advantages of microrheology include the requirement of a small amount of the material sample as well as the ability to determine the rheological properties at the microscale. At an even smaller length scale, i.e. the nanoscale, rheological properties of materials are significantly influenced by the nanoscale structure and the specific molecular interactions in the system. Molecular dynamics (MD) simulations can account for these detailed interactions in the system and provide a unique tool for systematic investigation of the nanoscale viscoelastic behavior. In this work, we have used MD simulations to perform 'active nanorheology' simulations consisting of an oscillatory motion of a nanoparticle in a matrix. The model systems studied are composed of a nanoparticle that is embedded in a matrix consisting of a polymer melt, a polymer solution or a suspension of nanoparticles. In these model systems, the nanoparticles are represented by a collection of beads, the polymer chains are modeled as bead-spring chains and the solvent is considered explicitly. All of the particles in the system interact with each other via the Lennard-Jones (LJ) or the purely repulsive LJ potential. The rheological properties are completely governed by the intermolecular interactions in these systems. The nanoparticle motion is studied over a range of frequencies and amplitudes and the response of the matrix is characaterized in terms of the local viscoelastic properties. Two different approaches for the active perturbation of the complex material by the probe nanoparticle and the subsequent calculation of the viscoelastic properties from the measured response are presented.

Monday 3:35 Hall of Ideas J MS10

Effect of shear and elongational flow on block copolymer/nanoparticle assembly: A coarse-grained molecular dynamics study

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Coarse grained, non-equilibrium molecular dynamics simulations have been conducted to model and simulate the behavior of symmetric diblock copolymer/nanoparticle systems under simple shear and planar elongational flow. The aim of our present study is to understand how the nanoparticles disperse in a block copolymer system under shear and elongational flow, and how the presence of nanoparticles influences the rheology and flow-induced morphology transition in block copolymers. We consider three different kinds of spherical nanoparticles (NPs) categorized with respect to their interaction potential with the polymeric blocks, 1) selective NPs, that show a preference towards one of the blocks of a model diblock copolymer, 2) non-selective NPs, that show equal attraction towards both blocks, 3) self-attracting NPs, that exhibit strong NP-NP attraction and have a tendency to aggregate. We also consider additional variants by changing the particle diameter and the particle-polymer interaction strength. We keep the volume fraction of nanoparticles low (0.1) to preserve lamellar morphology in the nanocomposites. For elongational flow, spatially and temporally periodic boundary conditions devised by Kraynik and Reinelt (Int. J. Multiphase Flow, 1992, 18, 1045) have been implemented for unrestricted simulation times. Our results show that shear and elongational flow can have a pronounced effect on the placement of nanoparticles in block copolymers and can therefore be used as another parameter to control nanocomposite self assembly. Furthermore, we found that the onset of shear induced lamellar transition from parallel to perpendicular orientation is also greatly influenced by particle-particle and particle polymer interactions. Finally, elongation induced, order to disorder transition in symmetric diblock copolymers and the effect of presence of different types of nanoparticles on such flow induced behavior are presented.

Monday 4:25 Hall of Ideas J MS11

Direct simulation of micro- and nano-fibre composites in shear and extensional flows

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CNT (carbon nanotube) and CNF (carbon nananofibre) have good mechanical, thermal, electrical conductivities with an ever increasing reasonable market price and are usually considered to be good candidates for polymer composites. Such composites, however, normally have the problem of formation of CNT/CNF aggregates that degrade their performance by a large margin. Experimentally, many studies have looked into how to get good dispersion and distribution. However, through experiments only it is difficult to analyze: 1) the maximum flow rate in order not to destroy the fibres, 2) the most adequate flow field and 3) the micro-structure that develops under flow. Thus, a working simulation technique could be very useful in this respect. A relatively large number of techniques for fibre-systems simulations have been developed for well dispersed rigid fibre systems but it was not until Yamamoto and Matsuoka [1] proposed the PSM (particle simulation method), that it has become possible to model fiber flexibility. In this work we resort to a a micro- and nano-fibre suspension simulation software based on PSM recently developed by Yamanoi and Maia [2], that considers van der Waals interactions, lubrication effects and repulsive potential to prevent fibres from overlapping. The software can treat high volume fraction and aggregated states and predict rheological properties under flow fields. The performance of the software is shown for glass fiber composites and nano-scale carbon fibre composites.

[1] S. Yamamoto and T. Matsuoka, J. Chem. Phys., 102 (1995) 2254-2260. [2] M. Yamanoi and J. M. Maia, J. Rheol., 2009, submitted.

Monday 4:50 Hall of Ideas J MS12

Modeling of fiber behavior during processing of fiber reinforced composite parts

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In some polymer composite manufacturing processes, the number of defective parts can be more than half of the total production. Mold filling phenomena play a significant role in fiber attrition, fiber orientation, fiber-jamming and fiber-matrix separation. The current approach to handle these problems has been based on simulation as well as trial and error techniques. In order to properly optimize these processes, a comprehensive understanding of the physics behind the process is required.

Mechanistic Computer simulations of flexible fiber suspensions are developed to study the molding of fiber reinforced composites. Fibers are modeled as chains or rigid beads connected by springs. Parameters such as fiber concentration, fiber length and stiffness can be modified to match specific processing conditions. Simulation results include final fiber orientations and fiber distributions within a molded part. Specific applications for these types of simulations are compression molding of sheet molding compound, and injection-compression molding.

The main goal of this work is to model the behavior of high fiber suspensions at polymer processing concentrations, which can be as high as 40% by volume. By using point wise potentials to model interactions between fibers, simulations at fiber concentrations up to a concentration of 10% have been performed. Fiber orientation distributions have been compared with those obtained with the model developed by Folgar and Tucker with good correlation. However, this model tends to predict faster fiber orientation development than observed in the simulations. This is attributed to the fact that the mechanistic model takes into account fiber interactions, interlocking and bending, factors that ultimately lead to a slower orientation of the fibers. It is expected that these types of simulations will provide a tool to optimize fiber distributions and orientations in the fabrication of fiber reinforced composite parts.

Monday 5:15 Hall of Ideas J MS13

Multiscale molecular simulation of linear viscoelasticity of entangled polymers by the molecular dynamics and primitive chain network models

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We propose a multiscale molecular simulation method for entangled polymers, based on the coarse-grained molecular dynamics (MD) and the primitive chain network (PCN) models. It is known that the coarse-grained MD models such as the Kremer-Grest model can simulate dynamics of entangled polymers well, but it requires large computational costs for long polymers. On the other hand, the PCN model can simulate entangled polymers with small computational costs while we need several phenomenological parameters which are not derived from microscopic models. In this work, we combine the coarse-grained MD and the PCN models to enable fast simulations based only on the MD parameters.

The PCN model describes entangled polymers as a network structure while the coarse-grained MD model describes polymers by the beads-spring type model. To connect the beads-spring polymers to a network structure, we use the primitive path extraction method. By extracting the primitive paths from MD snapshots and examining their statistics, we show that we can directly use the extracted primitive paths in the PCN simulations. The phenomenological parameters in the PCN model are also determined from the MD data.

As an application, we show the linear viscoelasticity of entangled linear polymer melts with various degrees of polymerization. It is shown that the shear relaxation modului can be calculated over 8 dicades with reasonable computational costs.

Monday 5:40 Hall of Ideas J MS14

A proposal to solve the time-stress discrepancy of tube models

Evelyne van Ruymbeke[1], Dimitris Vlassopoulos[2], Michalis Kapnistos[3], Chen-Yang Liu[4], and Christian Bailly[1]
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Recently, Liu et al.[1] have shown a systematic deviation of tube model predictions for describing the plateau modulus of short entangled linear chains. In the present work, we investigate the origin of this time-stress deviation by confronting our time-marching algorithm to experimental viscoelastic data of monodisperse linear polymers.

Our model is based on three viscoelastic material parameters, i.e., the Rouse time of an entanglement segment, the plateau modulus and the entanglement molecular weight, and uses the classical ingredients of the tube-based theories. There is however a key difference with the models proposed by McLeish and coworkers[2],[3]. In order to take into account the fact that reptation and contour length fluctuations do not have necessarily a cumulative effect, we propose a different description of the relaxation modulus, which allows us to analyze the contribution of each relaxation process to the total relaxation of the polymer, and to conclude that the Contour Length Fluctuations (CLF) of the outer molecular segments are overestimated in classical models.

We propose a way to correct this last issue, which ensures that, before the short but essential Rouse time of an entanglement segment, molecules do not relax. Results obtained with the corrected model show a very good agreement with experimental data. In particular, the Mw dependence of the plateau modulus, the zero-shear viscosity as well as the terminal relaxation time is now correctly predicted.

1: Liu, C.Y.; He, J.S., Keunings R., Bailly, C., Macromolecules, 2006, 39, 8, 3093.
2: Milner, S. T.; McLeish, T. C. B. Phys. Rev. Lett., 1998, 81, 725.
3: van Ruymbeke, E.; Liu, CY; Bailly, C., " Quantitative tube model predictions for the lineair viscoelasticity of linear polymers", rheology reviews 2007, The British Society of Rheology.

Monday 6:05 Hall of Ideas J MS15

Analyzing tube model assumptions for monodisperse LVE predictions

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Many refinements have been made to the Doi and Edwards tube model to improve predictions for linear viscoelasticity (LVE). For instance, Doi added contour length fluctuations modeled as a 1D Rouse chain; Graessley added constraint dynamics modeled as a single mode 3D Rouse motion of the segments of the tube and assumed factorization of relaxation processes; and Rubinstein and Colby improved constraint dynamics implementation by adding a continuous spectrum to the 3D Rouse modes. Later Neergaard and Schieber used a more-detailed slip-link model with the improved 3D Rouse motion of the entanglements as constraint dynamics. Several assumptions made in tube models were removed, however the agreement with data became worse. These results suggest that there might be a "cancellation of errors" in the tube model assumptions. In this work we present a discrete slip-link model (DSM). Use of slip-links instead of tubes allows a more natural way to include effects like contour length fluctuations and constraint dynamics. It has been shown that the DSM is a thermodynamically consistent model. We present a self-consistent model for constraint dynamics completely avoiding the 3D Rouse dynamics assumption. The model agrees with LVE monodisperse data and can be applied to polydisperse and branched systems without any modifications. The DSM has two adjustable parameters which are determined from a fit to a single-molecular-weight, monodisperse LVE experimental data for given chemistry and temperature. Finally, we compare the DSM with the Likhtman and McLeish tube model, which uncovers the source of the cancellation. First, the relaxation modulus, G(t), is not proportional to the fraction of survived primitive path in the DSM. Second, the constraint dynamics contribution to G(t) in the DSM is significantly different from the 3D Rouse implementation. Those assumptions create a "cancellation of errors" if both applied to the slip-link model.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Lecture Hall PL2

Interrogating the physics of amorphous solids: Rheological and mechanical measurements

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Rheological measurements offer a unique means of interrogating the physics of amorphous solids, including crosslinked rubbers and polymeric glasses. Here we present three vignettes to demonstrate the ability of classical and novel rheological experiments to resolve important questions in condensed matter physics. First, we describe results from classical torque and normal force measurements aimed at understanding the thermodynamics and mechanics of polymer networks in both dry and swollen states, and in particular, we examine the validity of the Frenkel-Flory-Rehner hypothesis. We then describe the use of a novel torsional dilatometer, which allows simultaneous measurement of mechanical properties and volume recovery, to investigate the aging and rejuvenation behaviors of glassy polymers. Finally, we describe a reduction in scale of the classical membrane inflation test to allow measurement of the biaxial creep compliance of nanometer thick polymeric films using an atomic force microscope. In each instance emphasis is placed on how the measurements are designed to interrogate the physics of interest in the materials investigated.

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Tuesday 9:45 Lecture Hall SC16

Direct measurement of suspension structure in pressure driven flow

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Many non-Newtonian properties of concentrated suspensions, including shear thinning, normal stress, and shear migration, are attributed to the evolution of structural anisotropy. Investigations of this anisotropy have largely been conducted using simulations such as Stokesian Dynamics and indirect measurement via scattering. Using high speed confocal laser scanning microscopy, we directly investigate the local structure via particle tracking after structural evolution in a pressure driven flow ranging from Péclet number (the ratio of convective to diffusive forces) of $0 < Pe < 2000$ over bulk volume fractions $0.2 = F = 0.4$. Due to the shear gradient, a single experiment allows both sampling over a range of Péclet numbers and concentrations that vary due to shear migration. Clear structural anisotropy similar to that demonstrated by simulations of Foss and Brady, 2000 and Morris and Katyal, 2002 show strong deviations from homogeneity in radial distribution profiles at high Péclet number and high volume fraction. Moreover, in regions of low Pe located in the center of the pressure driven flow, signatures of colloidal crystallization driven by the high concentration that results from the normal forces generated this anisotropy are apparent.

Tuesday 10:10 Lecture Hall SC17

Inertial effects in suspension mechanics: Rheology and constitutive modeling

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The literature on suspension mechanics over the last fifty years is largely focused on low Reynolds number theory, experiments and simulations; as a result a range of aspects of the flow including microstructure, rheology and shear-induced migration have been well understood. In the present study, the role of finite fluid inertia in a sheared suspension of noncolloidal and neutrally buoyant particles is addressed using numerical simulations. The Reynolds number characterizing the fluid inertia is defined on particle scale as $Re=\gamma a^2/\mu$, where μ and ρ are the viscosity and density of the fluid respectively, γ is the shear rate and a is the radius of the spheres. The numerical simulations are performed using the lattice-Boltzmann method with a wall-bounded geometry. The time averaged particle stress is computed and effective viscosity and normal stresses are presented over a range of Reynolds number and particle volume fraction (ϕ). The coupling between pair microstructure and rheology is also elucidated.

The suspension balance approach is then used to perform "computational suspension dynamics". Specifically we develop continuum modeling to predict the velocity and particle concentration profiles in a pressure-driven pipe flow. The particle-scale inertia is taken into account by modifying the model for particle stress and introducing the lateral force associated with inertial migration to the particle phase momentum balance. Case studies on cross-stream migration are provided and it is found that the predicted profiles show the influence of inertia in a manner consistent with the limited experimental data.

Tuesday 10:35 Lecture Hall SC18

Rheological and microstructural development as a function of strain in oscillating suspensions of non-colloidal spheres

Hyun-Ok Park and Jason E. Butler

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Rheological measurements are used to assess the existence and rate of microstructural changes in oscillating suspensions of non-colloidal spheres. Though slightly non-linear, naively separating the stress response into components in and out-of-phase with the strain reveals that the two components change at different rates. Rapid and large changes in the storage modulus occur over the first 15-20 oscillations for concentrated suspensions in the vicinity of a strain amplitude of one. The loss modulus is much larger than the storage modulus and appears to remain constant over the first twenty oscillations. However, the loss modulus does change slowly, consequently requiring large numbers of oscillations to reach steady state. The results are qualitatively independent of the shear cell geometry, suggesting that shear-induced particle migration is unimportant and that the observed behavior results from changes in the suspension microstructure. Comparison of the experimental results at small total strains to simulation results provides insight into the rapid changes of the storage modulus. Extending the range of volume fractions and total strains beyond previous investigations, as well as a more detailed study of the response at small total strain, has provided a more comprehensive view of the rheology.

Tuesday 11:00 Lecture Hall SC19

Particle migration in oscillatory torsional flows of concentrated suspensions

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Torsional flows of monomodal concentrated suspensions between parallel disks were previously considered to maintain uniform particle distributions. However, recent studies suggest that shear-induced particle migration or other microstructural ordering can occur over long time scales in steady and oscillatory torsional flows. In this study, we observe particle motion and rheology in oscillatory torsional flow of a 0.4 particle volume fraction suspension over a duration of 4800 oscillations. The oscillation amplitude covers the transition range below the minimum strain for the formation of steady-state microstructure and the oscillation frequency is also varied. We detect slow, radially outward drift of tracer particles, which is mainly a function of the oscillatory strain amplitude with slight dependence on the frequency of oscillation. We compare measured particle drift velocities to predicted values estimated from the suspension balance model. Simultaneously, we capture the torque evolution. At the largest strain amplitudes and lowest frequencies, the torque increases as the flow evolves, as was previously observed in steady flow, and a local minimum is detected at intermediate strain values, in agreement with other studies of oscillatory flow. Overall, the results suggest the interplay at intermediate oscillation amplitudes between radial particle migration driven by the overall particle stress balance and microstructural rearrangement driven by local self-assembly of the particles into layers. The results of this study can also assist in parameter selection for rheological measurements of suspensions in the parallel disk geometry.

Tuesday 11:25 Lecture Hall SC20

Mass transport enhancement to surfaces in dilute sheared suspensions

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Recently, Zurita-Gotor & Blawzdziewicz [J. Fluid. Mech. 592,447, (2007)] showed that the presence of a wall leads to a modification of binary particle interactions in bounded simple shear flows, resulting in a shear-induced self-diffusivity which scales linearly with concentration. This is the dominant source of self-diffusion in dilute sheared suspensions, and quantitatively agrees with the experimental measurements of Zarraga & Leighton [Phys. Fluids, 14(7), 2194 (2002)]. In addition to this effect, however, the wall reflection also causes a similar modification of solute (fluid particle) trajectories which gives rise to a shear-induced gradient diffusivity. This diffusivity, which scales as $\phi a^3/z$ where ϕ is the particle concentration, a is the suspension sphere radius, and z is the distance from the wall, has the potential to significantly decrease diffusional mass transport resistances to surfaces at large Peclet numbers. The magnitude of the gradient diffusivity is calculated in the far-field using a simple expression for the wall stresslet reflection, and in the near-field using the exact velocity distributions obtained by O'Neill [J. Fluid Mech. 27, 705 (1967), J. Inst. Math. Appl. 4,163 (1968)., Chem. Eng. Sci. 23, 1293 (1968).]. The 1/z far-field result is shown to lead to a modified Leveque-type self-similar solution for enhanced diffusion through a boundary layer.

Symposium SM
Polymer Solutions and Melts

Organizers: Ralph Colby, Jules J. Magda and Lynden Archer

Tuesday 9:45 Hall of Ideas G SM1

Single segment differential tube model with interchain tube pressure effect: Analysis of elongation and shear data of monodisperse polystyrene melts

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We present the comprehensive quantitative performance of our recently published single segment tube model with interchain tube pressure effect (ITPE) [1] in both versions (affine stretching and affine squeezing) for linear and non-linear rheometric flows. The mismatch originally observed between the model predictions and experimental data for transient elongational flows is improved by incorporating the Rouse relaxation modes into the relaxation mechanism. This simple model is tested with extensive data from Hassager's group [2-5] on transient and steady elongation flows, elongation relaxation and reverse elongation flows, as well as recent data on transient and steady high deformation shear flows by Schweizer et. al. [6]. New insights into the affine squeezing and the affine stretching assumptions are provided based on comparisons with the experimental data. Based on the quantitative performance of our model both in linear and non-linear regime, the role of ITPE in the relaxation mechanism of the polymer melt is clarified.

(1) S. Dhole, et al., A single segment differential tube model with interchain tube pressure effect, J.Non-Newtonian Fluid Mech. (2009), doi:10.1016/j.jnnfm.2009.03.014
(2) A. Bach et al., Elongational viscosity of narrow molar mass distribution Polystyrene, Macromolecules 36 (2003)5174-5179
(3) O. Hassager, Polymer fluid mechanics: Molecular orientation and stretching, Proc. XIVth International Congress on Rheology, NF01 (2004)
(4) H. K. Rasmussen et al., Elongational dynamics of narrow molar mass distribution linear and branched polystyrene melts. AIP Conference Proceedings (2008), 1027(Pt. 1, 15th International Congress on Rheology, 2008), 415-417
(5) J. K. Nielsen et al., Reversed extension flow, J. Non-Newtonian Fluid Mech. 155 (2008) 1519
(6) T. Schweizer et al., A shear rheometer for measuring shear stress and both normal stress differences in polymer melts simultaneously: the MTR 25, Rheol. Acta. 47 (2008), 943-957

Tuesday 10:10 Hall of Ideas G SM2

Rheological studies of biodegradable thermoplastic polyester-urethanes bearing POSS

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Bioabsorbable polymeric coronary stents have attracted great interest recently because of their potential for excellent long-term safety. A unique family of biodegradable thermoplastic polyester-urethanes synthesized in our group, polyhedral oligosilsesquioxane thermoplastic polyurethanes (POSS TPUs), exhibit many advantages for this application in terms of their superior mechanical properties and tailored biodegradability. In this work, we investigated the rheological properties of these polyurethanes to facilitate the optimization of an extrusion process for stent prototype fabrication. Specifically, we focused on the temperature-dependent viscosity, shear-thinning behavior, and thermal stability of the polymer melt. As expected, above the polyurethane melting temperature (ca. 120 °C), increasing the temperature was found to dramatically decrease the polymer viscosity very quickly and in a manner consistent with the WLF equation. Moreover, shear thinning was observed for the POSS TPUs for angular frequencies higher than 10 rad/s. The time- and temperature-dependences of the degradation behavior of the polymer melt were characterized by the rheological tests coupled with other polymer analysis methods, including TGA, DSC and GPC. We conclude that the polyurethanes exhibit excellent thermal stability up to 160 °C under a nitrogen environment, but slight degradation in the oxidizing air environment.

Tuesday 10:35 Hall of Ideas G SM3

A theoretical analysis of rheo-dielectric response of type-A polymer chains under steady shear and LAOS

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For type-A polymer chains having type-A dipoles parallel along the chain backbone (such as cis-polyisoprene), a theoretical analysis was conducted for the rheo-dielectric response to relate this response to the chain dynamics. The rheo-dielectric response in the shear gradient direction (y direction) under steady shear was analyzed on the basis of a Langevin equation. It turned out that the relaxation time is exactly the same for the rheo-dielectric relaxation function and the end-to-end vector auto-correlation function defined in the shear gradient direction and that the relaxation mode distribution also coincides for these functions at least up to second-order of the shear rate (corresponding to the lowest order of nonlinearities of these functions). Consequently, the Green-Kubo theorem holds satisfactorily, and the rheo-dielectric intensity is proportional to the squared chain size in y direction, $\langle R_y^2 \rangle$, averaged over the time-independent conformational distribution function under steady shear. The situation is more complicated under large amplitude oscillatory strain (LAOS) because the conformational distribution function F is synchronized with LAOS to oscillate at the LAOS frequency, O. The rheo-dielectric response under LAOS was found to detect this oscillation of F being coupled with the oscillation of the electric field, $E(t) = E_0 \sin \omega t$, and thus split into a series of components oscillating at frequencies ω and ω+kO (k = integer). Consequently, the rheo-dielectric intensity under LAOS, evaluated from the component oscillating at ω, is no longer proportional to $\langle R_y^2 \rangle$. However, the relative mode distribution and relaxation time of this component can be directly related to those of the end-to-end vector correlation averaged over a non-oscillatory part of the distribution function F.

Tuesday 11:00 Hall of Ideas G SM4

Rheology of gradient copolymer melts: Indications of both LCOT and UCOT in high molecular weight styrene/n-butyl acrylate systems

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We use rheology and small-angle x-ray scattering (SAXS) to explore the phase behavior of gradient copolymers with compositions varying across the entire copolymer backbone. Low-amplitude oscillatory shear (LAOS) was performed to study the impact of comonomer sequence on phase behavior in strongly segregating styrene/4-acetoxystyrene (S/AS) and moderately segregating styrene/n-butyl acrylate (S/nBA) systems with differing molecular weights (MWs). The higher MW S/AS gradient copolymer exhibits LAOS behavior similar to a highly microphase segregated S/AS block copolymer, while the lower MW S/AS gradient copolymer exhibits complex, non-terminal behavior indicative of a lower degree of microphase segregation. The S/nBA gradient copolymers demonstrate more liquidlike behavior, with the lower MW sample exhibiting near-Newtonian behavior, indicative of a weakly segregating structure, while the higher MW, steeper gradient sample shows behavior ranging from solidlike to more liquidlike as temperatures are increased from 353 K, indicative of a change from order to disorder or an upper critical ordering transition (UCOT). At temperatures above 453 K, the same higher MW S/nBA case shows evidence of re-ordering as measured by both LAOS and SAXS, indicative of a lower critical ordering transition (LCOT). This is similar to behavior seen in very weakly segregating S/n-butyl methacrylate block copolymers, where such dual ordering transitions were first detected by Russell et al. (Nature, 1994). Access to such behavior is very rare in blends and block copolymers, limited to low MW and/or very weakly segregating systems. The indication of both UCOT and LCOT in a 152k gradient copolymer thus demonstrates the potential for more complex phase diagrams through gradient sequencing.

Tuesday 11:25 Hall of Ideas G SM5

Linear viscoelasticity of solvated ionomer melts

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We report oscillatory shear data on a series of sulfonated ionomers with Li+ or Na+ counterions, made from condensation polymerization of poly(ethylene glycol) (PEG) with mixtures of sulfonated and non-sulfonated phthalates. These polyester copolymer ionomers have 9, 13 or 20 ether oxygens per phthalate, with the sulfonation level of the phthalates varying from 0% (neutral polymer) to 100%. Such an excess of ether oxygens solvates the ions, preventing the usual microphase separation of ions from polymer that occurs in conventional ionomers. As a consequence, time-temperature superposition works nicely and is utilized to construct master curves that cover all liquid-state relaxations from the glassy response to the terminal response. Glass transition temperature increases systematically with both ion content and phthalate content, the latter being adjusted by the length of the nearly monodisperse PEG spacers between phthalates. Dielectric spectroscopy determines the populations of ions existing in isolated ion pairs and quadrupoles, and this information is used to understand the linear viscoelasticity in terms of associating polymer models.

Symposium MR
Microrheometry and Microfluidics

Organizers: Daniel Blair and Amy Shen

Tuesday 9:45 Meeting Rooms OP MR16

Stability and breakup of confined threads

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Microfluidic devices are often used to generate drops, but confined morphologies with at least one dimension much longer than the wall spacing also exist. An example of this are long threads, either generated by jetting, or coalescence of drops. We use a three-dimensional periodic boundary-integral method to investigate the stability of such threads. Our algorithm incorporates Green's function who exactly satisfy the no-slip condition at the walls. The periodic version makes use of the Hele-Shaw form formulation, that the wall-corrected Green's functions take in the far field. We primarily focus on the stability of threads versus small amplitude disturbances. At large wall separations, we obtain an excellent match with Tomotika's theory. With increasing the confinement ratio, the growth speed reduces, but much more in the direction perpendicular to the walls. Also the wavelength with the fastest growth speed changes slightly. We find that all threads will break up in the confinement, as long as the undeformed drop fits between the plates (confinement ratio < 1), although the breakup time increases significantly. One other aspect we show is the response of threads laying close to each other. Depending on the distance between the threads, waves on neighboring threads form in an in- or out-of-phase pattern. The crossover distance in unconfined situations is in agreement with experimental data and analytical results. We find that the confinement promotes out-of-phase behavior. Finally, we show the influence of shear. If the shear flow can convect distortions before they can grow, shear flow acts to stabilize the thread. Our results match quite well with a simple scaling argument for the critical capillary number, above which the threads are stable.

Tuesday 10:10 Meeting Rooms OP MR17

Alteration of flow instability in planar contraction microchannels

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Flow instability of viscoelastic fluid in contraction geometry has been one of the benchmark problems in rheology field, and therefore has long been studied both in planar and axisymmetric configuration. In the recent decade, the attention has been turned to micro-contraction that has different physical phenomena and the different era of nondimensional numbers. In this study, the alteration in the flow instabilities in planar contraction microchannel was induced and visualized, by changing the channel dimension and by applying external field to the pressure-driven flow. Due to the limitation in fabrication method, these microchannels are only planar-shaped and aspect ratio of width and depth is fairly big. In the first part, the size of planar microchannel was gradually enlarged to millimeter range with varied aspect ratio and the different courses of instability development were visually recorded. In the next part, ac/dc electric field was perpendicularly applied to the pressure-driven flow and the flow stream of low viscosity polymer solution was interrupted depending on the electrical property of the fluid and the fluorescent seed particle with surface charge.

Tuesday 10:35 Meeting Rooms OP MR18

Oscillatory flow behavior of thermally responsive fluids in microchannels

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Microfluidic devices have the potential for a wide range of applications such as biological analysis, chemical reactors, and sensors. Recently, thermally responsive fluids have been successfully used for flow control in microchannels. At low temperatures these polymer solutions behave as a Newtonian fluid; however, above a critical temperature they (reversibly) form gel-like structures. Also, because of the small length scales involved in microchannel flows, viscous heating can become significant, and can lead to unexpected and undesired effects. In this work, we first derive a simple asymptotic model for flow of a thermally responsive fluid in a microchannel. The model takes into account viscous heating as well as possible convection through the channel walls. Using this model we then show that when the viscous heating exceeds a critical level, an oscillatory flow behavior can occur. These oscillations eventually become damped out as the system reaches a steady state; however, the time it takes for this to occur can become excessively large. We examine the physical mechanisms that cause the oscillatory behaviour, and determine the criteria for the oscillatory flow to occur. We also present some other interesting aspects of the flow.

Tuesday 11:00 Meeting Rooms OP MR19

Flow behavior of biopolymer solutions in a microfluidics flow contraction device

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The flow behavior of biopolymer solutions was studied in microfluidics contraction devices at UQ (Rodd et al. 2005) to gain insight into their behavior in extensional flow situations which is otherwise difficult to obtain. As far as we are aware, micro contraction flow data have not yet been published for low viscosity biopolymer solutions whereas data on their behavior in shear flow are abundant. Our interest in extensional flow data on biopolymer solutions is in the context of taste perception. At UNott we investigate which fundamental rheological parameters correlate to flavor perception from liquid foods modeled as biopolymer solutions (Gady et al. 2008). The hypothesis for this research is that the in-vivo flow behavior of liquid polymer based foods is complex and quantifying the extensional flow behavior of biopolymers in solution will complement current shear rheology - taste perception correlations as flow behavior in extensional flow situations also gives some insight into polymer behavior in solution (Rodd et al. 2005). The elastic behavior of a solution is related to both the elasticity of individual coils as well as entanglements between coils. However, very little data are available on extensional behavior of biopolymers. We characterized a large number of biopolymers of different molecular architecture in aqueous solution. Pressure drop was measured and recirculation patterns were analyzed to obtain apparent extensional viscosity data. For concentration below the coil-overlap concentration, c*, quantified in shear flow, the biopolymer solutions exhibited extensional thickening hypothesized to be due to the stretching of the polymer coils. On the contrary, for concentration above c*, extensional thinning was observed at low Reynolds numbers. We hypothesize that this is due to the disentanglement of polymer coils with the flow. In addition, differences in elasticity have been observed depending on molecular architecture.

Tuesday 11:25 Meeting Rooms OP MR20

Mass transfer kinetics and interfacial rheology in two-phase microchannel flows

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Multiphase liquid systems are essential to everyday life, e.g., foods, pharmaceutics, cosmetics, oil recovery, etc. The morphology and stability of such systems depend on dynamic interfacial properties and processes. Typical methods used to measure such properties often employ simpler flows and larger drops than those encountered in typical processing applications. Mass transfer mechanisms are governed by drop size; therefore experimentation at length scales typical of those encountered in applications is desirous. Using a microfluidic approach, dynamic structure and kinetics are measured in multiphase systems using drop sizes comparable to those seen in applications and easily adjustable flow complexity. Through drop deformation dynamics, the dynamic interfacial tension of aqueous, surfactant-containing drops in mineral oil is probed as a measure of surfactant mass transfer kinetics. Using particle tracers, the drop internal circulation velocity is used as a measure of interfacial mobility. Deformation dynamics, interfacial tension, and circulation patterns are measured in Poiseuille and transient elongational flows in a microchannel.

Experiments performed on drops of aqueous n-butanol solutions in mineral oil show that the interfacial tension decreases with interface age due to the diffusion of butanol from the drop to the oil. A shift from diffusion-controlled mass transfer to a regime where adsorption / desorption kinetics at the interface become limiting is verified for small drop sizes (tens of microns). Significant interfacial immobilization is seen at low surfactant concentrations, with remobilization at high concentrations. Internal drop circulation patterns are studied in more detail using a nearly index-matched system of ethylene glycol / water drops in silicone oil. Thus our microfluidic approach facilitates measurement of mass transfer kinetics and Marangoni effects in the same experiment utilizing industrially-relevant flows and drop sizes.

Symposium BR
Biorheology and Rheology in Biological Systems

Organizers: Prosenjit Bagchi and Michael R. King

Tuesday 9:45 Hall of Ideas J BR16

A constitutive equation for unidirectional flows of dilute deformable particles

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It has long been known that deformable particles and drops will migrate away from boundaries and from regions of high shear. The concentration distribution of such particles can be written as a balance between the drift flux arising from deformation and the flux due to shear induced migration. In the case of dilute emulsions, droplet drift flux can be modeled using the O(Ca) theoretical results of Chan and Leal [J. Fluid. Mech., 92, 131-170, 1979]. The flux due to shear-induced migration can be modeled using the suspension balance approach of Nott and Brady [J. Fluid. Mech., 275, 157-199, 1994], whereby particle migration is ascribed to normal stress gradients. In the limit of small deformation, the leading order contribution of the normal stresses in dilute emulsions arises from binary interactions and thus scales as $\tau\phi^2$, where ϕ is the droplet or particle volume fraction and τ is the local shear stress. In our model, the normal stress calculations of Zinchenko [Prikl. Matem. Mekhan., 47, 56-63, 1984] are connected to gradient diffusivity data computed from droplet trajectories [Loewenberg and Hinch, J. Fluid Mech., 338, 299-315, (1997)] via a reduced droplet mobility to derive a droplet flux due to shear-induced migration. As an example, the model is applied to the tube Poiseuille flow of a dilute emulsion at small Ca. It is demonstrated that the unsteady concentration distribution of droplets resulting from arbitrary time-dependent average velocity obeys a self-similar solution, provided the thickness of the droplet-depleted region near the walls is always non-zero. Application of the model to other systems such as vesicles and dilute RBC suspensions is discussed.

Tuesday 10:10 Hall of Ideas J BR17

Dynamics of suspensions of elastic capsules flowing in confined geometries

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Modeling the behavior of fluid-filled capsules (which can be considered as a simple representation of red blood cells and vesicles), is not only important to understand biological processes, such as blood flow in the microcirculation, but also to help design and improve microfluidic devices for characterizing or separating such particles. The present work describes simulations of large numbers of deformable capsules with various properties in confined geometries. Our algorithm incorporates a General-Geometry-Ewald-Like method (GGEM) for efficiently calculating hydrodynamic interactions (O(N)) in an immersed-boundary method. This allows for a detailed description of the particle interface combined with a large degree of freedom to model the confining domain (grooved channels, cylindrical and spherical obstructions). With our algorithm, we have addressed several issues. The ability to quickly simulate large number of particles enables examinations not only of the competition between shear-induced diffusion and wall-induced hydrodynamic migration of single particles, but also exploration of concentration effects and segregation by size, shape and/or deformability. The flow through a slit containing an array of pillars, which is a model representation of the interalveolar sheet structure of the capillaries in the lungs, has been examined as well. Combined with the simulation of grooved channels, we propose a methodology to separate these cells depending on their deformability and size. Finally, the effect of addition of long-chained polymer molecules in blood flow, known to lower blood pressure, is investigated.

Tuesday 10:35 Hall of Ideas J BR18

Simulation of red blood cell ghost deformation induced by linear diode bar optical stretchers

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The mechanical deformation of biological cells using optical forces is an efficient experimental method to study the cellular properties and identify diseased cells. Different types of optical stretchers have been successfully used to induce both small and large scale deformations. Optical stretchers generally require minimal direct contact, compared to other experimental techniques (micro-pipette aspiration, atomic force microscopy). A pseudo steady-state high-throughput optical stretcher can be implemented where anisotropic forces stretch red blood cells (RBC) ghosts within rapidly flowing microfluidic environments. This approach has the potential to be readily integrated with other cytometric optical-based detection technologies, lowering cost and increasing the availability of practical platforms for both laboratory and point-of-care applications. In this work we simulate an optical stretcher based only on a single, inexpensive light source. Cells are considered as 3D elastic capsules immersed in a fluid. The fluid-structure interaction is modeled using the Immersed Boundary Method (IBM). The transient deformation of an RBC ghost due to applied optical forces is calculated using the ray tracing method to obtain the force distribution on the cell surface. The optical force is removed and the relaxation of the red blood cell ghost is simulated. RBC ghost deformation and relaxation are simulated as a function of optical source power. The simulation results are used to develop methods for calculating membrane properties based on both the static deformation and the rate of relaxation.

Tuesday 11:00 Hall of Ideas J BR19

Simulation of cellular blood flow in the microcirculation

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We will present a simulation tool and results for cellular blood flow in geometries relevant to microcirculatory dynamics. The red cells are modeled as elastic membranes enclosing Newtonian fluid. The membranes are linearly elastic but finite deformation, however the numerical scheme is independent of this particular constitutive model, which could be changed in a straightforward way to a sophisticated constitutive model if needed. The plasma surrounding the cells is also Newtonian. The flow equations are solved with a specially designed fast boundary integral method, which is efficient enough to permit the simulation of hundreds of densely packed cells. Results will be presented matching experimental measurements of the resistance of flow in small straight tubes at different hematocrits (red-cell volume fractions) and flow rates. Results will also be presented for the complex geometry interactions between red cells and a wall-bound leukocyte and the flow of red cells in a model capillary network.

Tuesday 11:25 Hall of Ideas J BR20

Three-dimensional computational modeling of semi-dense suspension of O(1000) deformable capsules in channel flow

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Three-dimensional numerical simulations are presented on the motion of large ensembles of deformable particles (up to 1096 in number) in a channel flow at small inertia. Particles are modeled as capsules, that is, liquid drops surrounded by elastic membranes. The particle volume fraction considered is up to 29%. The numerical methodology is based on a mixed finite-difference/Fourier transform method for the flow solver and a front-tracking method for fluid/membrane interaction. In the simulations, the flow field is resolved using up to 288X288X288 grid points, and each particle surface is resolved by 1280 triangular elements. The database generated from the simulations provides a wealth of information on the dynamics of semi-dense suspension of liquid capsules, in particular, and of deformable particles, in general. The model retains two important features of the blood flow in the microcirculation, that is, the particulate nature of blood, and deformation of the erythrocytes. We present results on various physiologically relevant processes such as the development of the cell-free layer, and the Fahraeus-Lindqvist effect. We then use these results to calculate the core and plasma-layer viscosity, and show that the two-phase (or, core-annular) model of blood flow in microvessels underpredicts the blood velocity obtained in the simulations by as much as 40%. Based on a posteriori analysis of the simulation data, we develop a three-layer model of blood flow by taking into consideration the smooth variation of viscosity and hematocrit across the interface of the cell-free layer and the core. We then show that the blood velocity predicted by the three-layer model agrees very well with that obtained from the simulations.

Symposium MS
Molecular Modeling and Simulation in Rheology

Organizers: Rajesh Khare and Nicos Martys

Tuesday 9:45 Meeting Rooms QR MS16

Self-consisting modeling of entangled network strands and dangling ends

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We seek knowledge about the effect of dangling ends and soluble structures of stoichiometrically imbalanced networks. To interpretate our recent experimental results we seek a molecular model that can predict LVE data. The discrete slip-link model (DSM) has proven to be a robust tool for LVE and non-linear rheology predictions for linear chains, and it is thus used to analyze the experimental results. We divide the LVE predictions into three domains; 1) the low frequency region, where G' is a plateau, G_0, 2) the intermediate frequency region, where G' and G" are parallel and 3) the high frequency region, where G' levels off to an entanglement plateau, G_N^0, close to that of the linear polymer. The latter region is seldom obtained in experiments, while it is obtained in simulations since these start at zero time. Initially we consider a stoichiometrically balanced network, we call this an ideal entangled network (IEN). We simulate monodisperse polypropylene oxide with an average number of entanglements of ~3.8. Such lightly entangled networks show a G_0 that is about 24% lower than G_N^0. This decrease is a result of monomer fluctuations between entanglements. Additionally we observe that G' is dominating at all frequencies compared to G". Experimental observations of stoichiometrically imbalanced networks shows that G" and G' are of the same order of magnitude at intermediate frequencies, hence the DSM suggests that energy dissipation is largely a result of dangling ends and soluble structures. Energy dissipation is increased by adding a fraction of dangling ends, w_{DE}, to the ensemble. We find that when $w_{DE}=0.6$, G_0 is about 75% lower than G_N^0, this suggests that the fraction of network strands, $w_{NS}=1-w_{DE}$, largely influences the plateau value at low frequencies. Soluble strands can also be added to the theory which is expected to increase energy dissipation further.

Tuesday 10:10 Meeting Rooms QR MS17

Direct nonequilibrium Monte Carlo simulation of flow-induced crystallization of a linear short-chain polyethylene liquid in uniaxial elongational flow

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Nonequilibrium Monte Carlo simulations were performed for an atomistic model of a dense liquid composed of linear polyethylene chains undergoing uniaxial elongational flow. The simulations were conducted at four temperatures ranging from 300 K to 450 K. At the higher temperatures of 400 K and 450 K, simulation results revealed that the polyethylene chains were stretched significantly as a function of flow strength, but that the systems remained in the liquid phase. At the lower two temperatures of 300 K and 350 K, clear evidence was obtained of a flow-induced phase transition to a crystalline solid phase. This evidence included a structure factor for the multi-chain system that compared favorably with an experimental x-ray diffraction measurement of a crystalline linear polyethylene at all relevant length scales, including Bragg peaks at the correct k values. Simulated values of the internal energy (and the configurational temperature) revealed a flow-induced jump in absolute value, reminiscent of a first-order phase transition. The heat capacity of both phases could be calculated based on the configurational temperature. A distinct flow-induced enthalpy change was also evident between the liquid and crystalline states. Monitoring the configurational temperature of the system revealed a strong flow decrease with increasing flow strength, providing a plausible microscopic physical origin (i.e., related to the local conformation environment of the chains) for the flow-induced enhancement of the crystalline (or melting) temperature that have been reported in experiments.

Tuesday 10:35 Meeting Rooms QR MS18

Simulations of transient forces in soft matter: Applications to the rheology of tri-block copolymer telechelics and linear polymer melts

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In order to perform simulations of flowing soft matter in complex geometries, a minimum number of degrees of freedom must be used. A possible strategy in this situation is to simulate only the movements of the centers of mass of all particles, and to envisage the remaining degrees of freedom as constituting a thermodynamic bath. Such a coarse graining procedure inevitably leads to very soft interactions and usually to equations of motion that include memory of the recent history of the moving particles. In order to circumvent dealing with memory effects, we introduce an additional set of variables describing the thermodynamic state of the bath. Deviations of these variables from their equilibrium values give rise to transient forces in addition to the, usually very soft, thermodynamic mean forces. The model will be applied to study the rheology of solutions of tri-block copolymers in a solvent that does not accept the end blocks of the polymer, but does accept the middle block. In such a case the end blocks gather together in micellar spheres, while the middle blocks dissolve in the surrounding liquid. At high concentrations, micelles are connected by polymers with both end blocks taking part in different micelles. Such systems exhibit shear banding and sometimes even fluid fracture. I will show that a Brownian dynamics simulation model including transient forces can quantitatively reproduce all the rheological properties of such systems. Most model parameters will be estimated on the basis of the molecular architecture while some others are measured independently. A very bold application of the model is to simulate the rheology of melts of linear polymers. I will investigate the N-scaling of the model parameters of the single particle model and find that they are very similar to those of reptation theory and in agreement with experimental findings.

Tuesday 11:00 Meeting Rooms QR MS19

Magnetoviscosity of magnetic fluids under oscillating and rotating magnetic fields obtained through rotational Brownian dynamics simulations

Jorge H. Sanchez and Carlos Rinaldi
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The magnetic field dependent viscosity (magnetoviscosity) of dilute suspensions of magnetic spherical particles suspended in a Newtonian fluid subjected to both magnetic and shear flow fields was studied numerically. Brownian dynamics simulations were performed to compute the intrinsic magnetoviscosity of the suspension. Results are presented for the response of dilute suspensions of spherical particles to oscillating magnetic fields and magnetic fields that are co-rotating or counter-rotating with respect to the fluid vorticity. A decrease in the intrinsic magnetoviscosity is observed for oscillating and co-rotating magnetic fields. The frequency corresponding to zero viscosity and the minimum value in the negative viscosity are lower for co-rotating magnetic fields than for oscillating magnetic fields. In the case of counter-rotating magnetic field the results show a maximum in the intrinsic magnetoviscosity of the suspension. For both cases the frequency at which the viscosity achieves maximum or minimum values is dependent on the dimensionless shear rate, parameterized through the rotational Peclet number, and the dimensionless magnetic field strength, parameterized through the Langevin parameter.

Tuesday 11:25 Meeting Rooms QR MS20

Effect of extensional flow on phase transitions and orientational structure in binary carbonaceous mesophase mixtures

Mojdeh Golmohammadi and Alejandro D. Rey
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A Maier-Saupe model for binary mixtures of uniaxial discotic nematogens under extensional flow is formulated to describe phase ordering in carbonacoues mesophases, differing only in molecular weight. The orientational structure and the thermodynamic phase diagram depend on (i) the intrinsic properties of the mixture, i.e. molecular weight difference and the interaction parameter, (ii) the operating properties, i.e. concentration and temperature and (iii) deformation rates. The results obtained from our pervious study [Golmohammadi et al., L.C., 2008, Accepted] shows that depending on the intrinsic properties of the system, two types of uniaxial nematic mixtures arise: (i) non-ideal mixtures with a minimum in its Nemtic to Isotropic (NI) transition as a function of the concentration, and (ii) ideal mixtures with a monotonic trend of the NI transition temperature as a function of concentration. In the current work we study the effect of extensional flow on the phase transitions in ideal and non-ideal mixtures. A structural feature is the emergence of biaxiality which is characterized using X-ray scattering calculations.

Tuesday Afternoon

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Tuesday 1:30 Lecture Hall SC21

High-flux magnetorheology at elevated temperatures

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Applications of magnetorheological (MR) fluids often require operations at elevated temperatures caused by extreme environmental conditions or severe internal heating (viscous heating). A well-established theory of magnetorheological response at elevated temperatures does not exist. Although several recent studies have reported a reduction in the field-induced yield stress of MR fluids at elevated temperatures, the mechanism of thinning has been attributed to several different causes such as changes in the base fluid viscosity and Brownian excitation of the particle chains. In colloidal magneto-susceptible fluids such as ferrofluids, the changes in thermorheological response have been attributed to the reduction of magnetization with temperature. In the high-flux regime, the MR fluid response is primarily a function of saturation magnetization, which is also a temperature-dependent material property. We outline the development of a new parallel plate rheometer accessory designed for the AR-G2 controlled-stress rheometer which is capable of reaching 150°C and maintaining a magnetic flux density of 1T. Magnetic field non-uniformities are present in MR fixtures in regions where discontinuities in the local magnetic permeability are present (e.g. at magnetic solid/MR fluid interface, MR fluid/air interface). Using finite element methods, field uniformity throughout the sample space was evaluated and design features to maximize uniformity were implemented. These improvements were further validated by spatially-resolved measurements of magnetic flux using a Hall effect probe. Using the new magnetorheology accessory, the evolution in the MR fluid "gain" (i.e. the ratio of the flow stress with field-on as compared to field-off) is evaluated at ambient and elevated temperatures. We develop improved scaling laws that describe the evolution in the MR fluid response with changes in the applied field, shear rate (or shear stress), saturation magnetization and sample temperature.

Tuesday 1:55 Lecture Hall SC22

Simulation of fibrous electro- and magnetorheological fluids

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Experimental studies on the electro- and magnetorheological behavior of suspensions of polarizable and magnetizable fibers report substantial enhancements in the field-induced yield stress compared to responses observed for suspensions of spherical particles at the same particle volume fraction. This observation has a significant potential impact on commercial device development, where one objective has been to increase field-induced stresses in order to reduce device volume and cost. In this presentation, we report a study employing particle-level simulations to probe the behavior of suspensions of fibers in external electric or magnetic fields. The fibers are modeled as straight, rigid chains of osculating spheres suspended in a Newtonian liquid. Field-induced interactions are modeled as point-dipole interactions between the individual spheres. Hydrodynamic forces are treated in the free-draining limit, which restricts the validity of the method to vanishing shear rates. The simulations indeed show an enhancement of field-induced stresses at low volume fractions, as observed experimentally. We also observe slower structure formation, which is related to the tendency of the fibers to entangle. The entanglement is in part caused by the corrugation of the fiber surfaces, which produces a friction-like interaction between neighboring fibers.

Tuesday 2:20 Lecture Hall SC23

Electrorheology of nanocage based systems

Ernest C. McIntyre and Peter F. Green
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We show that mixtures of sulfonated polyhedral silsesquioxane cage structures (POSS) and silicone oil exhibit significant electrorheological activity. At low POSS concentrations less than 10% wt. stresses are comparable to the stresses exhibited by electrorheological polymer/silicone oil mixtures. It is well known that increases in sulfonation of polymer particles increases electrorheological activity and this could, in part, account for some of our observations. However, the effect is more significant than would be anticipated based on prior research. Extensive measurements of the conductivity and relative permittivity of the system indicate that the behavior of these materials cannot be reconciled with the conventional theory of electrorheological behavior, nor with the more recent extensions associated with polar molecule behavior.

Tuesday 2:45 Lecture Hall SC24

Rheology of calcium carbonate cuspensions with sodium polyacrylate dispersant

Gerard R. Gagnon[1], David J. Neivandt[1], Nigel D. Sanders[2], and Douglas W. Bousfield[1]
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The rheological behavior of high solids precipitated calcium carbonate suspensions dispersed with different sodium polyacrylate dispersants was characterized. The dispersants had different molecular weights and ionic group densities. The dose level was also changed. The zeta potential of the particles, divalent ion concentration in the aqueous phase, and the amount dispersant adsorbed onto the pigment particles was characterized. Viscosity was predicted by a particle level model. Dispersants with the same ionic group density had similar shear thinning behavior, but the behavior shifts depending on ionic group density. The molecular weight of the dispersant had little effect on the rheology. High ionic group density dispersants had a point for the onset of shear thickening at shear rates of around 300 s^{-1}. Oscillatory shear amplitude sweeps revealed that for each dispersant, low the elastic modulus versus strain and low the strain value at the edge of the linear elastic region correlates with shear viscosity at low shear rate. Dynamic medium-high shear rate measurements showed a shear thickening behavior for all dispersants. However, the onset shear rate was dependent on dispersant ionic group density. Model results predict the correct order of magnitude of shear thinning using electrostatic and van der Waals forces. The rheological behavior could be explained in terms of these colloidal forces between particles.

Tuesday 3:10 Lecture Hall SC25

Extensional rheology of shear-thickening nanoparticle suspensions

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A filament stretching rheometer is used to measure the extensional properties of shear-thickening nanoparticle suspensions as a function of concentration and extension rate. The experiments are performed using a series of colloidal suspensions consisting of concentrations of 17.5wt%, 25wt% and 30wt% of fumed silica nanoparticles in polypropylene glycol. The shear rheology of these suspensions was found to demonstrate dynamic shear thickening behavior owing to the formation of large hydrodynamic clusters. The critical value of angular frequency for the onset of shear-thickening was found to increase monotonically with decreasing strain amplitude. The extensional rheology of all the tested suspensions demonstrated modest strain hardening at low strain rates. At a critical extension rate, a dramatic increase in both the speed and magnitude of the strain hardening is observed for both the 25wt% and 30wt% suspensions with increasing extension rate. The steady state extensional viscosity as a function of extension rate shows a sharp extensional thickening transition very similar to shear flows. The increase in strain hardening is likely due to the formation of strings and clusters, ordered in the flow direction. This hypothesis is confirmed by small angle light scattering measurements on the flow of the nanoparticle suspension through a microfluidic hyperbolic contraction. The degree of alignment of nanoparticles is quantified from the analysis of the scattering patterns, and found to increase significantly with increasing extension rate.

Tuesday 4:00 Lecture Hall SC26

Flow induced orientation behavior of concentrated dispersions of multi-walled carbon nanotube suspension under shear flow

Saswati Pujari[1], Wesley R. Burghardt[1], Sameer Rahatekar[2], Jeffrey W. Gilman[2], Krzysztof K. Koziol[3], and Alan H. Windle[3]
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We report studies of average orientation state of concentrated dispersions of multi-walled carbon nanotube (MWNTs) in steady shear flow. Uncured epoxy was used as a viscous, Newtonian suspending medium, and samples were prepared from 'aligned' MWNTs using methods previously reported (Rahatekar et al., J Rheol 40:599, 2006). Flow induced structural measurements were made on a number of samples in the vorticity (1-3) plane of simple shear flow using in-situ x-ray scattering techniques in a rotating disc shear cell. Steady state anisotropy of MWNT dispersions decrease with increasing the length of the MWNTs. Surprisingly, the anisotropy is seen to increase with increasing concentration. For one of the samples (2wt% short MWNT), much detailed orientation dynamics is studied in steady shear and transient shear flow both in the 1-2 (flow gradient) and 1-3 (vorticity) planes of shear flow using small and wide angle x-ray scattering. Anisotropy induced in the 1-2 plane is found to be higher than anisotropy induced in the 1-3 plane. WAXS yields quantitatively a higher value of anisotropy than SAXS in the 1-3 plane. Measurements in 1-2 plane are done using an annular cone and plate x-ray shear cell.

Tuesday 4:25 Lecture Hall SC27

Transient behavior of carbon nanotube suspensions in an epoxy

Fatemeh Khalkhal and Pierre J. Carreau
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Carbon nanotubes (CNTs) have found a lot of applications in different industries recently. They are mainly used to enhance the electrical, mechanical and thermal properties of polymers. The rheology of CNT suspensions has been the subject of interest by many researchers recently, but very little can be found on the transient behavior of these suspensions. To better understand the evolution of the microstructure of CNT suspensions under flow the transient behavior of CNT suspensions in an epoxy was studied in the semi-dilute and concentrated regimes. The effect of rest time between two consecutive start-up tests in clockwise and counter clockwise directions was analyzed in order to monitor the structure recovery of the suspensions. Similar to other filled polymeric systems, stress overshoots were observed in the forward flow. If no rest time was given between two consecutive experiments, no overshoot was observed in reverse flow; however by increasing the rest time between two consecutive start-ups, stress overshoots appeared in reverse flow and their extent increased by the rest time. It was observed that most of the structure recovery occurs shortly after cessation of flow in time scales expected from the Brownian time scales. In the semi-dilute regime, the suspension structure was recovered at small applied shear rates in the reverse direction after sufficient rest time. However, at higher shear rates, the structure recovery was limited even after long rest times. In concentrated regime, the structure was totally recovered after cessation of flow after 1 h rest time. The complete structure recovery at high concentrations could be due to the tight arrangement of CNTs in the suspensions and formation of entangled nanotube networks that stores the stress work and reforms a similar structure to the initial one after cessation of flow.

Tuesday 4:50 Lecture Hall SC28

Viscoelasticity of single-walled carbon nanotubes (SWNTs) in superacids

Colin C. Young[1], Dmitri E. Tsentalovich[1], Virginia A. Davis[2], Micah J. Green[1], Alario N. Parra-Vasquez[1], Natnael Behabtu[1], Marco Banzola[1], and Matteo Pasquali[1]
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The dispersion of SWNTs at high concentrations in superacids is a promising avenue for the processing of macroscopic SWNT-based articles such as fibers, films, and composites. Rheological characterization is essential to understanding and controlling the microstructural evolution of such dispersions during processing. Here we report the viscoelastic behavior of solutions over a wide SWNT concentration range in both fuming sulfuric acid (oleum) and chlorosulfonic acid; the data are used to characterize percolation, liquid-crystalline phase transitions, and the microstructure of liquid-crystalline domains. The different scaling behavior for these two solvents reflect the qualitatively different liquid-crystalline microstructure present in each, which in turn reflects the differences in the ability of these acids to protonate and disperse SWNTs.

Tuesday 5:15 Lecture Hall SC29

Rheological properties and percolation behavior of polypropylene/multiwalled carbon nanotube composites

Pierre J. Carreau[1], Sameneh Abbasi[1], and Abdelsalim Derdouri[2]
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We present several issues related to the state of dispersion and rheological behavior of polypropylene/multiwalled carbon nanotube (MWCNT) composites. The composites were prepared by diluting a commercial masterbatch containing 20 wt % nanotubes using optimized melt-mixing conditions. The state of dispersion was then analyzed by scanning and transmission electron microscopy (SEM, TEM). To understand the percolated structure, the nanocomposites were characterized via a set of rheological and electrical conductivity measurements. No significant effect of the gap of the parallel plate geometry (or apparent slippage) was observed down to a 500 µm gap. G' measurements were found to be temperature dependent; the percolation threshold was lower at higher temperature suggesting stronger nanotube interactions. The nanotube networks (characterized by G') were also sensitive to the shear deformation, particularly at high temperature. The effect of shear deformation on the microstructure of the nanocomposites and nanotube networks was evaluated by subjecting each sample to different levels of shear stress for various periods of time. These results are further analyzed using simple models for suspensions of rod-like particles. Finally, the rheological and electrical conductivity percolation thresholds were compared. As expected the rheological threshold was found to be smaller than the electrical threshold: approximately equal to 0.2 and 0.5 wt % for the rheological and electrical conductivity measurements, respectively.

Tuesday 5:40 Lecture Hall SC30

Structural order induced by carbon nanotubes in surfactant solutions

Ofra Ben-David, Einat Nativ-Roth, Rachel Yerushalmi-Rozen, and Moshe Gottlieb
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The rheological behavior of aqueous dispersions of single walled carbon nanotubes (SWNT) in solutions of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) was investigated. The steady shear viscosity as a function of the applied shear rate was monitored in different concentrations of the surfactant which correspond to different mesophases. We found that the presence of SWNT had a dramatic effect on the behavior of the combined system not observed with other additives: A significant increase in the low shear-rate viscosity of SWNT dispersions, and shear thinning replacing Newtonian behavior were observed for CTAB concentrations below the onset of the surfactant hexagonal phase. As CTAB concentration increases the rheological behavior of SWNT-CTAB system and the native CTAB solutions become more alike. We suggest that the origin of the observed phenomena is the good size-match between SWNT and elongated CTAB micelles. Thus dispersed SWNT may induce the formation of size-matched elongated CTAB micelles that further orient under the action of external shear. A similar effect was not observed in dispersions of multi-walled carbon nanotubes or carbon black particles, suggesting that the cooperative behavior is not invoked when significant size-mismatch exists between the surfactant micelles and the dispersed additives.

Symposium SM
Polymer Solutions and Melts

Organizers: Ralph Colby, Jules J. Magda and Lynden Archer

Tuesday 1:30 Hall of Ideas G SM6

Rheological data and molecular modeling of polydisperse H-shaped polybutadienes

Si Wan Li, Hee Eon Park, and John M. Dealy
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A series of H-shaped polybutadienes were studied, which were polydisperse in terms of both molecular weight and structure. Details of the structures were revealed using temperature gradient interference chromatography (TGIC) and were compared using conventional analytical method such as size exclusion chromatography with laser light scattering detector (SEC-LS). Rheological characterizations were carried out over a broad frequency range using controlled-strain and controlled stress rheometers by small amplitude oscillatory shear (SAOs) and creep/recovery experiments. Time-temperature superpostion was found to work well on the SAOs data and dynamic modulus obtained from creep/recovery experiment agree well with the data. Simulations were carried out using models of Das et al.(1) and of Park et al.(2). Strengths and weaknesses of the models are discussed.

(1) Das, C., Inkson, N.J., Read, D.J., Kelmanson, M.A., and McLeish, T.C.B.,Journal of Rheology, 50 (2), 207-234 (2006). (2) Park, S.J., Shanbhag, S., and Larson, R.G.,Rheol Acta, 44 (319-330 (2005).

Tuesday 1:55 Hall of Ideas G SM7

Unique rheological properties and phenomena of a tree-like polybutadiene melt

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Long chain branching is known to dramatically change rheological behavior of entangled polymeric liquids. In this work, we study large deformation behavior under both simple shear and uniaxial extension of a 1,4-polybutadiene (PBD) melt with tree-like chain architecture, using both rheometric and particle-tracking velocimetric (PTV) methods. In striking contrast to the linear PBD melts, this hyper-branched PBD melt exhibits several remarkable characters. (a) It resists wall slip and does not undergo shear banding. (b) Being gel-like, it shows little rate dependence of its yielding characteristics during a startup shear and displays no shear stress maximum at strains as high as ten units. (c) It does not suffer elastic yielding after a large step shear, i.e., quiescent relaxation prevails. (d) Similarly, large step extension does not result in structural failure of the stretched specimen. (e) In both shear and tensile stress relaxation, the dynamics are found to be slower at higher amplitudes of step strain. Although most of these features can be expected from the emerging understanding of the cohesion in entangled liquids and elastic yielding [1], the last observation is clearly puzzling and opposite to what is seen in linear polymers.

[1] S. Q. Wang, S. Ravindranath, Y. Wang, P. E. Boukany, J. Chem. Phys. 127, 064903 (2007).

Tuesday 2:20 Hall of Ideas G SM8

Stress relaxation of comb polymer with short branches

Keith M. Kirkwood[1], L. Gary Leal[1], Dimitris Vlassopoulos[2], Paraskevi Driva[3], and Nikos Hadjichristidis[3]
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We measured the linear and nonlinear rheology of model polyisoprene comb polymers with a moderate number (5-18) of short (marginally entangled to unentangled) branches and highly entangled backbones. The hierarchical modes of relaxation were found to govern both the linear and nonlinear response. Appropriate modification of tube-model theory for entangled branches, inspired by recent work on asymmetric star polymers (where the short branch behaves as effectively larger on small timescales), provided a framework for quantitative predictions of the linear viscoelastic spectra. The extended nonlinear stress relaxation data over a wide time range (via time-temperature superposition) obeys time-strain separability and allows extraction of two damping functions, one for the branches at short times and one for the diluted backbone at long times. Both exhibit signatures of the comb architecture. The comb damping function at short times, shifted relative to the branch relaxation, is dominated by the retraction of branches and backbone end segments. The backbone damping function is rationalized by considering it as a linear chain that feels a smaller effective strain due to the prior branch relaxation.

Tuesday 2:45 Hall of Ideas G SM9

Self-similar dynamics of a flexible ring polymer in a fixed obstacle environment

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In this contribution we concern ourselves with modeling the dynamics of ideal flexible ring polymers constrained in an array of fixed obstacles. The fundamental issue in this problem is to understand how a topologically constrained polymer chain is able to relax its conformation in the

absence of chain ends. The key underlying physics was provided in an elegant scaling theory by Rubinstein and coworkers. In the current work we present a rigorous coarse-grained mean-field model based on the physical arguments of the scaling theory, and derive constitutive relations for rings in fixed obstacle environment. The model is built in three distinct steps: In the first step the dynamics of an arbitrary section of a ring chain is worked out based on fractal Blob-Spring (BS) dynamics and the center of mass diffusion and the relaxation spectrum of this section is determined. In the second step the center of mass diffusion obtained using the BS dynamics is used to understand the one dimensional diffusion of the section in a topologically constrained environment. Following Kapnistos et al, we assume that the relaxation of a non-concatenated flexible ring chain in an array of fixed obstacles occurs by the simultaneous relaxation of all possible sections of a ring chain in a self similar manner. In the final step we invoke this idea of dynamic self-similarity and argue that the dynamics described in the first and the second step, for any arbitrary section of the chain, applies to all sections of the chain. The constitutive relation is obtained consequently as the superposition of dynamic response of the sections of the chain.

Tuesday 3:10 Hall of Ideas G SM10

Melt dynamics of blended poly(oxyethylene) chains and rings

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Cyclic macromolecules exhibit dynamical behavior that is significantly different from their linear equivalents due to topological differences. Mixtures of cyclic and linear polymers offer added complexity due to the possibility of topological threading, which strongly affects melt dynamics and has been cited as an impediment to quantitative modeling of experimental data, since small fractions of linear contaminants significantly affect dynamics and are very difficult to remove or identify.

To better understand threading, we synthesized highly pure, monodisperse cyclic poly(oxyethylene) (CPOE) of relative low molecular weights (400-1500 g/mol) and blended it with linear POE (LPOE). The molecular weight range of the CPOE enables threading at the highest molecular weight, but not the lowest. The melt dynamics of these blends was examined with pulsed-field-gradient (PFG) 1H NMR and rheology to determine the self-diffusion coefficient and zero-shear viscosity. For blends prepared from components with equivalent molecular weights >400 g/mol, the diffusion is suppressed and the viscosity is enhanced in comparison with predictions based on a simple binary mixing rule. This is attributed to topological threading of rings onto linear chains. Blends of perdeuterated LPOE with hydrogenous CPOE (1500 g/mol) were also prepared and examined with PFG NMR. The resulting diffusion coefficients only represent the CPOE in the blends and are smaller than the average values measured for the fully hydrogenous blends at a given composition.

Extrapolation to zero CPOE concentration yielded the trace diffusion coefficient for CPOE in LPOE, which was assumed to represent the mobility of a threaded conformation. In combination with the pure-component diffusion coefficients and a three-term mixing rule, this value was used to determine the percentage of threaded rings as a function of CPOE concentration. The results are in qualitative and quantitative agreement with published modeling studies.

Tuesday 4:00 Hall of Ideas G SM11

Influence of long-chain branching on strain hardening of low density polyethylene

Florian J. Stadler[1], Florian Becker[2], Michael Buback[2], Joachim Kaschta[1], and Helmut Münstedt[1]
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Low density polyethylenes (LDPE) were synthesized in a laboratory scale autoclave under high pressure. These samples were found to possess a high molar mass tail, resulting in a distinctly bimodal molar mass distribution and a lower concentration of long-chain branching than typical of commercial LDPEs. Rheological experiments in elongation showed that these samples exhibit the highest strain hardening ever found in our investigations. The strain-hardening factor, i.e. the relation between the elongational and shear viscosity reaches ratios up to 40. Although the samples have an unusually high molar mass ($M_w = 2...4*10^6$ g/mol by SEC-MALLS), their zero shear-rate viscosities η_0 and their shear thinning behavior are still in a range, in which thermoplastic processing is possible. A qualitative explanation of these experimental results can be related to long-chain branches of very high molar masses using the Cayley-tree model. It was found that the average number of long-chain branches per molecules at $M=M_w$ is proportional to the maximum level of strain hardening obtained.

Tuesday 4:25 Hall of Ideas G SM12

Use of relaxation spectra for probing of polymers dynamics and architecture

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Spectra are the material function governing the rheological behavior in the linear viscoelastic regime, which can be understood as a combination of the spectrum and the excitation by the rheometer.

Determining spectra directly is not possible, but requires very time intensive calculations using special algorithms to overcome the difficulty that the calculation is an ill-posed problem. We have recently proposed a new algorithm, which can partially overcome these problems and is used in this presentation. (*Stadler and Bailly, A new method for the calculation of continuous relaxation spectra from dynamic-mechanical data, Rheol. Acta 2009, 48, 1, 33-49*).

One of the big challenges of molecular rheology has been to understand motions of the macromolecules in order to get an insight into the molecular structure. Several different molecular motions are found in even the simplest available linear monodisperse materials. The main and well-known relaxations are the glass transition at short times and chain reptation at long times. However, two other processes occur in between, which are weaker and thus harder to characterize -contour length fluctuations and the monomeric reequilibration relaxation. Only reptation and fluctuations are sensitive to architecture, as long as architectures with chain ends are involved. Rings have a totally different behavior.

The resolution of the various relaxations is affected by polydispersity. It is, nevertheless, possible to obtain a molar mass independent spectrum for linear metallocene catalyzed PE with $M_w/M_n=2$, from which long-chain branched (LCB) polymers deviate, as LCBs introduce additional relaxation mechanisms with a longer relaxation time.

Spectra, therefore, present a powerful toolbox to analyze architecture-dependent molecular relaxations and also their temperature dependence in a clearer fashion than conventional rheological plots.

Tuesday 4:50 Hall of Ideas G SM13

Effect of sparse long-chain branching on the step-strain behavior in a series of well-defined HDPEs

Donald G. Baird, Christopher D. McGrady, and Christopher W. Seay
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The effect of sparse long chain branching, LCB, on the shear step-strain relaxation modulus is analyzed using a series of eight well-characterized, high-density polyethylene (HDPE) resins. The motivation for this work is in assessing the ability of step-strain flows to provide specific information about a material's branching architecture. Fundamental to this goal is proving the validity of relaxation moduli data at times shorter than the onset of time-strain separability. Strains of 1% to 1250% are imposed on materials with LCB content ranging from zero to 3.33 LCB per 10,000 carbon atoms. All materials are observed to obey time-strain separation beyond some characteristic time, t_k. The presence of LCB is observed to increase the value of t_k relative to the linear resin. Furthermore, the amount of LCB content is seen to correlate positively with increasing t_k. The behavior of the relaxation modulus at times shorter than tk is investigated by an analysis of the enhancement seen in the linear relaxation modulus, $G^0(t)$, as a function of strain and LCB content. This enhancement is seen to 1) increase with increasing strain in all resins, 2) be significantly larger in the sparsely-branched HDPE resins relative to the linear HDPE resin, and 3) increase in magnitude with increasing LCB content. The shape and smoothness of the damping function is investigated to rule out the presence of wall-slip and material rupture during testing. The finite rise time to impose the desired strain is carefully monitored and compared to the Rouse relaxation time of the linear HDPE resins studied. Sparse LCB is found to increase the magnitude of the relaxation modulus at short times relative to the linear resin. It is shown that these differences are due to variations in the material architecture, specifically LCB content, and not because of mechanical anomalies.

Tuesday 5:15 Hall of Ideas G SM14

Parameter-free predictions of the linear rheology of commercial ethene/α-olefin copolymers with and without long-chain branching

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We derive a method of obtaining all three key "tube" model parameters, namely the plateau modulus GN0, the entanglement molecular weight, Me, and the frictional equilibration time τe, from the molecular weight per backbone bond of polyethylene copolymers of ethylene with longer comonomers, ranging from C4 (butylene) to C26 (hexacosene). The molecular weight per backbone bond is easily calculated from the co-monomer composition. The plateau modulus is obtained from a correlation by Fetters et al.[2002], and the entanglement molecular weight is obtained from this using the standard tube-model formula. The equilibration time is obtained from a remarkable finding by Stadler et al. [2008] that the zero-shear viscosity of linear ethene/α-olefin copolymers is independent of co-monomer type and content, over a wide range of /α-olefin co-monomers. From this observation, and the values of GN0 and Me, using the tube theory, we construct a method to obtain τe from the co-monomer type and content. We show that these a priori values of the tube model parameters, when used in a general model (the "Hierarchical Model") for predicting linear rheology, yield accurate predictions for a wide range of polydisperse copolymers. We finally design a series of mixtures of commercial copolymers with long chain branching (LCB), with those without LCB, and measure their rheological behavior. Our predictions of the linear rheology of these using the "Hierarchical model" are in good agreement with our measurements. These results show that a priori predictions of linear rheology of complex commercial polyolefin copolymers is now possible.

Tuesday 5:40 Hall of Ideas G SM15

Computational models for predicting the linear rheology of branched polymer melts

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We present a detailed investigation of the similarities and differences between the Hierarchical [1,2] and "BOB" (or branch-on-branch) [3] models, for predicting the linear rheology of general mixtures of polydisperse branched polymers. These two models are based on a similar tube-theory framework, but differ in their numerical implementation and details in relaxation mechanisms. We examine the effects of these differences on the predictions of the linear viscoelastic properties of a set of polymer materials for which we could find suitable rheological data in the literature all at the same, or nearly the same, temperature for several different architectures and molecular weights. We confirm the success of these two models in quantitatively predicting the linear rheology for a certain range of branched polymer melts, and also point out the remaining open questions that need to be resolved in future work. An updated version of the Hierarchical model, which shows improved computational efficiency and refined relaxation mechanisms, is also introduced.

[1] R. G. Larson, Macromolecules **34**, 4556 (2001).
[2] S. J. Park, S. Shanbhag, and R. G. Larson, Rheol. Acta **44**, 319 (2005).
[3] C. Das, N. J. Inkson, D. J. Read, M. A. Kelmanson and T. C. B. McLeish, J. Rheol. **50**, 207 (2006).

Symposium EB
Emulsions, Blends and Multiphase Systems

Organizers: Michael Loewenberg and Rekha Rao

Tuesday 1:30 Meeting Rooms OP EB1

Dynamics of polyisoprene-poly(p-tert-butyl styrene) diblock copolymer in disordered state

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Linear viscoelastic and dielectric behavior was examined for a diblock copolymer composed of cis-polyisoprene (PI) and poly(p-tert-butyl styrene) (PtBS) blocks of the molecular weights MPI = 53K and MPtBS = 42K. These blocks were miscible and the copolymer was in the disordered state at temperatures examined, 20 = T/°C = 120. (LCST-type phase separation occurs only at inaccessibly high T > 250°C.) PI has the type-A dipole parallel along the chain backbone while PtBS does not. Thus, the dielectric response at low frequencies exclusively detected the global motion of the PI block. The dielectric data of the PI block exhibited prominent thermo-rheological complexity. Since the PI and PtBS blocks behaved as the fast and slow blocks at low T while these blocks exhibited equally fast motion at high T, this complexity was related partly to the dynamic frictional heterogeneity for the PI block resulting from this motional difference of the blocks. However, it turned out that the complexity was more importantly related to the connectivity between the PI and PtBS blocks: The PI block would essentially behave as a tethered chains at low T (where the slow PtBS block effectively anchored the PI block) while the two blocks would behave as portions of a free linear chain at high T (where this anchoring effect vanished), and this change in the motional mode of the PI block should have dominated the thermo-rheological complexity of the PI block. In the iso-relaxation-time state for the Rouse segment defined with respect to bulk PI, the dielectric data for the copolymer were compared with those of bulk linear/star PI. Good agreement seen between the copolymer at low T and star PI and between the copolymer at high T and linear PI lent support to the above molecular picture. The viscoelastic behavior of the copolymer was in accord to this behavior of PI block.

Tuesday 1:55 Meeting Rooms OP EB2

Coupling of component dynamics in miscible polymer blends

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Dynamic heterogeneity, and the resulting failure of time-temperature superposition (tTS), is widely observed for miscible blends of two polymers with a large difference between their glass transition temperatures. It is attributable to the fact that each component senses its own effective local concentration and glass transition temperature, as described for example by the self-concentration model. However, the presence of stronger interactions such as hydrogen bonding can potentially couple the relaxation of the two components, leading to a restoration of tTS. To quantify the effects of hydrogen bonding on the viscoelastic response, blends of styrene-co-vinyl phenol (PSVPh) and poly(vinyl methyl ether) (PVME) were explored in detail. The amount of hydrogen bonding was modulated by varying the vinyl phenol content in the PSVPh copolymer, and tTS was attempted for the linear viscoelastic data obtained. As expected, tTS failure was observed for PS/PVME blends, whereas tTS was successful for PVPh/PVME, despite the fact that the difference in component glass transition temperatures was greatly increased in the latter system. tTS was obeyed for blends of PVME and a PSVPh copolymer with 50 mol % vinyl phenol units, but not for one with only 10% phenol units. By utilizing established models for the extent of hydrogen bonding in these systems, it is possible to extract the size of a control volume, whereby one hydrogen bond per control volume is sufficient to couple the component dynamics. In accordance with expectation based on the self-concentration model, this volume corresponds approximately to the Kuhn length cubed.

Tuesday 2:20 Meeting Rooms OP EB3

Shear and extensional rheology of nylon 6 nanocomposites based on polyacrylic nanoparticles

Estefania Huitrón-Rattinger[1], Angel Romo-Uribe[1], and Carlos A. Cruz-Ramos[2]
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The incorporation of nanoparticles into polymeric materials can lead to dramatic improvements in polymer properties. These enhancements have been shown to apply to a wide range of thermoplastics and a few thermoset systems. We have incorporated polyacrylic nanoparticles into a commercial Nylon 6 by melt extrusion at a concentration of 3 wt%. The microstructure, thermal properties and shear and extensional rheological behavior were investigated. Although the polymer nanoparticles did not influence the melting temperature, the decomposition temperatures were increased. Moreover, the degree of crystallinity and crystal size were reduced relative to the neat polymer. The shear rheological properties showed that the nanoparticles induced a predominantly elastic behavior, as measured by the mechanical damping, in an otherwise viscous melt.

On the other hand, extensional rheometry demonstrated that the nanoparticles induced strain hardening. Incorporation of maleic anhidride into the polymer nanoparticles enhanced the strain hardening behavior in the nanocomposites.

Tuesday 2:45 Meeting Rooms OP EB4

Rheological behavior of thermoplastic polyurethane/layered silicate nanocomposites

Tannaz Ebrahimi and Hossein Nazockdast
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We have studied the roll of anisometric organoclay plettlets on microphase separation and morphological development of Thermoplastic Polyurethane (TPU) by using.93 linear and nonlinear rheological approach. The results of the isothermal frequency sweep tests at elevated temperatures performed on the organoclay containing samples were found not to be reproducible due to side reactions. Monitoring the time evolution of storage modulus during annealing process at different temperatures showed that the chemical functionality of organoclay modifier has a strong influence on the extent of side reactions and morphology development. This was evidenced by the results of in- situ FTIR, H1NMR spectroscopy and GPC. Thus the master curves were constructed using the time-temperature superposition principle at temperatures below 170oC. As expected a breakdown of TTS at low frequency range was observed at lower temperatures for the samples which was intensified for organoclay containing samples. This could be explained in terms of interfacial enhancing effect of organoclay on the extent and the rate of morphology development of the samples. An attempt was also made to predict the nonlinear viscoelastic behaviour of the samples by using K-BKZ equation and the experimentally measured linear stress relaxation results. The linear relaxation modulus and damping functions were simulated by curve fitting into Maxwell and Osaki model respectively. The results showed that Wagner model, derived from the K-BKZ constitutive equation, could successfully be used to simulate the start up of shear flow test especially at lower shear rates. However the Wagner model failed to predict the nonlinear behaviour at high shear rates in particular for nanocomposites samples. This could be attributed to changing of microstructure of percolated layered silicates at high steady shear rates which may not necessarily accrue during step-strain relaxation tests. This can also be due to the concentration fluctuation of TPU matrix in measurement temperature.

Tuesday 3:10 Meeting Rooms OP EB5

Rheological properties of natural fibre/polymer composites

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In this work, the shear and uniaxial elongational rheology in the melt state of polypropylene (PP) blended with hemp fibres was investigated. The parameters studied were hemp concentration (0-30% by weight) and the addition of a coupling agent: maleic anhydride polypropylene (MAPP) (0-0.6% by weight). The shear rheological data reveals that fibre content mainly influences the low shear rate properties like yield stress and zero-shear-viscosity. On the other hand, the addition of a coupling agent mainly influences intermediate to high shear rate parameters like relaxation time and power-law index. From uniaxial elongational results, a strain softening behaviour of the composites was observed with increasing consistency and decreasing strain at break as fibre concentration increases. MAPP addition was shown to improve the fibre-polymer adhesion, but at the same time produces a plasticizing effect.

Tuesday 4:00 Meeting Rooms OP EB6

Rheo-SALS study of shear induced phase separation (SIPS) in aqueous solutions of cationic surfactant and salt

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Cationic surfactants in the presence of salt can self - assemble into long, flexible chains, known as "thread" or "worm like micelles" (WLM) that may or may not branch and form viscoelastic networks. Recent studies elucidating the formation of shear banding, i.e., the splitting of a viscometric flow into bands of different local shear rates, show important differences in the underlying microstructure and mechanism of shear banding. In the present study, we investigate further the nonlinear shear rheology of branched, cationic wormlike micellar surfactant solutions with in situ small angle light scattering (SALS): specifically near the miscibility gap of 40mM Erucyl bis(hydroxyethyl) methylammonium chloride (EHAC) and sodium salicylate (NaSal). We employ a new rheo-SALS instrument (TA instruments) developed in our group at the University of Delaware to identify shear-induced phase separation as the existence of a butterfly SALS pattern under flow. Isotropic solutions of a high NaSal concentration (200-800mM), show shear-banding that manifests rheologically as a stress plateau between 25 to 45°C. Interestingly, this stress plateau is observed to be very weakly dependent on the temperature, but the critical shear rates vary systematically with temperature. The SALS pattern in flow-vorticity plane show no scattering below the critical shear rate and a "butterfly" pattern with enhanced scattering in the flow direction. This is indicative of a shear induced phase separation (SIPS) with large structures aligned along the vorticity direction. The morphology characterization and rheology are used along with the phase behavior to understand the mechanism of shear-banding as shear-induced phase separation.

Tuesday 4:25 Meeting Rooms OP EB7

Nonlinear dynamics of coiling and buckling in viscoelastic jets

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Free surface continuous jets of non-Newtonian fluids, although relevant for many industrial processes like bottle filling, remain poorly understood in terms of fundamental fluid dynamics. Instability in viscous jets leads to regular periodic coiling of the jet, which exhibits a non-trivial frequency dependence with the height of the fall. Here we examine free surface non-Newtonian jets impacting on a surface and present a systematic study of the effect of viscoelasticity on the dynamics of continuous jets of worm-like micellar surfactant solutions of varying viscosities and elasticities. We use two different model fluids (Sodium Lauryl Ether Sulphate (SLES) and Cetyl Pyridinum Chloride (CPyCl)), which span a wide range of viscosities and viscoelastic relaxation times. We systematically vary the height of the drop and the flow rate in order to study the effects of varying geometric and kinematic parameters. We examine these different dynamical regimes in terms of scaling variables, which depend on the geometry (dimensionless height), kinematics (dimensionless flow rate), and the fluid properties (elasto-gravity number) and present a "state diagram" of the dynamics of the jet in terms of these dimensionless variables. We observe that for fluids with higher elastic relaxation times (CPyCl), folding is the preferred mode. In contrast, for low elasticity fluids (SLES) we observe complex nonlinear dynamics consisting of coiling, folding, and irregular meandering as the height of the fall increases. Beyond this regime, the jet dynamics smoothly crosses over to exhibit the "leaping shampoo" or the Kaye effect. Upon increasing the flow rate to very high values, the "leaping shampoo" state disappears and is replaced by a pronounced mounding or "heaping". A subsequent increase in the flow rate results in finger-like protrusions to emerge out of the mound and climb up towards the nozzle. This novel transition is currently under investigation and remains a theoretical challenge.

Tuesday 4:50 Meeting Rooms OP EB8

Piling up of high speed, yield stress fluid jets: Experimentally observed flow regimes

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Piling up of a non-Newtonian jet occurs during many industrial processes. Flow regimes observed as non-Newtonian jets pile up are experimentally examined and summarized in this effort. Novel flow visualizations of experiments are shown where industrially relevant fluids impact a fluid surface and pile up. We show distinct flow characteristics and flow regimes that occur when a fluid with an apparent yield stress strikes a surface of the same fluid. We also show observed flow features for viscoelastic jets and jets of wormlike micelle solutions. We show attempts to correlate effects of jet diameter, jet velocity, and fluid rheological properties. Finally, we show how well computational fluids dynamics simulations using a Generalized Newtonian Fluid with various viscosity models are able to retrodict experimental results.

Tuesday 5:15 Meeting Rooms OP EB9

Measurements of viscoplastic fluid flow through an axisymmetric sudden contraction with particle image velocimetry

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In this work, we carry out an experimental investigation of viscoplastic flow through an axisymmetric sudden contraction in different flow regimes. The working fluid (aqueous solution of Carbopol) is modelled as a generalized Newtonian fluid with a Herschel-Bulkey viscosity function. The experiments are conducted for laminar and turbulent flow regimes with Reynolds number (Re') ranged between 500 and 8000. In addition, the flow of Newtonian fluid in the same contraction is studied for comparison. The Particle Image Velocimetry technique (PIV) is used to obtain two-dimensional velocity vectors at the geometry vertical center plane. The focus of this work is to investigate the flow kinematics upstream of the contraction plane and Reynolds number's influence in the formation of vortex zone in the corner contraction, rigid static zones and rigid move zones (commonly called Plug-flow zones). The experimental setup is designed to provide turbulent and laminar flow at different flow rates. The experimental system is a closed loop composed of series of PVC pipes, a bypass, a return line, a test section, temperature and pressure sensors, a variable-speed AC motor-driven and other devices. The flow rate is monitored by a Coriolis mass flowmeter and capacitor transducers measure the pressure difference through the contraction. A National Instruments board captures both signals, which are treated in Lab View software. The test section is built of transparent Plexiglas, and consists of inlet and outlet pipes, attached as to provide a ß =2/1 contraction ratio. The fluid tested is pumped from the reservoir with a positive-displacement pump through a 25,4mm inner diameter smooth plexiglass to the test section. In order to minimize optical distortions produces by the curvature of the pipe and refractive index, is proposed a rectangular Plexiglas pipe box filled with glycerol that encloses the contraction. The results show good agreement with others previous works, indicating the reliability of experimental procedure.

Tuesday 5:40 Meeting Rooms OP EB10

Rheological properties of metallocene-catalyzed ethylene copolymers and morphology control of their blends with polypropylene

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With the development of metallocene catalysts technology, a new generation of ethylene a-olefin copolymers with fairly controlled co-monomer compositions and also narrow distributions of molecular weight have been commercially produced. These copolymers are widely used as the toughening compound in thermoplastic olefin (TPO) blends and the rheological behavior of these copolymers as well as morphological aspects of the TPOs based on these elastomers have gained a great interest. In this study, rheological properties of a series of ethylene-octene copolymers (with co-monomer compositions ranging between 0 and 38 wt%) and morphology evolution of their blends with polypropylene have been investigated. Thermo-rheological measurements showed that the copolymers of low level of octene content are slightly long-chain branched, though extensional measurement (using a SER geometry) showed that this level of branching does not result in a pronounced difference in the melt strength of these elastomers. However, using a Palierne emulsion model, it was found that the increase in the octene content improves the interfacial miscibility between the polypropylene and the copolymers, and this can result in a finer droplet-matrix morphology. Transient morphology obtained at high shear rate showed that even when the Capillary number is large, flow-induced coalescence plays a major role in the morphology evolution of these blends. A series of random copolymers was used as surface modifiers to prevent the coalescence and control the morphology. These formulations were compared to a blend which was compatibilized with a di-block copolymer synthesized in a grafting reaction, and the impact of the compatibilizers on the transient rheological/morphological properties in shear and elongational flow was also investigated.

Symposium GG
Gels, Glasses and Jammed Systems

Organizers: Corey O'Hern and Subramanian Ramakrishnan

Tuesday 1:30 Hall of Ideas J GG1

Thermoreversible gel formation and aging in concentrated nanoparticle suspensions

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We report a combined x-ray photon correlation spectroscopy (XPCS) and rheometry study of the evolution of concentrated suspensions of nanometer-scale colloids undergoing gelation and aging. 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. At high temperatures, decalin is a good solvent for the chains, which form a solvated brush that stabilizes the colloids. At low temperature, the solvent quality is poor, leading to a weak, temperature-dependent, short-range attraction between the colloids that drives a reversible gel transition. Following a quench through this transition, the shear modulus grows at a rate that depends strongly on temperature. The intermediate scattering function measured with XPCS displays two features, a plateau value that provides information about constrained local dynamics in the gel and a terminal relaxation time that provides information about relaxation of residual stress. From the wave-vector dependence of the plateau value, a localization length can be extracted. At lower colloidal volume fraction, the relationship between the localization length and the shear modulus agrees quantitatively with the prediction of Chen and Schweitzer based on a simplified mode coupling theory [1], but deviations from the prediction are observed at early times for higher volume fraction.

[1] Y.-L. Chen and K. S. Schweitzer, J. Chem. Phys. 120, 7212 (2004).

Tuesday 1:55 Hall of Ideas J GG2

Aging of soft colloidal suspensions studied by macro- and micro-rheology

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Soft colloidal suspensions at high concentrations, form glasses, which show aging behavior. The mechanical relaxation processes in these materials slow down with their age and equilibrium is never reached. This has not only consequences for practical materials like cosmethic creams and pastes but, from a fundamental point of view, it has also influence on the dynamical behavior of these materials, which is not well understood. We studied both the macro- and micro- rheology of soft thermosensitive microgel particle suspensions that can be tuned continuously and reversibly between the glassy state at low and the liquid state at high temperature. In the glassy state, the rheological properties (G', G", and J) of the suspensions depend strongly on their age [1]. They can be described quantitatively by the soft glassy rheology (SGR) model. The underlying mechanism for the aging is the increase of the structural relaxation time t_s as the system ages. To test for micro-rheological properties we determined the mean square displacement (MSD) of probe particles, embedded in the system. The MSD values were obtained from particle tracking using a Confocal Scanning Laser Microscope. This technique provides not only the MSD values but also the displacement distributions and the time evolution of single particle displacements, which are indicative for heterogeneity of the suspension.

[1] Eko H. Purnomo, Dirk van den Ende, Siva Vanapalli and Frieder Mugele; Phys. Rev. Lett. 101, 238301: 1-4 (2008)

Tuesday 2:20 Hall of Ideas J GG3

Dynamics of internal stresses and scaling of strain recovery in aging colloidal gels

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On cessation of flow, dilute suspensions of carbon black particles undergo rapid gelation and display instantaneous residual or internal stresses which relax slowly with time. We monitor the evolution of these stresses (under zero strain) and find a weak power law decay, $\sigma_i{\sim}t_w^{\alpha}$ over 5 decades of time where α˜0.07. The system exhibits aging, with the elastic modulus scaling as a weak power law of elapsed time, $G'{\sim}t^{\beta}$, with β˜α. Imposition of zero stress conditions after waiting time t_w, at internal stress $\sigma_i(t_w)$, results in strain recovery as the system relaxes without the zero strain constraint. Older systems exhibit less recovery than younger ones. Remarkably, strain recoveries at different t_w can be shifted to construct a single master curve in which the magnitude of the recovery is shifted vertically according to $\sigma_i(t_w)^{-1}$ and horizontally simply with elapsed time. The scaling of the strain recovery with internal stress suggests that the internal stress state is characteristic of the age of the system and of the manner in which the system will continue to evolve. This result has important implications for our understanding of glassy behavior in soft materials.

Tuesday 2:45 Hall of Ideas J GG4

Effect of interparticle attractions on the shear thickening phase boundary

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We investigate the effect of interparticle attractions on shear thickening in suspensions. We find thresholds where increasing the yield stress due to attractions first increases the onset stress of shear thickening then eliminates shear thickening. For example, 100 micron glass spheres with a hydrophobic coating cluster in water due to interparticle attractions which jam the system, preventing shear thickening because the yield stress exceeds the shear thickening stress range. When surfactant is added, the yield stress is reduced and shear thickening is recovered. We quantify and show the generality of these stress thresholds by tuning attractive yield stresses due to electrorheological and magnetorheological effects, as well as for geometric, non-attractive yield stresses due to approaching the jamming transition by increasing particle packing fraction.

Tuesday 3:10 Hall of Ideas J GG5

Re-entrant state behavior in an anisotropic colloid system

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Upon increasing the volume fraction of colloidal particles in a suspension, the system will undergo a state transition from an ergodic fluid state where particles are free to diffuse throughout the suspension to a nonergodic state where particles are trapped by their neighbors. The most commonly reported value for this glass transition volume fraction (ϕ_g) is 0.58, which is for spheres interacting with so-called hard core repulsions. Recent theoretical and experimental work has shown that it is possible to maintain the fluid state at even higher particle densities either by making the particles weakly attractive or by altering the particle shape.

The work described in this paper will demonstrate an experimental system in which both weak attractions and anisotropic particle shape are combined to reach a maximum glass transition volume fraction of 0.62, well in excess of the so called hard sphere value.

Using seeded emulsion polymerization (with or without divinyl benzene crosslinker), polystyrene particles are synthesized with a tunable particle shape. In addition, the particle interaction potentials are varied from soft repulsions to near hard conditions to weak attractions by coating the particles with a monolayer of nonionic surfactant and varying the ionic strength of the solvent. The shape of the interaction potential is determined by the degree of screening of electrostatic forces which is a function of ionic strength and a constant van der Waals attractive force.

The results of this work demonstrate three experimental "firsts" in the field of colloids. 1) Confirmation of an increase in the glass transition volume fraction for moderately anisotropic homonuclear dicolloids compared to spheres as predicted by theory. 2) A "van der Waals" system the exhibits re-entrant state behavior. 3) A system of anisotropically shaped particles that exhibit re-entrant state behavior.

Tuesday 4:00 Hall of Ideas J GG6

Aging dynamics of a flow-quenched colloidal glass

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Glassy dynamics are displayed in colloidal systems although many features of the glass transition as commonly encountered in polymer and molecular glasses are not conserved. In particular, an effective cooling rate has not been well established experimentally for colloidal glasses. Given the thermalizing effect of shear flow in these systems, a natural question is whether the flow cessation rate is a determinant of the aging response and whether it may parameterize the system's departure from equilibrium. We investigate the aging behavior of a repulsive colloidal glass and follow the dynamics of internal stresses immediately after the flow arrest as a function of the rate of arrest. We find striking parallels between the stress relaxation and the aging of the system, both dependent on the flow arrest rate. Our results point to this flow "quench" rate as an explicit mechanical variable that characterizes the departure from equilibrium. Slower quenches produce more slowly aging glasses with smaller internal stresses at short times which relax at long times by smaller extents. This implies a frustrated approach to an ideal stress-free state that succinctly reflects the frustrated nature of glassy dynamics.

Tuesday 4:25 Hall of Ideas J GG7

Aging of colloidal suspensions of thermosensitive particles

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We use a concentrated suspension of thermosensitive particles as an example of colloidal systems which have been claimed to be good models for glass-forming systems and to form an amorphous, glass-like structure. Using multispeckle, diffusing wave spectroscopy we monitor the aging of the dynamics in shear melting and in temperature jump experiments. The results are consistent with aging in conventional colloidal glasses subjected to shear melting treatments. Our results in temperature jumps, where the thermoresponsive particles change size and, therefore, volume concentration, are the first to show aging in such conditions. Interestingly, in both cases the relaxation times follow a power law in the aging time but we find that the aging exponents are different for two cases with temperature quenching giving rise to much higher aging exponents. We are also investigating whether the system exhibits asymmetry of approach behavior as already found in molecular and polymeric glasses; we find that although the up-jump and down-jump in temperature (volume fraction) of the colloid results in different (asymmetry) aging behavior, the nature of asymmetry is not the same as in conventional glass formers. We also find that this colloidal system does not exhibit the viscoelastic memory effect known to occur in molecular glass formers.

Tuesday 4:50 Hall of Ideas J GG8

Photogelling colloidal dispersions based on light-activated assembly of nanoparticles

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Photorheological (PR) fluids, i.e., fluids whose rheology can be tuned by light, have been a recent focus for our laboratory. We are interested in low-cost approaches to PR fluids using molecules or materials that are readily available. Toward this end, we report a new concept for such fluids based on light-activated assembly of nanoparticles into a physical network (gel). Our system consists of disk-like nanoparticles of laponite along with a surfactant stabilizer (Pluronic F127) and the photoacid generator (PAG), diphenyliodonium-2-carboxylate monohydrate. Initially, the nanoparticles are sterically stabilized by the surfactant, and the result is a stable, low-viscosity dispersion. Upon UV irradiation, the PAG gets photolyzed, lowering the pH by 3 units. In turn, the stabilizing surfactant is displaced from the negatively charged faces of the nanoparticle disks while the edges of the disks become positively charged. The particles are thereby induced to assemble into a three-dimensional "house-of-cards" network that extends through the sample volume. The net result is a light-induced sol to gel transition, i.e., from a low, water-like viscosity to an infinite viscosity and yield stress. The yield stress of the photogel is sufficiently high to support the weight of small objects. The gel can be converted back to a sol by increasing either the pH or the surfactant content.

Tuesday 5:15 Hall of Ideas J GG9

Thermoreversible gels composed of monodispersed rod-like particles: Rheology and light scattering

Naveen K. Reddy[1], Zhenkun Zhang[1], Jan Vermant[1], Pavlik Lettinga[2], and Jan Dhont[2]
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In the present work we present a study of the rheological and structural properties of model thermoreversible rodlike particles. The aim is to evaluate the effect of shape and structure on the rheological properties of gels. to this end thermoreversible gels composed of model rod like particle (fd-virus). The fd-virus is a monodisperse particle with 880 nm length, 6.6 nm in diameter and it is typically negatively charged (10 e/nm) at neutral pH. Thermoreversible gels of fd-virus are obtained by grafting thermoreversible poly(N-isopropylarcylamide) (PNIPAM) onto the virus. The length of the double layer and the length of the PNIPAM layer provide us with two independent control parameters for the range of the electrostatic and hydrophobic interactions, respectively. As a consequence, the temperature, at which gelation occurs and the associated structure, is shown to depend on ionic strength. Results of rheological characterization in the linear viscoelastic regime for fd-PNIPAM in two different ionic strengths will be presented as a function of volume fraction. Oscillatory measurements, creep ringing, yield stress measurements and selected non linear measurements will be presented. The rheological measurements will be evaluated against measurements of the gel structure by light scattering, SAXS and cryoSEM.

Tuesday 5:40 Hall of Ideas J GG10

Thermoreversible gels from triblock copolymers and ionic liquids

Timothy P. Lodge[1], Yu Lei[1], and Atsushi Noro[2]

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An "ion gel" consists of a polymer network swollen with an ionic liquid. As ionic liquids combine several attractive properties, include negligible vapor pressure, high ionic conductivity, and exceptional thermal and chemical stability, they are being incorporated as key components of materials systems for numerous applications, including actuators, gas separation membranes, fuel cells, batteries, gate dielectrics, supercapacitors, and sensors. By utilizing a modest amount of polymer to produce an ion gel, the high mobility of the constituent ions can be maintained within a soft elastic solid. We have produced ion gels by utilizing self-assembly of various ABA triblock copolymers, such as poly(styrene-b-ethylene oxide-b-styrene) (SOS), poly(styrene-b-methyl methacrylate-b-styrene) (SMS), and poly(N-isopropyl acrylamide-b-ethylene oxide-b-N-isopropyl acrylamide) (NON), where the mid-block is soluble in the ionic liquid and the end-blocks are not. Of particular interest are thermoreversible gels, where the A blocks self-assemble on cooling, thereby allowing liquid state processing at higher temperatures. The NON gels are such a system, as PNIPAM exhibits a UCST phase diagram in certain ionic liquids. Another strategy is to utilize A blocks that can form hydrogen bonds with a third polymeric component, C, as a "crosslinker". Examples of this include poly(2-vinylpyridine-b-ethyl acrylate-b-2-vinylpyridine) (VEAV) and poly(2-vinylpyridine-b-ethylene oxide-b-2-vinylpyridine) (VOV), crosslinked with poly(hydroxystyrene) (HS). The rheological properties of these ion gels are fascinating, as the strong temperature dependence of the hydrogen bonding, and the significant temperature dependence of the ionic liquid viscosity, provide access to an unprecedent wide range of reduced frequency (15 decades).

Symposium VS
Viscoplasticity and Soft Solids

Organizers: John De Bruyn and Ian Frigaard

Tuesday 1:30 Meeting Rooms QR VS1

Modeling the thixotropic behavior of viscoplastic liquids

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A novel approach for modeling the mechanical behavior of thixotropic viscoplastic liquids is presented. Non-monotonic flow curves, stress overshoot during microstructure breakdown flows at constant shear rate, and viscosity bifurcation are some of the common aspects of viscoplastic liquids that are predicted by the new model. It involves two evolution equations, one for the stress and the other for the structure parameter. Simple ideas are employed to describe the microstructure, and, as a result, a model with a clear physical basis is obtained. In addition to the flow curve, which by construction is exactly predicted, it is shown that the model is able to predict correctly the behavior observed in the usual rheometric transient flows, among which: abrupt changes in shear rate (microstructure buildup or breakdown experiments); abrupt changes in shear stress (viscosity bifurcation experiments); and oscillatory tests (amplitude sweep and frequency sweep). The model is frame-indifferent and applicable to complex flows.

Tuesday 1:55 Meeting Rooms QR VS2

Large amplitude oscillatory shear of pseudoplastic and elastoviscoplastic materials

Randy H. Ewoldt and Gareth H. McKinley

Hatsopoulos Microfluids Laboratory, Dept. of Mech. Engr., Massachusetts Institute of Technology, Cambridge, MA 02139, United States

We explore the utility of strain-controlled large amplitude oscillatory shear (LAOS) deformation for identifying and characterizing apparent yield stress responses in elastoviscoplastic materials. Our approach emphasizes the visual representation of the LAOS stress response within the framework of 3D parametric response curves (i.e. Lissajous-Bowditch curves with strain, strain-rate, and stress as the coordinate axes), in conjunction with quantitative analysis of the corresponding cyclic behavior. This approach enables us to explore how the material properties characterizing the yielding response depend on both strain amplitude and frequency of deformation. Canonical constitutive models are used to illustrate the characteristic features of pseudoplastic and elastoplastic material responses under large amplitude oscillatory shear. Experimental results are presented for a pseudoplastic shear-thinning solution and an elastoviscoplastic material. We also propose several quantitative measures for aiding the identification of plastic behavior. The first measure, which we refer to as the perfect plastic dissipation ratio, compares the dissipated energy of the material response to that of a perfect plastic response. Additional quantitative analysis involves concepts from the differential geometry of closed space-curves and the computation of measures such as the curvature and torsion for the 3D parametric response curves, which we examine in the context of identifying critical transitions such as a yield stress or yield strain. The LAOS test protocols outlined and the associated material measures provide a rheological fingerprint of the yielding behavior of viscoplastic soft solids that can be compactly represented within the domain of a Pipkin diagram defined by the amplitude and timescale of deformation.

Tuesday 2:20 Meeting Rooms QR VS3

Predicting slump lengths in the setting of annular plugs and chemical packers

Ian A. Frigaard[1] and Gideon A. Ngwa[2]

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In conventional well construction, primary cementing involves displacement flows in narrow eccentric annuli and cement plugs are set in tubular geometries. However, in an increasing number of scenarios plugs are being set in annular geometries, whether as cement plugs or simply in the form of chemical packers. The generic reason for setting of such plugs is to hydraulically isolate different regions of a wellbore (or hole). An interesting practical problem in such situations is to predict the rheological properties that are necessary in order to prevent the annular plug fluid from flowing under the action of buoyancy, or indeed to predict how far the plug material may flow for given rheological properties. The answers to these questions provide valuable information for operational design. Mechanically, the above questions result in a Hele-Shaw type flow of two visco-plastic fluids in an enclosed annulus, driven only by the density difference between the fluids. We present estimates of the necessary yield stresses to resist motion, showing that the estimates are necessary as well as sufficient, by comparison with numerical solutions using an augmented Lagrangian method. Finally, when these conditions are not met, we predict the final shape of the interface when a long slumping flow occurs.

Tuesday 2:45 Meeting Rooms QR VS4

Finite perturbations of static wall layers in the Couette flow of a Bingham fluid

Ian A. Frigaard[1], Cherif Nouar[2], and Monica Naccache[3]

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Couette flows of a yield stress fluid permit axisymmetric solutions in which the fluid rotates rigidly in a static layer attached to the outer cylinder. It is interesting that the existence of the static layer on the outer cylinder does not apparently retard the occurrence of Taylor vortices, as was shown by Landry et al (2006), using a linear stability analysis. We explore nonlinear stability effects on these basic flows, using both numerical simulations and a weakly nonlinear stability analysis. The latter is significantly complicated by the singularity at the yield surface. We present a range of analytical and numerical results.

Tuesday 3:10 Meeting Rooms QR VS5

Different experimental methods to characterize the non-linear behavior of gels

Joerg Laeuger, Patrick Heyer, and Heiko Stettin

Anton Paar Germany GmbH, Ostfildern, Germany

Various techniques have been proposed to characterize the cross over from linear to non-linear behavior and the behavior in the non-linear regime. A widely used method is the so-called Fourier Transform rheology in which not just the base wave but also the higher harmonics are measured in oscillatory testing. The rising of higher harmonics is associated with the onset of non-linear behavior. However, no clear physical meaning can be attributed to the higher harmonics itself. A new theoretical framework as proposed recently by Ewoldt et al. (J. Rheol. 52(6), 1427-1458, 2008) provides a quantitative analyzes of Lissajous figures during Large Amplitude Oscillatory Shear (LAOS). Intra- and intercycle nonlinearities, strain-stiffening and -softening, and shear-thinning and -thickening are described and can be distinguished. A similar method is the so-called cyclic loading testing where a triangle function in strain is applied. In this case the rheometer is operated in an rotational mode, the strain triangle function is applied as a succession of shear rate steps in clockwise and counter clockwise directions. The resulting shear stress is plotted as a function of the applied strain similar to the Lissajous plots of the oscillatory testing. A somewhat different approach is the technique of Strain-Rate Frequency Superposition (SRFS) as described by Wyss et al. (Phys. Rev. Lett. 98, 238303, 2007). Here the strain rate is kept constant during frequency sweeps by increasing the strain parallel to decreasing the frequency. The observed scaling suggests that the linear and the nonlinear viscoelastic response of soft materials can be described within a single physical picture. The aim of this paper is to present results from these different techniques on a typical gel samples. FT-Rheology and quantitative LAOS analyzes during SRFS testing reveal further insight into the the cross over from linear to non-linear behavior.

Tuesday 4:00 Meeting Rooms QR VS6

In-situ velocimetric measurements and studying the rheological behavior of wax-oil systems for the purpose of flow assurance

Christopher J. Dimitriou[1], Gareth H. McKinley[1], Alberto Montesi[2], and Rama Venkatesan[3]

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Flow Assurance is a critical problem in the production of remote, deep-water crude oil. It entails the development and adoption of strategies that allow for continuous flow of oil in the presence of precipitates such as waxes, hydrates and asphaltenes. In this talk we present experimental data that elucidates the rheological properties of model oil-wax systems that closely mimic the behavior of waxy crude oil (e.g. temperature dependent rheology, dependence on thermal and shear history). Velocimetric and birefringence imaging techniques are used in order to probe the microstructure of wax-oil gels that form at temperatures below the wax appearance temperature (T_{wa}). The wax appearance temperature is the temperature below which wax solids first begin to precipitate out of the solution. This can be readily detected by identifying the temperature at which the viscosity-temperature dependence of the sample departs from Arrhenius like behavior. The data from the imaging techniques, together with the corresponding rheological data, show that the structure formed by wax crystallites can be irreversibly broken down by high stresses, and may then reform only through a subsequent heating and cooling "rejuvenation" step to temperatures below T_{wa}.

In addition we present a discussion on modes of failure (yielding) in the wax-oil systems. Specifically, the use of direct velocimetric measurements in the rheometer allows us to determine whether a sample yields in its bulk, or whether interfacial slip occurs whereby low shear rates appear in the bulk with high shear rate regions near the wall. This is of practical importance in Flow Assurance because in many instances one is interested in determining the most efficient way to restart the flow of a gelled pipeline.

Tuesday 4:25 Meeting Rooms QR VS7

Dimensionless durometry

Adam W. Mix[1] and A. Jeffrey Giacomin[2]

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Durometry is the measurement of the hardness of materials, such as, plastics, metals, wood, and rubber. Many different hardness scales and indentor geometries have been standardized for durometry. The deformation caused by indentation into a solid is governed by linear elastic mechanics, and we relate the Young's modulus to standardized hardness scale reading. We adimensionalized these indentation mechanics, and uncovered a normalized Young's modulus, Ψ, and the dimensionless hardness, H. We then discovered a new dimensionless indentor stiffness which we call mechanical indentability, Mi , which can be used for classifying hardness scales. The result of our analysis allows practitioners to determine the Young's modulus from measured hardness. Further, our results can be used to convert between different hardness scales, not only between hardness scales of the same indentor geometry, but also between those differing in geometry.

Tuesday 4:50 Meeting Rooms QR VS8

Nanoindentation characterization of viscoplasticity

Joseph E. Jakes[1], Charles R. Frihart[1], and Donald S. Stone[2]

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Nanoindentation has the potential to characterize the rheology of solids at sub-micron length scales, making it a unique tool for probing local variations in properties within microscopic structures. It is difficult, however, to relate results made with nanoindentation to measurements made using more conventional experiments. Deformation in polymers is pressure sensitive, and for this reason the hydrostatic pressure beneath the indenter will affect the measured properties. Therefore, the effect of the hydrostatic pressure must be taken into consideration when comparing nanoindentation results to conventional testing results. To investigate this effect, we developed an experimental technique, called broadband nanoindentation creep or BNC, to assess the hardness-strain rate properties across 5 decades of strain rate (10^{-4}-10 s^{-1}). We compare BNC-derived stress-strain rate data with literature uniaxial data for poly-methylmethacrylate and propose a method for estimating the pressure activation volume for plastic deformation based on BNC.

Tuesday 5:15 Meeting Rooms QR VS9

Wrinkling and strain softening in thin films of single-wall carbon nanotubes on elastic substrates

Erik K. Hobbie, Daneesh O. Simien, Jun Young Chung, Jeffrey A. Fagan, Jan Obrzut, Steven D. Hudson, and Christopher M. Stafford

NIST, Gaithersburg, MD, United States

Thin films of purified single-wall carbon nanotubes (SWNTs) are uniaxially compressed by depositing them on prestretched substrates of polydimethylsiloxane (PDMS). After the strain is released, the mechanical response of the films is characterized through a combination of optical microscopy, light scattering, atomic force microscopy, electron microscopy and in-plane impedance spectroscopy. Above a well-defined critical concentration or thickness, films composed of SWNTs of varied length (100 nm to1000 nm) exhibit nonlinear mechanical response under compressive strains between 2 % and 20 %, wrinkling and yielding in a strongly strain-softening fashion. Associated with this softening is a fracture of the SWNT film at a periodicity commensurate with the wrinkling wavelength. The fracture pattern exhibits extended spatial correlation along the direction normal to the strain, which causes a substantial reduction in film conductivity. We discuss the practical implications of this instability and model the nonlinear response.

Tuesday 5:40 Meeting Rooms QR VS10

The affect of prestrain on non-linear modulus characterization of filled elastomers

Christopher c. White, Don l. Hunston, and Kar Tean Tan

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Although filled elastomers represent a commercially important class of materials, there are challenges to effectively characterize their rheological properties. The materials are complex exhibiting both non-linear viscoelastic behavior and the Mullins effect. To effectively minimize the impact of the Mullins effect, a prestrain is often imposed on the material prior to characterization. The focus of this presentation is understanding how presence or absence of the prestrain and the level of the prestrain affects the characterization results. Stress relaxation was selected as the characterization method with the strain levels less than the maximum prestrain. For a model material, it was found that increasing the prestrain simply shifted the stress relaxation curves down without changing the time dependence or strain level dependence. Over the range of conditions tested, time-strain master curves could be constructed, and the data could be fit with a Mooney-Rivin type equation. When no prestrain was imposed before characterization, however, the behavior was more complex. Moreover, in tests where the strain level in the characterization was higher than that in the prestrain, the results were the same as for characterization test with no prestrain. Some of the results could be explained by a model that assumes the strength of the temporary junctions in the material that are broken during the prestrain depends on both strain level and time.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Lecture Hall PL3

Spatio-temporal chaos and negative shear rate fluctuations in sheared soft matter systems

Ajay K. Sood
Department of Physics, Indian Institute of Science, Bangalore, India

Soft matter under shear is a paradigm for fascinating non-equilibrium physics. My talk will showcase this by taking examples from our work related to spatio-temporal rheochaos in sheared gels [1,2,3] and anomalously large fluctuations in shear rate (or viscosity), showing positive and negative values, at a constant shear stress in a jammed state [4]. In the last few years, rheochaos - irregular time dependence in the stress at constant shear rate or vice versa, has been established to be a flow instability that occurs practically at zero Reynolds number in systems who flow curve is intrinsically non-monotonic or multivalued. Our experiments using time-dependence of stress and polarized light scattering establish the spatially inhomogeneous orientational dynamics for shear thinning worm-like micellar gels en route to rheochaos. The dynamics of 2D Taylor like velocity rolls, stacked along the vorticity direction, is correlated with the stress fluctuations. Our experiments on the stress induced jammed state have revealed [4] that the shear rate at a fixed shear stress in a micellar hexagonal phase exhibits large fluctuations, including several negative values. The probability distribution functions (PDF) of the global power flux to the system derived from the shear rate fluctuations are Gaussian or non-Gaussian, depending on the external drive (applied stress) on the system. In both cases, the PDF is consistent with the Gallavotti-Cohen steady state fluctuation theorem. In the last part of my talk, I will present our rheology experiments on two-dimensional films at liquid-liquid interface, revealing shear banding and jamming transitions [5].

[1]. R. Bandyopadhyay, G. Basappa and A.K. Sood, Phys. Rev. Lett. 84, 2022 (2000). [2]. R. Ganapathy and A.K. Sood, Phys. Rev. Lett. 96, 108 301 (2006). [3]. R. Ganapathy, S. Mazumdar and A.K. Sood, Phys. Rev. E 78, 021 504 (2008). [4]. S. Mazumdar and A.K. Sood, Phys. Rev. Lett. 101, 078 301 (2008). [5]. R. Krishnaswamy, S. Mazumdar, V. Rathee and A.K. Sood (2009).

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Wednesday 9:45 Lecture Hall SC31

Shear induced ageing and slow dynamics in hard sphere glasses

Pierre Ballesta, Nick N. Koumakis, and George Petekidis
IESL, FORTH, Heraklion, Greece

Hard sphere glasses, like many frustrated soft matter systems exhibit ultraslow dynamics which slow down with aging time revealing a departure from ideal glass behavior where a frozen out of cage motion is expected. Such behavior is related with dynamic heterogeneities, i.e. regions with enhanced cooperative particle motions that have been monitored both by dynamic light scattering and microscopy experiments. At the same time, whereas hard sphere glasses under shear exhibit a yield stress behavior, when lower stresses are applied they reveal a non-ideal solid-like response as for exampled is manifested by a slow long lasting creep with progressively decreasing shear rate. Here we follow such creeping behavior as a function of applied stress, below and near the yield stress and show that a complicated interplay between ageing and shear takes place. Moreover we simultaneously perform multispeckle diffusive wave spectroscopy measurements to investigate the progress of microscopic particle dynamics under shear as a function of waiting time and relate them with the mechanical response of the sample.

Wednesday 10:10 Lecture Hall SC32

Charge effects on microstructure, rheology and order-disorder transitions for sheared colloidal crystals and suspensions

Amit Kumar and Jonathan L. Higdon
Chemical and Biomolecular Engineering, University of Illinois, Urbana, IL 61801, United States

Fast Lubrication Dynamics simulations are employed to study the phase behavior and rheology of charged colloidal suspensions at a volume fraction of 0.33. For a given screening length of the repulsive interaction, there exists a range of surface potential for which both the ordered and disordered metastable states exist. This range is found to have a strong dependence on shear rate having a maximum width around Pe = 0.5. Phase diagrams are presented showing ordered, disordered and metastable regions as a function of surface potential and Pe. The presence of both ordered and disordered metastable states allows for the characterization of both the branches of viscosity as a function of shear rate. In contrast to common experience, the disordered branch may exhibit a lower viscosity than the ordered branch at low shear rates ($Pe < 0.05$). This result is attributed to the smaller short time diffusivity in the ordered state, which leads to a greater distortion of the microstructure and hence greater stress at the same shear rate. At the higher shear rates, ordered states with close packed planes aligned in the flow-vorticity direction minimize the distortive effect of shear, and hence show lower viscosity than the corresponding disordered states. This anomalous behavior is consistent with the stress reduction results and hysteresis loops reported in experiments on charge stabilized suspensions by Chen, Ackerson and Zukoski. The simulations provide detailed microstructures which confirm and refine comments by Chen et al regarding the structure in the ordered and disordered states.

Wednesday 10:35 Lecture Hall SC33

Step strain induced crystallization in concentrated colloidal suspensions

Laura T. Shereda, Ronald G. Larson, and Michael J. Solomon
Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

Under shear flow, concentrated colloidal suspensions show shear thinning and shear thickening rheological behaviors that are of fundamental interest to colloidal crystal formation under shear flow (Krishnamurthy, 2005, J. Rheol). Early work by Ackerson et al (Ackerson, 1991, Physica A) established stress and strain criteria for colloidal crystal formation under shear flow; however, direct visualization of the microstructural changes that result in the disorder to order transition (Cerda, 2008, Phys Rev E) could clarify how this transition occurs. Here we seek to better understand the formation of colloidal crystals under shear flow by studying the structural changes that occur upon shearing using confocal microscopy. Because of an indication from recent work (Shereda, 2008, Phys Rev Lett) that crystallization occurs given only small strains in the non-uniform flow of spin coating, we study the structural response to a step strain deformation. A parallel plate assembly with a stationary bottom plate and a top plate moved by a stepper motor was loaded with suspensions of charge stabilized, refractive index matched poly(12-hydroxystearic acid) stabilized poly(methyl methacrylate) colloids of size about one micron. These particles were suspended in the viscous solvent dioctyl phthalate (colloid volume fraction ~ 0.35) and small quantities of photopolymer. Samples were imaged both before and after a step strain was imposed. Strain amplitudes varying from 1 to 10 were applied upon which samples were immediately immobilized by exposure to UV light. Particle centroids were located in 3D by means of quantitative image processing. Local crystallinity was determined by application of local bond order parameter criteria (ten Wolde, 1996, J Chem Phys). We quantify the effect of strain and shear rate on local crystallinity on an axis perpendicular to the substrate in simple shear flow. Additionally, we compare these data to the stress and strain criteria for crystal formation developed in our previous spin coating study.

Wednesday 11:00 Lecture Hall SC34

Contact and stress anisotropies in the start-up flow of colloidal suspensions

Nicos S. Martys[1], Didier Lootens[2], William L. George[1], and Pascal Hebraud[3]
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Spatio-temporal correlations in start-up flows of attractive colloids are explored by numerical simulations as a function of their volume fraction and shear rate. The suspension is first allowed to flocculate for a given time, then the stress necessary to induce its flow is computed. We find that, at low volume fractions, the stress is a universal function of the strain. On the contrary, at high volume fractions, this scaling behavior is no longer observed and a supplementary stress becomes necessary to induce flow. To better understand the physical origin of the supplementary stress, we examine the creation, disruption and orientation of contacts between the particles, and the corresponding contribution to stress as a function of strain. Our simulations show that the onset of flow is dominated by the creation of contacts between the particles at low shear rates, and by their disruption at high shear rates. However, neither the evolution of the number of contacts with strain, nor their orientation can fully account for the non-scaling behavior of the stress at high volume fractions. At small strains, the relative importance of forcing in the compression quadrant increases with volume fraction, and with flocculation time. This mechanism of stress transmission through the compression quadrant is not accounted for in the usual description of yield stress, which considers the breaking of bonds oriented in the extension quadrant.

Wednesday 11:25 Lecture Hall SC35

Study of the flow dynamics of solid and liquid phases of a colloidal suspension in a microcapillary using NMR

Einar O. Fridjonsson[1], Sarah L. Codd[2], and Joseph D. Seymour[1]
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In this study the dynamics of solid and liquid phases of hard sphere poly methylmethacrylate (PMMA) colloidal suspensions ($a = 1.25 \pm 0.46\mu m$, $\phi = 0.22$) were studied in a 252μm ID capillary for $a/L > 2000$ using dynamic NMR. Both phases were detected simultaneously by using oil (Hexadecane) filled colloidal particles allowing spectrally resolved Pulsed Gradient Spin Echo (PGSE) techniques to probe the motion of each phase at $Pe_B = 410$ and 820 over a time scale of $\Delta = 25ms$ to 500ms. This allowed for the determination of the concentration profiles of the colloidal phase across the capillary which were fitted to the theoretical model of Morris and coworkers [1]. Also, by probing the displacement scale dependence of both phases simultaneously by varying the displacement observation time Δ allows for the observation of microstructural details in the colloidal system due to the low thermal motion of the colloids relative to the suspending fluid ($D_c/D_s \sim 10^{-4}$), allowing the hydrodynamic dispersion of water in the colloidal suspension to probe this microstructure.

[1] M. Frank, D. Anderson, E.R. Weeks and J.F. Morris, *Particle migration in pressure driven flow of a Brownian suspension*, Journal of Fluid Mechanics, 493 (2003), 363-378.

Symposium SM
Polymer Solutions and Melts

Organizers: Ralph Colby, Jules J. Magda and Lynden Archer

Wednesday 9:45 Meeting Rooms KLOP SM16

Extensional flow induced crystallization of poly-1-butene using a filament stretching rheometer

Manojkumar Chellamuthu[1], Deepak Arora[2], H. Henning Winter[2], and Jonathan P. Rothstein[1]
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A filament stretching rheometer with a custom-built oven is used to measure the extensional flow induced crystallization of isotactic poly1-butene as a function of strain and extension rate. The Janeschitz-Kriegel protocol is used to study the extensional flow induced crystallization of the polymer melts. All the samples are stretched and crystallized at 98^{o} C. Using Differential Scanning Calorimetry, the degree of crystallinity of the stretched samples was found to increase from 45% to 62% with the increase in extension rate from $\dot{e} = 0.01s^{-1}$ to $\dot{e} = 0.5s^{-1}$ at a fixed strain. We believe that the increase in crystallinity is due to the effective orientation and alignment of polymer molecules with increasing extension rate. No significant difference in crystallinity was observed with varying strains. The extensional flows were also found to significantly impact polymorphic transformation of the isotactic poly1-butene crystals from type II to type I. Finally, the effect of extensional flow induced crystallization was also studied for linear and branched poly-propylene.

Wednesday 10:10 Meeting Rooms KLOP SM17

Shear-induced crystallization studied by simultaneous measurement of rheology and turbidity

Jen Shueng Tiang and John M. Dealy
Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

The effect of shearing at high rates on the crystallization of isotactic polypropylene was studied in a sliding-plate rheometer in which the sample undergoes uniform shear. Nucleation and growth stages were revealed by the simultaneous measurement of the response to small-amplitude oscillatory shear and the turbidity. To make this possible, a shear stress transducer and a fiber-optic probe were mounted in the stationary plate of the rheometer. The effects of molecular weight, nucleating agent, shear rate and strain were determined. After erasing the previous thermo-mechanical history, the sample is cooled to 155.5°C and held at that temperature. A brief period of shearing at a high rate is imposed, and then small-amplitude oscillatory shear is imposed continuously to provide a rheological indication of crystallization. It had been previously demonstrated that the oscillatory shear has no effect on crystallization kinetics. The results showed that rheology responds primarily to the growth phase, while turbidity responds primarily to the nucleation phase. An increase in the molecular weight was found to hinder quiescent crystallization but accelerate nucleation under shear. The presence of a nucleating agent enhances both nucleation and growth kinetics. Shear rate and strain were found to be of equal importance in controlling the crystallization rate.

Wednesday 10:35 Meeting Rooms KLOP SM18

Structure-property evolution during crystallization of isotactic poly-1-butene: Shear rheology, DSC, optical microscopy, small angle light scattering and transmission intensity measurements

Deepak Arora[1], Manojkumar Chellamuthu[2], Jonathan P. Rothstein[2], and H. Henning Winter[3]
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Isothermal crystallization experiments were performed on isotactic poly(1-butene). Optical microscopy, DSC, SALS, and rheology, at early stages of spherulite growth, provide quantitative information about nucleation density, volume fraction of spherulites and their crystallinity, and the mechanism of connecting into a sample spanning structure. An understanding of the kinetics of nucleation helps predicting the crystal growth, in particular for early stages of crystallization. An attempt is made to connect the crystal fraction inside spherulites with the average crystallinity of the entire sample. The crystal fraction inside spherulites is very small initially but increases with time and catches up with the sample crystallinity later on. Optical microscopy near the fluid-to-solid transition suggests that the transition, as determined by rheology, is not caused by packing/jamming of spherulites but by the formation of a percolating structure. At percolation, the absolute crystallinity is about 7-8 vol%. This shows that spherulites are mostly amorphous before impingement. The effect of strain, Weissenberg number (We) and specific mechanical work on rate of crystallization (nucleation followed by growth) and on growth of anisotropy is studied for shear-induced crystallization. The samples were sheared for a finite strain at the beginning of the experiment and then crystallized without further flow (Janeschitz-Kriegl protocol). Steady shear conditions were achieved for all the experiments as the Deborah number (De) remained < 1. Spherulitic growth is observed under quiescent conditions (We = 0) and at small strains and We. Strain-effect on rate of crystallization seems to level off for very high values of strain for isotactic poly (1-butene). The strain requirements for oriented growth become less and less for higher We indicating a criterion based on specific work. We can be interpreted as the interplay between the rate of molecular relaxation and rate of producing orientation.

Wednesday 11:00 Meeting Rooms KLOP SM19

Flow induced crystallization of polylactide: Accurate determination of induction time

Yury Yuryev and Paula M. Wood-Adams
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Viscoelastic properties of polymer melts are highly sensitive to any structural changes, including molecular weight changes and the formation and growth of crystallites. We have made use of this sensitivity to study the homogeneous and flow induced crystallization of polylactide. Since this polymer is rather quickly susceptible to thermal degradation even at moderate temperatures it is essentially impossible to study homogeneous crystallization in the absence of degradation. The evolution of complex viscosity of a polylactide during simultaneous crystallization and mild thermal degradation was therefore studied. A simple empirical model is used to characterize the variation of complex viscosity due to thermal degradation and when combined with a statistical analysis of residuals to determine the induction time of homogeneous crystallization at low supercooling. This technique allows for highly accurate and repeatable measurements of induction time which then opens the possibility for studying in detail the effect of flow on this parameter. We have performed a series of experiments looking at the effect of shear rate and shearing time on the induction time. These data were then used to evaluate a flow induced crystallization model a which is based upon the independent alignment approximation of the Doi-Edwards model.

Wednesday 11:25 Meeting Rooms KLOP SM20

Simultaneous rheometry and FT-IR for the determination of molecular structures as a function of the deformation

Manfred Feustel[1], Cornelia Kuechenmeister[2], and Jint Nijman[2]
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For a comprehensive understanding of a material, usually more than just one analytical technique is required. Techniques complementing rheological measurements are for example GPC, thermal analysis, microscopy, or FT-IR spectroscopy. By combining two analytical techniques in one instrument and measuring two properties simultaneously, the amount of information gathered from one single sample is maximized.

In this paper we present the combination of a rheometer and a FT-IR spectrometer. With the Rheonaut module the HAAKE MARS rheometer can be coupled to a FT-IR spectrometer to collect rheological data and IR spectra simultaneously using a plate/plate or cone/plate measuring geometry.

The patented Rheonaut module consists of an optical unit which is fully integrated in a temperature controlled measuring geometry. Infrared data are collected using the ATR (attenuated total reflection) principle in which the sample dependent absorption of infrared light is obtained from the attenuation of the total reflection at the interface between sample and optical sensor. A pyroelectric detector made of deuterated triglycene sulfate (DTGS) is used to detect the infrared beam. Since IR light stimulates the vibrational energy of a molecule due to changes in the internuclear distance of two or more atoms, this process generates an infrared spectrum. Thus, chemical information of the sample under investigation is provided simultaneously to its rheological data.

For the investigation of polymerization reactions, the change of functional groups of reacting molecules as well as the (long time) stability of chemical structures such as the enzymatic or hydrolytic structural interruptions of biopolymers can be monitored using a single reflection sensor. The influence of different shear stresses and the resulting deformations on long-chain and complex molecules can be measured using a multiple reflection sensor.

Details of this unique new set-up as well as selected measuring results will be presented.

Symposium EB
Emulsions, Blends and Multiphase Systems

Organizers: Michael Loewenberg and Rekha Rao

Wednesday 9:45 Hall of Ideas G EB11

Numerical simulation of drop retraction after a large strain jump

Yuriko Renardy[1], Michael Renardy[1], Souad Assighaou[2], and Lazhar Benyahia[2]
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A spherical drop of one liquid suspended in another is subjected to an instantaneous initial shear. We simulate the retraction of the drop to its spherical equilibrium and compare the results with recent experiments. In agreement with the experiments, we observe a two step relaxation process.

Wednesday 10:10 Hall of Ideas G EB12

Direct numerical simulations of emulsions immersed in electric fields

Arturo Fernandez
Mechanical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, United States

Direct Numerical Simulation is used to examine the effects of electric fields on the microstructure and properties of emulsions. The response of the fluids to the electric field is described using the leaky dielectric model proposed by Taylor. A simple-shear flow is adopted in order to be able to compare our numerical results versus other results without electric fields. An electric potential difference is applied perpendicular to the sliding plates. The numerical simulations show that the response of the emulsions is governed by the competition between the electric attraction and the fluid shear. The former leads to the aggregation of the drops in chains parallel to the electric field, while the latter tries to break-up the aggregated chains. The emulsions exhibit a strong shear-thinning response with a strengthening of the normal stress differences especially at low shear rates. The significance of the electrical field strength on the bulk properties will be discussed. Also, some results concerning the effects of confinement on the rheological properties will be presented.

Wednesday 10:35 Hall of Ideas G EB13

Slender-body theory for low-viscosity drops in confined geometries

Pieter Janssen[1], Patrick D. Anderson[2], and Michael Loewenberg[3]
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A slender-body analysis is presented for low-viscosity drops in confined geometries. The dynamics of confined drops in the shear flow generated by the tangential motion of parallel rigid boundaries is explored. It is shown that the boundaries generates a disturbance flow that tends to align drops in the flow direction, away from the straining component of the flow. Drop deformation is thereby reduced. For wall separations in an intermediate range, the critical capillary number is increased by a factor of $3^{1/2}$. This result help to explain recent experimental observations of drop breakup in confined geometries.

Wednesday 11:00 Hall of Ideas G EB14

Combined effect of confinement and compatibilization on the dynamics of droplets

Anja Vananroye, Peter Van Puyvelde, and Paula Moldenaers
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Nowadays, downsizing of equipment is omnipresent in process industries, a tendency that is also emerging in the processing of blends such as in micro-mixers. In that case, the blend morphology is not only affected by the characteristics of the components and type of flow, but also by the presence of the walls. During the past years, much research has focused on the behavior of blends in confined geometries during shear flow. However, most studies were limited to systems containing Newtonian components. In real-life, additional effects such as viscoelasticity of the components and compatibilization are commonly present, which are expected to affect the morphological processes. Therefore, the effect of confinement on the behavior of compatibilized droplets is investigated here. The experiments are performed in a counterrotating plate-plate device, in which a compatibilized droplet is positioned in a Newtonian matrix. The shape and breakup behaviour of such droplets in shear flow is microscopically observed. Compatibilizer concentration, capillary number and degree of confinement are systematically varied, and the resulting behavior at a viscosity ratio close to unity is compared to the predictions of the Minale model for confined droplets. The experiments indicate that the presence of compatibilizer decreases the interfacial tension of the droplet. However, taking into account this reduction in interfacial tension, droplet deformation is slightly reduced with respect to the uncompatibilized case for all compatibilizer concentrations. It is observed that confinement increases droplet deformation in the same manner for uncompatibilized and compatibilized droplets at a viscosity ratio of unity. At this viscosity ratio, droplet breakup is more or less unaffected by the degree of confinement both in the compatibilized and in the uncompatibilized case. However, compatibilized droplets tend to break up at a higher critical capillary number, the latter is essentially independent of the amount of compatibilizer.

Wednesday 11:25 Hall of Ideas G EB15

Effect of compatibilizer concentration and volume fraction on model immiscible blends with interfacial crosslinking

Candice L. DeLeo and Sachin S. Velankar
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Reactive compatibilization - generating a compatibilizer by an interfacial chemical reaction between functional polymers in immiscible phases - is a well-established method in the polymer blend industry. Typically, an end-functional polymer in one phase reacts with a multifunctional polymer in the other phase to form a graft copolymer. In this paper we investigate reactively-compatibilized blends in which **both** reactive species are multifunctional, and thus form a crosslinked network at the interface. Experiments are conducted on a model system composed of two immiscible homopolymers, and two reactive species added to each homopolymer. We focus on varying the concentration of the reactive species (i.e. the compatibilizer concentration), and the relative volumes of the two homopolymers.

At sufficiently high amounts of compatibilizer, the blends show a droplet-matrix morphology with non-spherical drops, sometimes with wrinkled interfaces, which forms a space-spanning network of drops. It is possible that such a robust interface can be used to stabilize morphologies of highly elongated drops.

The rheological properties (creep, recovery, and dynamic oscillatory) also depend on compatibilizer concentration. At adequately high concentrations, the blends exhibit gel-like behavior and coalescence is suppressed. Upon shearing, these blends shows a large viscosity and creep recovery at short shearing times suggesting a breakdown of the network structure upon shearing. These non-Newtonian properties strongly increase with increasing compatibilizer concentration. At lower compatibilizer concentrations, the rheological properties of the blends are similar to uncompatibilzed blends studied previously. Varying the volume fraction results in a sharp increase in the viscosity and creep recovery near the phase inversion point. Interestingly, when PDMS is the majority phase, no gel-like behavior is observed, even at high compatibilizer concentrations.

Symposium GG
Gels, Glasses and Jammed Systems

Organizers: Corey O'Hern and Subramanian Ramakrishnan

Wednesday 9:45 Meeting Rooms MNQR GG11

Rheological characterization of a discotic colloidal clay at bulk and microscopic scales

Jason P. Rich[1], Gareth H. McKinley[2], and Patrick S. Doyle[1]

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Charged colloidal clays are frequently employed as rheological modifiers in a number of applications, from oil drilling fluids to consumer products. Achieving the desired performance of these materials relies upon understanding and control of the rheological properties at both microscopic and bulk scales. For example, a drilling fluid must entrain rock cuttings of various sizes and prevent their sedimentation, while in toothpaste the micro-scale texture and foaming properties are important for consumer satisfaction. As a step towards advancing applications such as these, we perform rheological measurements at both macroscopic and microscopic length scales on a dispersion of Laponite RD in water (a synthetic discotic colloidal clay). Significant rheological aging is observed, including a cross-over from viscous-dominated to elastic-dominated behavior (gelation) with age time, and an order-of-magnitude growth in the elastic modulus as the system continues to age. By comparing bulk rheology results to those from microrheology experiments, we find that the clay is a significantly more fragile gel at microscopic scales than bulk measurements would indicate. Microrheology measurements further reveal strong probe-size effects, as well as the development of a pronounced heterogeneous structure in the gelling Laponite dispersions. By considering these observations in the context of the phase behavior that arises due to clay-clay and clay-solvent charge interactions, we propose a microstructural description of the clay and address implications for applications.

Wednesday 10:10 Meeting Rooms MNQR GG12

Rheological properties of temperature sensitive composite hydrogels

Judith Meid and Walter Richtering

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Hydrogels are of high interest for technical and medical applications. Especially stimuli responsive or so called "smart" polymer gels have been studied extensively during the past decades. These gels react to external stimuli, as e.g. temperature or pH-value, by a drastic change of their volume. Poly-N-(isopropyl)-acrylamide (PNIPAM) is one of the best studied thermo sensitive polymers ever. PNIPAM hydrogels undergo a reversible phase transition temperature (VPTT) in pure water (1). The response time of hydrogels is proportional to the square of the size of the hydrogels thus the response rate of the microgels is very fast due to the micrometer size compared to millimeter sized hydrogels. It is possible to incorporate temperature responsive PNIPAM microgel in a non temperature sensitive poly-acrylamide matrix to induce the fast swelling behavior of the microgel particles into a macroscopic scaled hydrogel, a so called composite material was prepared. The temperature sensitivity of the composite material which maintains the fast responsibility of the microgels was investigates by SANS measurements (2,3). Rheology measurements demonstrated that the incorporation of the microgels changes the viscoelastic properties of the composite materials significantly. In principle a higher volume fraction of embedded microgels leads to a more rigid composite material. The volume fraction of the incorporated microgels decreases by increasing temperature and so a change of the viscoelastic properties of the whole composite network is observed. The structural behavior of the embedded microgels under shear stress can be monitored by a combination of rheological measurements and small angle neutron scattering (SANS).

1. Nayak, S.; Lyon, L. A., Angew. Chem. Int. Ed. 2005, 117, 7886-7709. 2. Soddemann, M.; Richtering, W., Progr. Colloid Polym. Sci. 2004, 129, 88-94. 3. Musch, J; Schneider, S.; Lindner, P.; Richtering, W., J. Phys. Chem. B 2008, 112, 6309-6314.

Wednesday 10:35 Meeting Rooms MNQR GG13

Characterization of sheared compressed emulsions using confocal rheology

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We have investigated the properties of a dense oil-in-water emulsion under shear stress. Measurements of the jammed emulsion were taken with a customized confocal rheometer, which is capable of acquiring three-dimensional images while simultaneously applying a precise shear stress. Images acquired deep inside the emulsion are detailed enough to determine the position and shape of individual emulsion droplets. The motion of the drops and the forces on each droplet can be calculated as a function of shear stress during continuous and oscillatory deformations. This information allows us to link the bulk rheological properties of the emulsion to local structural relaxation and the force distribution measured at the single droplet level.

Wednesday 11:00 Meeting Rooms MNQR GG14

Soft glassy rheological features of nanoscale ionic materials (NIMs)

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Nanoscale ionic materials (NIMs) are a recently discovered class of organic-inorganic hybrid materials which are able to relax to equilibrium in absence of any solvent. Linear rheology of these materials manifest classical traits of soft glasses, including a yield stress, slow dynamics and divergence of the viscosity. The frequency response of NIMs in the nonlinear shear regime reveals several heretofore unexplored features of soft glasses. In particular, we report that the dynamic response of NIMs at multiple, discrete strains can be superimposed to produce universal master curves spanning fifteen or more decades in time. This universal behavior, termed 'time strain superposition' (TSS), is analogous to time temperature superposition in many regards, including the fact that the shift factors obey a WLF-like relation. We discuss these findings using recent models for soft glasses, as well as older phenomenological models based on the free-volume concept.

Wednesday 11:25 Meeting Rooms MNQR GG15

Periodic transformation of a dense suspension into a deforming porous medium

Sandeep D. Kulkarni[1], Bloen Metzger[2], and Jeffrey F. Morris[1]
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[2]CNRS Laboratoire IUSTI, Marseille, France

We experimentally examine flow of an extremely concentrated non-Brownian suspension through an abrupt channel contraction. Without external loading, the material is able to flow smoothly as a viscous mixture, but when solid load is applied by adding weight to a piston on top of the suspension, the flow becomes intermittently either nearly jammed or smoothly flowing for particle volume fraction ϕ approximately equal to $\phi_c = 0.58$. The intermittent cycles of alternating fast and slow motion exhibit a well-defined periodicity. The phenomenon occurs for a range of contraction width, solvent viscosity and applied load. In case of these intermittent flows, we observe a consistently lower concentration in the effluent material relative to the input concentration. This self-filtration indicates that the mixture exhibits characteristics of both a porous medium and a viscous fluid.

The internal stress state of the mixture during both smooth flow and intermittent jamming is explored through systematic measurement of the liquid pressure at various points along the channel boundary, focusing on the region near the throat of the contraction. This is combined with particle tracking velocimetry. The results indicate that there is a strong correlation of the liquid pressure with the intermittency. We consider the relation of this liquid pressure to the shear induced particle pressure Π, which is strongly dependent on ϕ and shear rate [Deboeuf *et al.*, Phys. Rev. Lett. **102**, 108301 (2009)] in sheared suspensions.

Symposium FM
Non-Newtonian Fluid Mechanics and Stability

Organizers: Radhakrishna Sureshkumar and Yong Joo

Wednesday 9:45 Hall of Ideas J FM1

Inertial and elastic instabilities in shear layers

Alexander Morozov
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In Newtonian fluids, free shear layers -- 1D velocity profiles with a velocity jump across an (imaginary) interface -- are known to exhibit Kelvin-Helmholtz (KH) instability which plays a crucial role in sustaining coherent structures that organise dynamics in weakly turbulent flows. Addition of small amounts of polymer was previously shown [1] to inhibit Newtonian KH instability and was argued to be a possible explanation for the drag-reduction phenomenon.

Here we perform the linear stability analysis of a viscoelastic shear layer of Oldroyd-B and FENE-CR fluids and show that this picture is incomplete. At large values of the Reynolds number, increasing the Weissenberg number indeed results in a decrease of the most unstable eigenvalue. However, when the Reynolds number is decreased at moderate fixed Weissenberg number, the eigenvalue first decreases and then increases again. At Re = 0 and Wi > Wi_{crit}, we find a purely elastic shear layer instability. This points to a switching between inertial and purely elastic (due to the normal stresses) mechanisms of the instability.

[1] J. Azaiez and G.M. Homsy, Journal of Fluid Mech. 268, 37 (1994)

Wednesday 10:10 Hall of Ideas J FM2

Non-modal amplification of disturbances in channel flows of viscoelastic fluids: A possible route to elastic turbulence

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Non-modal amplification of disturbances in channel flows of Oldroyd-B fluids is studied from an input-output point of view by analyzing the ensemble-average energy density associated with the velocity field of the linearized governing equations. The inputs consist of spatially distributed and temporally varying body forces that are harmonic in the streamwise and spanwise directions and stochastic in the wall-normal direction and in time. Such inputs enable the use of powerful tools from linear systems theory that have recently been applied to analyze Newtonian fluid flows. It is found that the energy density increases with a decrease in viscosity ratio S (ratio of solvent viscosity to total viscosity) and increase in Reynolds number Re and elasticity number E. In most of the cases, streamwise constant perturbations are most amplified and the location of maximum energy density shifts to higher spanwise wavenumbers with an increase in Re and E and decrease in S. For streamwise constant flows with high E and finite Re, we establish that the energy density scales as $O(ERe^3)$, indicating that large velocity variances can be sustained in weakly inertial/strongly elastic stochastically driven channel flows. The underlying physical mechanism involves polymer stretching that introduces an effective lift-up of flow fluctuations similar to vortex-tilting in inertia-dominated flows. The mechanism examined here provides a possible route for a bypass transition to elastic turbulence and might be exploited to enhance mixing in microfluidic devices

Wednesday 10:35 Hall of Ideas J FM3

The effect of viscoelasticity on the probability density functions in turbulent channel flow

Gaurab Samanta[1], Kostas D. Housiadas[2], Robert A. Handler[3], and Antony N. Beris[1]
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In an effort to better understand the interactions with viscoelasticity with turbulence at the smaller scales (as opposed to the larger scales, as for example, examined through a coherent structures analysis) we present here results on higher order statistics of third (skewness factor) and fourth order (flatness factor) and the underlying probability density functions (PDF) of the velocity fluctuations and their derivatives of a viscoelastic turbulent channel flow and compared them against those for a Newtonian fluid at a friction Reynolds number 180. The velocity fields in both cases are obtained from Direct Numerical Simulations. In the viscoelastic case, the Giesekus model is used. With the presence of viscoelasticity the non-Gaussian character of the PDFs is significantly enhanced. In particular, larger in magnitude skewness factors and much longer tails are typically observed in the viscoelastic case. This indicates higher intermittency in the viscoelastic turbulent flow along with strong correlations between all scales of turbulence. The most notable differences are seen in the PDFs of the shear and spanwise velocity components in the buffer and log-law regions as well as in most of the components of the first and second order velocity derivatives. It is also found that whereas in the log-law layer the PDF of the logarithm of the pseudodissipation rate for both the Newtonian and the viscoelastic cases are almost Gaussian, in the viscous sublayer and the buffer layer significant deviations from the Gaussian shape are observed.

Wednesday 11:00 Hall of Ideas J FM4

Understanding the dynamics of viscoelastic turbulent flows and polymer drag reduction in minimal flow units

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Adding a small amount of flexible polymers into a turbulent flow can cause substantial reduction in its friction drag by influencing the fundamental dynamics of the self-sustaining turbulent structures. In this study, we isolate the essential components of the self-sustaining process by conducting direct numerical simulations (DNS) in minimal flow units (MFU) of viscoelastic turbulent flows. These MFU solutions obtained at various polymer parameters recover all key transitions in viscoelastic turbulent flows reported previously in experiments at much higher Re, including the onset of drag reduction, low degree of drag reduction (LDR), high degree of drag reduction (HDR) and maximum drag reduction (MDR). At the MDR regime, the mean velocity profile is insensitive to changing polymer parameters. The LDR-HDR transition is characterized by a sudden increase in the minimal box size of sustaining turbulence, which may correspond to a qualitative change in the self-sustaining mechanism. With these solutions, we study the effects of polymer on turbulent coherent structures and the dynamics of the self-sustaining process, based on which the mechanism behind the multistage transition scheme in viscoelastic turbulent flows can be better understood.

Wednesday 11:25 Hall of Ideas J FM5

Effect of Karhunen-Loeve optimization criterion on the reconstructed conformation field in viscoelastic turbulent channel flow

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Karhunen-Loeve (KL) method has been regularly used to decompose direct numerical simulation (DNS) generated velocity realizations of a viscoelastic turbulent channel flow, [1] into a more manageable data set. The basis set thus created is optimal in the sense that fewest number of these basis set functions could represent through a linear superposition, a particular fraction of the average kinetic energy of the set of velocity realizations. Recently, using a selected set of these basis functions, velocity and conformation fields are reconstructed, [2]. Comparison of velocity statistics shows good agreement with the corresponding DNS results. However, conformation statistics do not match well against DNS results, [2]. In order to be able to enhance our capability to properly reconstruct the conformation field, the objective function in the KL method is modified in the present work such that different physical flow measures (i.e. other than kinetic energy, such as dissipation) can be optimized. A study of the effect of using different optimization criteria in the KL method, on the reconstructed conformation fields will be presented. This is of significance for any future work for systematic evaluation of low-dimensional models for viscoelastic turbulence, of importance to applications such as drag reduction.

[1] G. Samanta, G. M. Oxberry, A. N. Beris, R. A. Handler, and K. D. Housiadas, "Time-evolution K-L analysis of coherent structures based on DNS of turbulent Newtonian and viscoelastic flows", J. turbulence, 9 (41): 1-25 (2008). [2] G. Samanta, A. N. Beris, R. A. Handler, and K. D. Housiadas, "Velocity and conformation statistics based on reduced Karhunen-Loeve projection data from DNS of viscoelastic turbulent channel flow", J. Non-Newtonian Fluid Mech., doi:10.1016/j.jnnfm.2009.02.003 (2009).

Wednesday Afternoon

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Wednesday 1:30 Lecture Hall SC36

Suspensions of bubbles in yield stress fluids

Michael Kogan[1], Julie Goyon[1], Xavier Chateau[1], Olivier Pitois[2], and Guillaume Ovarlez[1]
[1]Ur Navier, Université Paris Est, Champs sur Marne 77420, France; [2]Université Paris-Est, Laboratoire de Physique des Matériaux, Marne la Vallée, France

We studied the rheological behavior of yield stress fluids which contained known volume fractions of monodisperse air bubbles. Using a new model system, well-controlled suspensions of monodisperse bubbles in a yield stress fluid were prepared by a method that consisted of mixing a foam with a dense water in oil emulsion, both having the same continuous phase of a surfactant solution. We measured the change in the elastic modulus in the linear regime due to the addition of air bubbles to the fluid, and the change in the yield stress under the same conditions.

Two different results were found depending on the size of the bubbles. For large bubbles, as the volume fraction of air was increased, the relative elastic modulus decreased at low and moderate volume fractions, followed by an increase at high volume fractions. Surprisingly, the relative yield stress showed no change at low and moderate volume fractions, and showed a sharp increase at high volume fractions. The high volume fraction limit corresponds to the case of foamy yield stress fluids where the bubbles form a contact network, when the bubble volume fraction is higher than 60%. For small bubbles, both the yield stress and the elastic modulus of the suspension were found to increase with the bubble volume fraction.

We show that the location of the transition in the behavior corresponds to a change in the capillary number, as the location of the transition can be adjusted by a change of either the bubble size or the yield stress of the fluid. In other words, this corresponds to a transition from deformable to non-deformable bubbles. Finally, the impact of the boundary conditions at the bubble interface will be addressed by studying different surfactant solutions. A micromechanical analysis of the results will also be presented.

Wednesday 1:55 Lecture Hall SC37

Set-on-demand cement, a novel approach to cement rheology

Brian D. Figura and Robert K. Prud'homme
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In energy recovery, time is expensive: a mere day of platform downtime can cost more than $500,000. In order to minimize costs and promote more efficient energy recovery, we examine a method of achieving set-on-demand cements whose rheology and setting time can be tuned over a wide range. In this system, a set of admixtures are chosen and mixed into the cement in order to provide the desired rheological properties and setting times. We also describe advances in cement rheological methods that enable more accurate and relevant measurements.

Wednesday 2:20 Lecture Hall SC38

Suspensions of polydisperse particles in yield stress fluids

Xavier Chateau, Thai Son Vu, and Guillaume Ovarlez
Ur Navier, Université Paris Est, Champs sur Marne, France

We studied theoretically and experimentally the behavior of suspensions of polydisperse noncolloidal particles in yield stress fluids. Bidisperse suspensions have been prepared by suspending spherical beads of various sizes in an emulsion. We used rheometrical procedures that allow studying homogeneous and isotropic suspensions. We measured the elastic modulus and the yield stress of the suspensions as a function of the suspending paste mechanical properties and of the particle volume fraction. We observed that both the dimensionless elastic modulus and the dimensionless yield stress fall along master curves when these quantities are plotted as a function of the ratio of the particle volume fraction to the maximum particle volume fraction. We show that this maximum particle volume fraction can actually be predicted by using a packing model of the literature. The elastic modulus/particle concentration relationship is well fitted to a Krieger-Dougherty law. We propose a very simple law for the yield stress/particle concentration relationship, and shows that our experimental data are vey well fitted to this law. These laws are in agreement with what we observe on monodisperse suspensions. Finally, we show that it is possible to integrate the packing model to a morphologically representative pattern-based model of the suspension.

Wednesday 2:45 Lecture Hall SC39

Rheological variability of Savannah River Site (SRS) high level waste (HLW) sludges

John M. Pareizs, Scott H. Reboul, and Erich K. Hansen
Savannah River National Laboratory, Aiken, SC 29808, United States

The Department of Energy's Savannah River Site (SRS) in Aiken SC produced nuclear materials from the mid 1950s to the late 1980s. One of the by-products of this production is caustic high level waste (HLW) sludge currently stored in underground tanks. There are two main types of sludges, HM (high aluminum) and PUREX (high iron). The rheological properties of this sludge at various stages of processing must be either measured or predicted to develop strategies to transfer the sludge using centrifugal slurry pumps to other waste tanks or to SRS's waste stabilization facility, the Defense Waste Processing Facility. Transfer distances range between 1000 and 5000 feet. This presentation compares the rheological properties of the two SRS sludge types. Because of major differences in chemical composition, mineralogy, and solid phase morphology, variations in the sludge rheology can be extreme. SRS sludges are non-Newtonian. The rheological data are analyzed as a Bingham Plastic fluid. The Bingham Plastic parameters for the two main sludge types are presented as functions of weight percent undissolved solids, weight percent total solids, and mean particle size. This presentation also describes the methodology and equipment used to measure the properties of these radioactive materials.

Wednesday 3:10 Lecture Hall SC40

Study of shear induced particles sedimentation and bubbles rising in yield stress fluids through MRI

Julie Goyon[1], François Bertrand[1], Olivier Pitois[2], and Guillaume Ovarlez[1]
[1]Université Paris Est, Laboratoire Navier, Champs sur marne 77420, France; [2]Université Paris-Est, Laboratoire de Physique des Matériaux, Marne la Vallée, France

We study experimentally the behaviour of suspensions of non colloidal particles and bubbles in yield stress fluids. The samples we study are stable at rest: the gravity does not induce motion of the objects. We use a controlled shear rate Couette cell rheometer to shear the samples. Thanks to a Magnetic Resonance Imaging (MRI) technique, we can have access to the local concentration as function of the position in the gap. We observe that at rest the non colloidal particles, whose density were not matched with the one of the yield stress fluid, are motionless. This is because the shear stress induced in the material by the gravitational force exerted by the object is much lower than its yield stress. On the other hand, when sheared, we observe that the particles fall down in all conditions: the particles do not meet any yield resistance to sedimentation. We study the sedimentation velocity for suspension of non colloidal particles in an emulsion as function of the local shear rate, the yield stress of the fluid, the size and the volume fraction of the particles. At low shear rates, we find that the sedimentation velocity is basically the one of a sphere falling in a Newtonian fluid of viscosity equal to the apparent viscosity of the sheared yield stress fluid. At higher shear rates, some discrepancies with this basic analysis are observed. In the case of suspensions of bubbles, as the volume fraction of bubbles in the yield stress fluid increases, one can have a yield stress foam, which is stable in time i.e. does not drain. We find that drainage can be induced by shearing the sample in a Couette cell. We investigate the drainage velocity by MRI techniques as function of the bubbles size, the local shear rate and the yield stress of the fluid. The drainage velocity is found to be very fast. We find that drainage leads to a very dry and stable yield stress foam.

Symposium IC
Industrial and Complex Systems Rheology

Organizers: Matt Liberatore and Jim Oberhauser

Wednesday 4:00 Lecture Hall IC1

Fluid mechanics of pretreated corn stover slurries in process equipment

Bradley J. Niesner[1], Vinay Raman[1], Jinyoung Baek[1], Jonathan J. Stickel[2], Clare J. Dibble[2], and Robert J. Fisher[1]
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The conversion of biomass, specifically ligno-cellulosic biomass, into fuels and chemicals has recently gained national attention as an alternative to the use of fossil fuels. Current biochemical conversion processes in research and development typically use high concentrations of water and hence low concentrations of biomass solids. Increasing the concentration of the biomass solids has a large potential to reduce the cost of conversion. The detailed rheological behavior of dilute-acid pretreated corn stover slurries was previously investigated for a range of concentrations and extents of enzymatic hydrolysis, where it was found that the slurries have a significant yield stress and are shear thinning. Data from these rheology experiments were used to select an appropriate generalized Newtonian constitutive model and to determine model coefficients. The selected model included the concentration of solids as an independent variable so that a single set of coefficients could be used for a range of slurry concentrations. Using computational fluid dynamics with the selected constitutive model, simulations of the slurry flow were made for relevant process geometries, specifically a straight pipe, a horizontal reaction vessel, and a vertical reaction vessel. The simulations show that the yielding behavior results in plug flow in the pipe and dead zones in the vertical mixer that depend on the concentration of the slurry. Power requirements for mixing and pumping were calculated from the simulations. The pipe flow simulations were verified by measuring the flow rate and pressure drop of pretreated corn stover slurries flowing in a straight pipe.

Wednesday 4:25 Lecture Hall IC2

Investigating the changing rheology of high-solids biomass slurries during enzymatic saccharification

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Although exceptionally difficult to transport due to their high viscosities, processing of high-solids slurries will be necessary for the economic operation of lignocellulosic biorefineries. In this work, we examine the changing rheology of high-solids pretreated corn stover (PCS) slurries prior to and during enzymatic saccharification. Prior to saccharification, PCS slurries with fractions of insoluble solids (FIS) ranging from 5-20% (w/w) were found to exhibit rheological properties characteristic of soft solids, including the presence of an apparent yield stress and shear-thinning behavior. Notably, yield stress and viscosity were found to be strong functions of PCS concentration, decreasing roughly ten-fold for each 5% decrease in FIS. During saccharification, FIS drops as glucose and other sugars are liberated by the hydrolysis reaction and move into the liquid phase. As a result, the viscosity and yield stress of PCS slurries within a saccharification reactor diminish rapidly with conversion, by more than an order of magnitude within a few hours. The rheological properties of unsaccharified and saccharified stover agree well when compared at equivalent volume fractions of insoluble particles. Because the rapid drop in yield stress with conversion is an important design parameter, indicating when a suspension becomes "pourable" or "pumpable", this work will help the process designer identify an optimal residence time during saccharification. In this light, we also present preliminary results suggesting that viscosity-modification / flow-assurance additives may significantly reduce the yield stress and viscosity of PCS slurries, ensuring their downstream processability.

Wednesday 4:50 Lecture Hall IC3

Rheology of model invert emulsion drilling fluids containing nanoparticles

Sushant Agarwal[1], Lynn M. Walker[2], Dennis C. Prieve[2], Phuoc Tran[3], Yee Soong[3], and Rakesh K. Gupta[1]
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Oil-based muds (OBM) are widely used as drilling fluids in high-temperature, high-pressure (HTHP) drilling operations in the oil and natural gas industry. OBMs are generally water-in-oil invert emulsions containing many additives such as clays, emulsifiers and surfactants to manage their rheology and stability. In this work, we show the effect of adding hydrophilic and hydrophobic nanoparticles to model invert emulsions in terms of their gel behavior and plastic viscosity. These model fluids consist of organically modified montmorillonite clay dispersed in water-in-polydecene invert emulsions. It is found that by adding only a small volume fraction of hydrophobic nanosilica particles, significant increase in the gel strength can be obtained without causing a significant increase in plastic viscosity. In addition, we also show the effect of high temperature and high pressure aging on the rheology of these model drilling fluids.

Wednesday 5:15 Lecture Hall IC4

Rheological characterization of unconventional oil resources

John R. Dorgan[1], Jyoti Bechura[2], and Michael Batzle[2]
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Remarks will be made on the relationship between rheology and seismology used in resource exploration and production. Subsequently, rheological characterization of two unconventional petroleum resources are discussed. As heavier oils become of increasing interest, there is a need to relate the viscoelastic properties of complicated geologic composite structures to their seismic properties. Data on a heavy oil containing sandstone as well as an oil bearing shale are presented. Sectioning of the aniosotropic shale and the measurement of samples of various orientation enables the determination of the matric of elastic coefficients for the anisotropic rock. The characterization of complex viscoelastic behavior of these important two phase systems is an area where rheologists and geophysicists can work across interdisciplinary lines to provide a knowledge base which can help ensure energy supplies into the foreseeable future.

Wednesday 5:40 Lecture Hall IC5

Temperature and pressure effects on suspension rheology

Jason Maxey
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It has been noted that, for Newtonian liquids, pressure effects on rheological properties only become significant at pressures around 1,000 atmospheres; this is not the case, however, when the fluid in question is a complex suspension - e.g. invert-emulsion drilling fluids. An invert-emulsion drilling fluid (IEDF) generally consists of an oil external phase, emulsified brine internal phase, various organophilic clay and polymer viscosifiers, and up to 80%wt (45%v) of barium sulfate (barite) to control density. The resulting system is elasto-visco-plastic, with strong shear-thinning, time-dependant, and yield characteristics. The normal operating environment for a drilling fluid can range in temperature from 4°C to upwards of 250°C in pressures that range from atmospheric (at the surface) to over 40,000 psi. At these pressures, rheological changes are observed from compressibility of the oil external phase, emulsion droplets, and effects on organophilic clay interactions. In this work, rheological studies of a series of IEDF have been conducted. Shear and oscillatory tests have been performed in the range of 0 - 2000 psi and 32°F - 250°F. The flow profiles, yield stress, thixotropy, and viscoelasticity are examined compared to results from traditional measurement

devices. In addition, the behavior of the base oil and viscosified emulsion, without weight material, are examined and compared to the whole mud properties.

Symposium SM
Polymer Solutions and Melts

Organizers: Ralph Colby, Jules J. Magda and Lynden Archer

Wednesday 1:30 Meeting Rooms KLOP SM21

An experimental study of slip flow in capillaries and semi-hyperbolically converging dies

Prajakta A. Kamerkar[1] and Brian J. Edwards[2]
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Slip velocity is measured in straight-walled capillary dies and semi-hyperbolically converging dies (SCHDs) in three industrial polymer melts, with and without the presence of a viscosity reducing stearic acid additive. Data taken in shear flow through capillary dies indicated a substantial increase in the slip velocity caused by the addition of the stearic acid. An extended Mooney analysis was developed to allow quantification of the slip velocity in the SHCDs. Data taken from these dies showed much less of an increase in the slip velocity of the polymer/additive system relevant to the neat polymer. One possible explanation of this observation is that the magnitude of the slip velocity is directly related to the degree of orientation within the flowing polymeric material.

Wednesday 1:55 Meeting Rooms KLOP SM22

Understanding the origin of flow inhomogeneity in entangled fluids by direct visualization of individual DNAs during flow

Pouyan E. Boukany[1], Orin L. Hemminger[1], Shi-Qing Wang[2], and L J. Lee[1]
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[2]Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, United States

No-slip boundary condition and uniform deformation are the most important assumptions in studies of fluid rheology. Violation of these convenient premises in entangled liquids has been noticed in the literature for quite some time [1-2]. Using spin-disk confocal microscopy, we investigate dynamic responses of individual DNA chains in entangled DNAs from simple shear to contraction and channel flow. Several new experimental findings will be presented to further elucidate the origins of flow inhomogeneity from wall slip to shear banding.

[1] "Observations of wall slip and shear banding in an entangled DNA solution", P. E. Boukany, Y. T. Hu and S. Q. Wang, Macromolecules 41, 2644 (2008). [2] "Exploring the transition from wall slip to bulk shearing banding well-entangled DNA solutions during shear", P. E. Boukany, and S. Q. Wang, Soft Matter 5, 780 (2009).

Wednesday 2:20 Meeting Rooms KLOP SM23

Influence of viscosity and elasticity on the diameter distribution of meltblown polymer fibers

Dawud H. Tan, Chunfeng Zhou, Satish Kumar, Christopher W. Macosko, Frank Bates, and Christopher J. Ellison
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Melt blowing is a commercial processing technique that produces a significant portion of nonwoven fiber products. It utilizes two streams of hot air to stretch an extruded polymer strand into a fiber, typically 2 μm in diameter. We have demonstrated the capability of producing defect-free fibers with an average diameter of roughly 400 nm using a lab-scale melt blowing device designed after typical commercial equipment[1]. A systematic study of melt blowing of Boger liquids with increasing relaxation times, obtained by mixing low and a high molecular weight polystyrenes, will be presented. Slender-jet modeling (1D) and finite element simulations (2D and axisymmetric) of the experimental result will also be presented. Results from these parallel studies demonstrate the impact of melt viscosity and elasticity on the average diameter and diameter distribution of melt blown fibers. In particular, the model analysis predicts that the polymer melts with higher elasticity yield thicker fibers due to the strong elastic tensile stress. This agrees qualitatively with the experimental result.

[1] C.J. Ellison et al., *Polymer* **48**, 3306-3316, 2007

Wednesday 2:45 Meeting Rooms KLOP SM24

Stress relaxation in polymer melts following equibiaxial step strain

Teresita Kashyap and David C. Venerus
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We report measurements of the stress relaxation modulus for two polymer melts following step equibiaxial strain using the Lubricated Squeezing Flow (LSF) method. The LSF method is validated for Hencky strains up to approximately 1.5 by demonstrating results do not depend on lubricant viscosity or sample geometry. Measurements were performed on a linear polystyrene melt (PS158K), and on a branched polyethylene melt (LDPE 1810H). These two melts have been previously characterized in both step shear strain flows and constant strain rate

equibiaxial elongational flows. Time-strain factorability was observed for both materials. These data were used to determine the damping function, which is compared to data from the literature. In addition, we compare measured damping functions with predictions from the Tube Model and the Pom-Pom Model. We find reasonably good agreement between data on the linear polymers and the Tube Model predictions, while significant differences are found between the Pom-Pom Model and data for the branched polymer.

Wednesday 3:10 Meeting Rooms KLOP SM25

A continuous lubricated squeezing flow technique to study the rheological behavior of polymer melts in equibiaxial elongational flow

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Despite its technological significance, the rheological behavior of polymer melts in equibiaxial elongational flow is largely unexplored and, consequently, is inadequately understood. The simple reason for this is that methods for generating equibiaxial elongational deformations are either very complicated or not reliable. The most widely accepted method for generating rheologically controlled, equibiaxial elongational flow is the rotating clamp method, or MultiAxiale Dehnung (MAD), developed by Meissner. However, the extremely complicated nature of the MAD rheometer has resulted in a relatively limited set of experimental data. A promising method that has been used with some success is known as Lubricated Squeezing Flow (LSF), where a polymer melt is squeezed between lubricated solid surfaces. Unfortunately, uncontrolled lubricant thinning limits the LSF technique to rather modest strain levels. Previously, we have shown by direct comparison of data obtained with the LSF and MAD techniques, that the LSF technique fails at Hencky strains of less than one. In our laboratory, we have been developing a modified LSF technique that involves the continuous injection of lubricant through porous metal plates, which we refer to as Continuous LSF (CLSF). In our most recent work, we have used a combination of experimental tests and a hydrodynamic model of CLSF to significantly improve the CLSF setup and methods. We report measurements of transient equibiaxial elongational viscosity obtained using the CLSF technique on a linear polystyrene melt and a branched polyethylene melt. Good agreement is observed between data obtained using the CLSF technique and data from the MAD rheometer.

Wednesday 4:00 Meeting Rooms KLOP SM26

Anisotropic thermal conduction in polymers subjected to uniaxial elongation

David C. Venerus, Jay D. Schieber, Sahil Gupta, and Nakhaie Shahab

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Polymer processing flows involve a strong coupling of mechanical and thermal effects that have a significant impact on the final properties of the material. Simple molecular arguments suggest that Fourier's law must be generalized to allow for a tensorial thermal conductivity in polymers subjected to deformation. In our laboratory we have developed a novel, optical method to obtain quantitative measurements of anisotropic thermal diffusivity in polymers subjected to deformations. In this paper we report measurements of anisotropic thermal diffusivity, stress and birefringence in both molten and solid polymers in uniaxial elongation. One set of data consists of time-dependent measurements the anisotropic thermal diffusivity on a polyisobutylene melt following the cessation of constant strain rate flow. A second set of data involves anisotropic thermal diffusivity measurements made on solid polystyrene samples that have either been quenched immediately after deformation in the molten state, or that are under stress in an unoriented state. These data are used to test the stress-thermal rule, and to study the molecular origins of anisotropic thermal transport in polymers.

Wednesday 4:25 Meeting Rooms KLOP SM27

What is chain disentanglement during or after external deformation?

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In quiescence and over time scales much shorter than the longest molecular relaxation time associated with thermal fluctuations, chains of sufficient length are unable to move past one another and are effectively trapped in their spatial positions, leading to effects often associated with the phrase "chain entanglement". Any deformation that is not sufficiently large and fast may not force the chains to pass around one another. In this linear response regime, entanglements are effective, and the deformation is elastic. Conversely, startup continual deformation could cause an entangled polymeric liquid to yield at high rates. Flow is a dynamic state where chains are mutually sliding past one another on the experimental time (i.e., the reciprocal shear rate). Thus, in the state of flow, the system loses chain entanglement, i.e., disentanglement takes place. Loss of chain entanglement could also occur during shear cessation from a large stepwise deformation when residual elastic retraction forces allow the chains to pass around one another. Protocols of parallel oscillatory shear superposition and sequential startup shear are applied to look for more evidence of the structural rearrangements due to external deformation. This presentation reports new information that depicts the state of partial chain disentanglement.

Wednesday 4:50 Meeting Rooms KLOP SM28

Brittle failure of entangled melts in rapid uniaxial extension

Yangyang Wang and Shi-Qing Wang

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We have performed rapid uniaxial extension on a series of entangled polymer melts and solutions to explore the transition from ductile yielding to brittle failure above glass transition temperature. These samples show an engineering stress maximum and subsequently fail in a ductile way when the Hencky strain rate is below a critical value that depends on the Rouse relaxation rate, where the force maximum scales linearly with the Hencky strain at the maximum. This yielding and ensuing failure can be understood in terms of inter-chain sliding (i.e., chain disentanglement) leading to non-uniform stretching. At Rouse Weissenberg numbers higher than a critical value, the engineering stress rises sharply with the Hencky strain until the point of brittle fracture. There is evidence that the strain-hardening stems from non-Gaussian response of the elastic entanglement network, whose onset appears to be independent of the entanglement spacing. Data from different melts and solutions appear to collapse onto a master curve upon normalization of the engineering stress by the elastic plateau modulus and the strain rate by the Rouse relaxation time. (The provision of the SBR sample by Dr. Xiaorong Wang from Bridgestone-Americas is gratefully acknowledged.)

Wednesday 5:15 Meeting Rooms KLOP SM29

Shearing entangled polymer solutions at small gap distances

Sham Ravindranath[1], Pouyan E. Boukany[2], Shi-Qing Wang[1], and L J. Lee[2]

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Well-entangled polymeric liquids have been observed to undergo inhomogeneous yielding upon a sudden startup shear and non-quiescent relaxation after a large step strain in absence of any edge complications. These particle-tracking velocimetric (PTV) observations, published in over a dozen papers since 2006, invite the question of what happens in simple shear at gap distances as small as dozens of microns. We have recently clearly established that most entangled polymers would prematurely undergo interfacial yielding before failure in the sample interior can be observed. In other words, it can be demonstrated, when the Weissenberg number $Wi < 2b/H$, interfacial wall slip is dominant so that the sample bulk would still undergo terminal flow [1-2]. Here b is the slip length that can be either minimized using a polymeric solvent for solutions or reduced to zero by adhering samples to the fixture surfaces, and H is the gap distance. Shear banding is possible to observe, typically, only when $Wi > 2b/H$. The value of $2b/H$ also controls whether interfacial slip is the origin of non-quiescent relaxation from step shear [3]. Thus, we can predict what would happen when H is greatly reduced: interfacial slip would dominate the phenomenology. It is possible to observe shear banding, however, when sheared deep in the stress plateau region where $Wi > 2b/H$. We have carried out a combination of rheometric and PTV measurements based on an advanced fluorescent-confocal microscope to elucidate the physics governing the rheological responses of entangled polymeric solutions at small gaps.

1. P. E. Boukany, and S. Q. Wang, Soft Matter 5, 780 (2009). 2. P. E. Boukany and S. Q. Wang, Macromolecules 42, 2222 (2009). 3. S. Ravindranath and S. Q. Wang, Macromolecules 40, 8031(2007).

Wednesday 5:40 Meeting Rooms KLOP SM30

Passive breakup of viscoelastic droplets and filament self-thinning at a microfluidic T-junction

Gordon F. Christopher[1] and Shelley L. Anna[2]

[1]Polymers Division, NIST, Gaithersburg, MD 20899, United States; [2]Depts. of Chemical and Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

In this talk, we examine a simple experiment in which pre-formed droplets containing a dilute polymer solution enter a T-shaped microfluidic junction and stretch as they pass through the stagnation point. Depending on the initial aspect ratio and speed, droplets may break into two segments. We characterize the breaking-nonbreaking behavior of these droplets and find that viscoelastic droplets are less stable than Newtonian droplets of comparable shear viscosity. When droplets break, we observe that viscoelastic droplet segments are connected by persistent filaments that first undergo stretching due to drag of the outer viscous liquid on the large connected segments. Later, filaments undergo iterated stretching and develop a series of beads along their length. Secondary filaments between beads no longer stretch with the outer flow, but rather they exhibit an exponentially decreasing diameter consistent with elasto-capillary breakup. The relaxation time obtained from the filament diameter profiles is close to the estimated Zimm relaxation time for the polymer solution, but depends on the global flow parameters, including the initial size and speed of the droplet prior to entering the T-junction. Based on the microscale diameters of the filaments, we suggest that splitting of droplets at microfluidic T-junctions may be a useful way to characterize the extensional rheology of low viscosity elastic liquids.

Symposium EB
Emulsions, Blends and Multiphase Systems

Organizers: Michael Loewenberg and Rekha Rao

Wednesday 1:30 Hall of Ideas G EB16

Linear and non-linear rheology of cocontinuous blends during coarsening

Carlos R. Lopez-Barron and Christopher W. Macosko
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The evolution of the microstructure during annealing of cocontinuous blends was studied with 3D imaging and both linear and non-linear rheology. 3D images of a symmetric blend made of fluorescently labeled polystyrene and styrene-ran-acrylonitrile copolymer were obtained with laser scanning confocal microscopy. Applying the coordinate transformation method (Lopez-Barron and Macosko, 2009) on the 3D images, we were able to compute the local curvature of the blend interface. Images were analyzed for time evolution of interfacial area, curvature and curvature distributions. Two regimes of coarsening were observed: an early linear (self-similar) growth followed by a gradual decrease of the coarsening rate. The growth of the microstructure and the regime transitions were correlated to a decrease on the elastic modulus which is faster in the early stage and slows down in the late stage. Fourier transform rheology was used to study the non-linear viscoelastic behavior of the blend during coarsening. The relative intensity of the 3rd harmonic and the fundamental frequency, represented by the normalized quantity $I_{3/1}=I(3w_1)/I(w_1)$, gives the non-linear character of the blend. A decrease of I_3 during coarsening was observed, which indicates an abatement of non-linearity due to a decrease in the interfacial area.

Wednesday 1:55 Hall of Ideas G EB17

Rheology of explosive emulsions: Viscosity, elasticity, tiime effects, transportation

Irina Masalova
Material Science and Technology Centre, Cape Peninsula University of Technology, Cape Town, South Africa

Explosive emulsions are highly concentrated w/o emulsions (up to 90 volume % of dispersed phase), where dispersed phase comprises the over-cooled, highly concentrated inorganic salts solution. Rheological properties of these emulsions demonstrate the variety of effects including non-Newtonian behavior, yielding at low shear stresses and the effect of rheopexy occurs at low shear rates. Viscous properties and yielding was studied in detail, including droplet size, oil phase concentration dependencies and estimation of pumping characteristics taking an account refinement of droplets as a function of pumping speed. The normal stresses in shearing were also measured. Normal force in the low-shear-rate domain does not depend on shear rate. This was explained in the frames of the Reynolds mechanism of dilatancy, while at a high shear rate the Weissenberg mechanism of normal stresses as the consequence of elasticity becomes dominant. The two-step model of flow of the emulsions under study was proposed, based on the whole complex of experimental evidences including direct microscopic observations. It was demonstrated that at low shear rates, the flow of emulsions proceeds by rolling larger drops over smaller ones, while the dominant mechanism of flow above some shear stress threshold is droplet deformation. Three levels of time effects related to the evolution of rheological properties of the emulsions were found: rapid viscoelastic process, rheopexy due to structure rearrangements during flow and slow aging due to crystallization of the super-cooled phase. Finally the problem of modeling long distance transportation of the emulsions (corresponding to their technological applications) was discussed. This problem is related to the choice of the appropriate rheological model to describe flow properties and to find correlation between rheological parameters and shelf-life stability of the emulsions. The results of the calculations were confirmed by real industrial applications.

Wednesday 2:20 Hall of Ideas G EB18

Evolving structure and rheological properties of an emulsion undergoing internal phase solidification

Prasad U. Karanjkar, Jae W. Lee, and Jeffrey F. Morris
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Rheological properties of multiphase systems including emulsions, suspensions, and polymer blends predominantly depend on the microscopic structure of the internal or dispersed phase. Hence morphological characterization is an integral part in understanding the complex fluid's behavior. To this end, we describe development and application of a *flow rheometer* providing the capability of measurement of mechanical properties together with morphological characteristics through visualization. The device uses an oscillatory pressure-driven flow under temperature controlled conditions, with imaging and light transmission combined with pressure drop measurements as the primary diagnostic tools.

We describe calibration, over a range of temperatures, against standard rotational rheometry for both Newtonian and phase-change fluids (wax forming oils). We also apply the system to a more complex case of an emulsion in which the internal phase solidifies, considering both simple water-in-oil emulsion and a clathrate hydrate-forming emulsion. The motivation is to address hydrate plug formation inside transport pipelines, a source of concern for the petroleum industry. Our study includes water-in-oil emulsions which model oil- field emulsions; these are characterized inside the flow rheometer under hydrate forming conditions. We describe the particle agglomeration and related rheological changes which take place as the reaction (or phase transition) takes place.

Wednesday 2:45 Hall of Ideas G EB19

Linear viscoelasticity of organic foams: Relaxations, temporal dependencies, and bubble loading phenomena

Jamie M. Kropka, Lisa A. Mondy, and Mathew Celina
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It is not initially intuitive that adding a gas to a liquid would give you a solid, but that is exactly what happens with foams. At sufficiently high gas concentrations, the bubbles within foam become jammed and merely distort under small shear deformations. This distortion increases the gas-liquid interfacial area, and thus energy per unit volume, and results in an elastic restoring force. Actually, liquid foams are viscoelastic liquids, exhibiting a fast response attributed to local bubble motions and a slow response due to structural evolution of the intrinsically unstable system. In this work, these processes are examined in novel organic foams that exhibit physiochemical characteristics that vary substantially from the typically investigated aqueous systems. Transient and dynamic relaxation responses are evaluated to understand their dependence on physiochemical properties and to probe the physical mechanisms responsible for energy dissipation. The fast response is found to closely resemble that of aqueous foams despite the organic foams exhibiting continuous phase viscosities orders of magnitude higher than their aqueous counterparts. The slow response is attributed to a combination of (1) the collective effect of many localized rearrangements of cells and (2) foam softening due to increasing cell size with time. The temporal dependencies of the linear viscoelastic response are also assessed in the context of the foam structural evolution due to cell coarsening. In addition, particular attention is paid to the development of elasticity in the foam with gas fraction. The transition from a simple liquid to one that is strongly viscoelastic, due solely to bubble interactions, is captured.

Sandia is a multi-program 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.

Wednesday 3:10 Hall of Ideas G EB20

Foam drainage equation

Fahir T. Akyildiz[1] and Dennis A. Siginer[2]
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The numerical solution of the free boundary evolution equation for foams is investigated. The free boundary problem is first transform to the fixed domain in terms of change of independent variable; the resulting singular nonlinear partial differential equation is transform to the nonlinear partial differential equation by change of dependent variable. After using the domain truncation, convergence of the variable step size backward Euler discretization is discussed. Numerical algorithms based on the backward difference and implicit Crank-Nicolson are proposed for solving the field equations and comparative results are presented . Furthermore, it is shown that the reaction-diffusion problem with free drainage represented by a degenerate parabolic partial differential equation is covered by analytic semi-groups set in an abstract Banach space.

Wednesday 4:00 Hall of Ideas G EB21

A novel miniature mixing device for polymeric blends, nanocomposites and food compounds

Martin Sentmanat[1], Christos Stamboulides[2], and Savvas G. Hatzikiriakos[2]
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Polymeric composites and blends are typically developed via a mechanical mixing process during which time the ingredients are subjected to both shear and extensional deformations. The overall integrity of polymeric compounds strongly depends upon the shear and extensional rheological properties of the polymeric matrix the morphology and concentration of solids. In addition, the rheological properties also control the final quality and commercial attractiveness of the final products. Often times when working with new experimental fillers and polymers, material quantities may be available in extremely limited amounts thereby constraining material compounding protocols and the physical property characterizations associated therewith. A new miniature mixer has been developed to monitor and optimize the preparation protocol of various polymeric compounds and blend systems. The effect of mixing time and other basic processing parameters on the shear and extensional rheological properties of said compounds is examined in order to understand the effect of undermixed and/or overmixed conditions on the rheological properties and thus the quality of the final products. Results from the new miniature mixer are compared with the results from other conventional mixing techniques in order to assess the scalability of the new mixing protocol. Examples include, those of polymer blending, nanocomposite and dough formation.

Wednesday 4:25 Hall of Ideas G EB22

Control of filament formation in microfluidic flow focusing

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When droplets form in a microfluidic flow focusing geometry, the presence of slowly-desorbing surfactant molecules at the interface can retard pinch-off and lead to the development of a sustained thread via a tipstreaming-like mechanism. Likewise, a small amount of dissolved polymer in the bulk phase is well known to lead to the formation of persistent viscoelastic threads between pinching droplets. In this talk, we investigate the interplay between these two stabilizing mechanisms for the purpose of controlling the formation of fine liquid threads. Surfactants are

dissolved in the outer oil phase, and the tipstreaming behavior is characterized as a function of surfactant concentration and capillary number. The dispersed phase liquid consists of a well-characterized elastic liquid. Droplet pinchoff and thread formation are characterized as a function of the relaxation time of the viscoelastic dispersed phase liquid. We show that the thread formation process can be controlled by tuning the timescales for surfactant dynamics, viscoelasticity, and interface stretching in the elongation-dominated flow.

Wednesday 4:50 Hall of Ideas G EB23

Co-extrusion of polymers filled with particulates and a eutectic alloy

Lisa A. Mondy[1], Rekha R. Rao[1], Lothar Bieg[1], John L. Schroeder[1], Mark Stavig[1], Duane Schneider[1], Scott Spangler[1], Phillip Cole[1], Randy A. Mrozek[2], and Joseph L. Lenhart[2]

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We are developing structured composites composed of alternating layers of conductive and dielectric polymers through a process called multi-layered coextrusion. Here, the two polymers are extruded through a feedblock, then the extruded material is split vertically and recombined by stacking the segments horizontally to multiply the number of layers. Intrinsically conductive polymers are typically difficult to extrude due to their conjugated backbones. Our approach is to melt process a polymer composite composed of a polymer matrix, conductive nickel particulates, and a eutectic alloy. The eutectic alloy melts during processing leading to a combination of emulsified liquid metal and solid metal particles, with a lower composite viscosity than using solid particles alone for the same fraction of metal. Upon cooling the eutectic forms a network of connective bridges between the nickel particles leading to low resistivity values. Extrudable dielectric materials can also be formed using particle fillers in a polymer matrix. Finite element modeling is used to examine the practical limits of density or viscosity mismatches of the two materials in the coextruder. Examination of microstructure and measurements of rheological and electrical properties, combined with the modeling, are used to optimize the formulations.

[1] 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.

Wednesday 5:15 Hall of Ideas G EB24

Microfluidic forced assembly of polymer blends: Mixing and layering

Doyoung Young and Kalman B. Migler

Complex Fluids Group, Polymers Division, NIST, Gaithersburg, MD 20899, United States

We present a novel microfluidic mixer for high temperature polymer melts based on the platform of the Multi-sample Micro-slit Rheometer (MMR). The device is essentially a static mixer with ten consecutive units of splitting and recombination flow formed by stacking three stainless steel shims (50 µm thickness, 45 mm in diameter). The mixing results show an evolution of the morphology for the polystyrene/polypropylene blend, cylindrical domain/matrix or the transition of a multilayer to a domain/matrix or a co-continuous morphology depending on the channel configuration and the number of mixing unit passed by. This mixer will be particularly useful not only as a polymer melt mixer but as a multilayer processor when a limited material quantity (only 1 or 2 pellets) is available. The microfluidic platform is based on flow through shim slits and is easily reconfigurable so that it can emulate other kind of polymer melt processing such as capillary rheometer or micro-injection molder.

Wednesday 5:40 Hall of Ideas G EB25

Influence of rheological properties on the electrospinning of chitosan/PEO solutions

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CREPEC - Chemical Eng., École Polytechnique, Montreal, QC, Canada

Electrospinning is a recently developed spinning technique which enables producing ultrafine fibers at the nanoscale, and with distinctly high surface area in the form of non-woven mats. These properties have attracted great attention for their applications in various fields such as biomedical engineering, food science, pharmaceuticals and nanocomposites. In spite of the simplicity of the electrospinning process, many polymers, and especially natural ones, are not readily electrospun into defect-free nanofibers. Chitosan is one of the polymers that is still challenging to electrospin, mainly due to its polycationic nature and rigid structure in the solution state. The viscosity of most chitosan solutions is very high in the concentration range required to provide enough chain entanglements that are crucial to successful electrospinning. However, the unique properties of this polymer like biodegradability, biocompatibility and antifungal effects have led to various attempts to improve its electrospinnability. Adding a second polymeric phase such as PVA, PEO and PLA as a co-spinning agent and plasticizer is an efficient way to decrease the viscosity and create composite nanofibers of chitosan. Based on preliminary trials, PEO has been chosen because of its excellent electrospinnability and ability to make nanofibers. In this research a high temperature electrospinning setup is used to decrease the viscosity of chitosan and its blends with PEO and to improve its spinnability. The purpose of this investigation is to focus on the impact of rheological properties and viscous forces on the electrospinning of chitosan solutions. The use of this high temperature setup makes it possible to separate the effect of rheology from other controlling parameters. The rheological behavior of the various solutions is characterized in steady simple shear and small angle oscillatory shear flow (SAOS). The effects of the second phase content and temperature on the electrospinning process and the final produced nanofibers are discussed.

Symposium GG
Gels, Glasses and Jammed Systems

Organizers: Corey O'Hern and Subramanian Ramakrishnan

Wednesday 1:30 Meeting Rooms MNQR GG16

Microrheology of microtubule solutions and microtubule-actin composite networks

Maria Kilfoil
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In this talk, I will discuss the first local/microrheological measurements on microtubule solutions, as well as composite networks. The viscoelastic properties of microtubules as reported from two-point microrheology agree with the macroscopic measurement at high frequencies, but appear to show a discrepancy at low frequencies, at time scales on the order of a second. A composite of F-actin and microtubules has viscoelastic behavior between that of F-actin and pure microtubules. I will further show that the Poisson ratio of the composite, measured by the length-scale dependent two-point microrheology, is robustly smaller than that of the F-actin network at timescales >1 s, suggesting that a local compressibility is conferred by the addition of microtubules to the F-actin network.

Wednesday 1:55 Meeting Rooms MNQR GG17

The effect of crosslink density on the viscoelastic bulk modulus

Jiaxi Guo and Sindee L. Simon
Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

In an effort to test Leaderman's hypothesis that the bulk and shear responses arise from different molecular mechanisms, the viscoelastic bulk modulus is measured for polycyanurate networks of two crosslink densities and compared to previously obtained shear relaxation data. We perform the pressure relaxation experiments in the vicinity of the pressure-dependent Tg after step changes in volume using a custom-built pressurizable dilatometer. Reduced master curves are formed by time-temperature superposition using horizontal shifts to account for the temperature dependence of the relaxation time, along with small vertical shifts to account for the temperature dependence of the glassy and rubbery bulk moduli. The results indicate that the shape and placement of the dispersion is independent of crosslink density when Tg is taken as the reference temperature. In addition, the horizontal and vertical shift factors show a similar dependence on temperature when plotted as the departure from Tg. The horizontal shift factors also agree well with those from the shear viscoelastic response. The relaxation spectra obtained from the pressure relaxation measurements is compared to those obtained from shear stress relaxation experiments. The results support the conclusions from our previous measurements on polystyrene, as well as those of Bero and Plazek, and indicate that Leaderman's hypothesis is incorrect. More specifically, although the long-time chain modes are unavailable to the bulk deformation, the short-time mechanisms for the bulk and shear responses appear to have the same underlying molecular mechanisms.

Wednesday 2:20 Meeting Rooms MNQR GG18

Direct measurement of molecular mobility in actively deformed PMMA glasses

Mark D. Ediger[1], Hau-Nan Lee[1], Robert A. Riggleman[2], and Juan J. de Pablo[2]
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We use an optical photobleaching technique to quantitatively measure changes in molecular mobility during the active deformation of a polymer glass (PMMA). Segmental mobility increases by up to a factor of 1000 during uni-axial tensile creep. While the Eyring model can describe the increase in mobility at low stress, it fails to describe mobility after flow onset. In this regime, mobility is strongly accelerated and the distribution of relaxation times narrows significantly, indicating a more homogenous ensemble of local environments. At even larger stresses, in the strain-hardening regime, mobility decreases with increasing stress. Consistent with the view that stress-induced mobility allows plastic flow in polymer glasses, we observe a strong correlation between strain rate and segmental mobility during single-step creep; more complicated deformations break this correlation. Coarse-grained molecular dynamics simulations reproduce all the qualitative features of the experimental measurements. The simulations reveal that "enhanced mobility" is a conceptually reasonable description of the behavior observed in simulation and experiment.

Wednesday 2:45 Meeting Rooms MNQR GG19

Topological changes during the gel transition of a reversible polymeric network

Arlette R. Baljon[1], Joris Billen[1], Mark Wilson[1], and Avinoam Rabinovitch[2]
[1]Physics, San Diego State University, San Diego, CA, United States; [2]Physics, Gurion University of the Negev, Beer-Shava, Israel

The sol/gel transition is studied in model telechelic polymers. We find that, as in the case of glass-forming liquids, the transition range is very broad. Four characteristic temperatures for gel formation are calculated: (1) the temperature below which relaxation times no longer show Arrhenius dependence on temperature; (2) the Vogel-Fulcher temperature at which the structural relaxation time extrapolates to infinity; (3) the analogue of the crossover temperature defined by Mode Coupling Theory; (4) a "jamming" transition temperature at which the number of reversible bonds sharply increases and their distribution over micelles changes qualitatively. Graph theoretical concepts are applied to further quantify these topological changes: telechelic polymers serve as "links" between "nodes", which consist of aggregates of their associating

endgroups. Our analysis shows that the degree distribution of the systems is bimodal and consists of two classes of nodes.. so-called "superpeers" with a large average number of links per node and "peers" with a much smaller number. At high temperature the system consists of separate peer- and superpeer-networks. At lower temperatures links between peers and superpeers form. The fraction of superpeer nodes increases as well. This increase is steepest at the "jamming" transition. The eigenvalue spectra of the networks reveal that in the jammed state peers are only connected to superpeers, a topology known to be very robust.

Wednesday 3:10 Meeting Rooms MNQR GG20

Catastrophic breaking of polymer gels

Matthew L. Lynch[1] and Alan L. Graham[2]
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Polymer gels prepared from synergistic blends of xanthan and Konjac gums exhibit remarkable flow characteristics. Creep measurements indicate that when the applied stress leads to a deformation of gel in excess of critical strain the gel readily breaks and flows, and when the applied stress leads to a deformation far less than the critical strain, there is essentially no creep of the gel. Remarkably, when the applied stress results in strains approaching a critical strain, the gels hold for an extended period of time at which point it breaks catastrophically and the gel flows. There is a power-law relationship between this 'incubation' time and the applied stress. Electron microscopy measurements suggest that the gel forms from interlocked bundles of aggregated molecules. The microstructure of the bundles dictates the bulk modulus. However, creep recovery measurements suggest that applied stress slowly breaks the molecular filaments of each bundle leading to gradual weaken of the gel structure and finally catastrophic breakage of the polymer gel. Together, this provides unique insights into the yield-stress properties of synergistic gum gels.

Wednesday 4:00 Meeting Rooms MNQR GG21

Nonlinear viscoelastic response of a colloidal system near the glass transition concentration: Superposition experiments and rejuvenation

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There is currently considerable interest in the behavior of colloidal dispersions near to the glass or jamming transitions. One aspect of the behavior is that it is considered as a model of the behavior of glassy materials. One aspect of the behavior of glassy polymers has been the so-called mechanical rejuvenation phenomenon and this has been partially investigated in experiments in which small deformations are superimposed upon large deformations. Here we examine this paradigm by looking at concentrated polybutadiene carboxylate (200 nm diameter) particles subjected to shearing histories in which small deformations are superimposed on large deformations. In the case of polymer solutions and polymer glasses, such histories have a signature that looks much like the system was initially softened by the imposed large strain and then, either due to a viscoelastic fading memory or rejuvenation followed by aging, the material stiffens. In no instance, however, have there been reported effects of loading sequence on the apparent aging response. Here we find that in the concentrated colloidal suspensions there is a strong sequence effect. We also find that the direction of the superposed strain (add a small strain to the large strain or subtract the strain) also makes a large difference in the observed "aging". The importance of the findings in terms of the behavior of the colloid-glass paradigm will be discussed.

Wednesday 4:25 Meeting Rooms MNQR GG22

Nanostructure and rheology of concentrated nanoparticle & colloidal gel suspensions

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Chemical Engineering, University of Delaware, Newark, DE 19716, United States

Nanoparticle and colloidal gels, flocculated suspensions, and attractive driven glasses are of fundamental scientific interest and pose challenges to industrial formulation and application because of the hierarchy of structures that connect particle properties to bulk material properties. In many cases the processing of these materials relies on the fact that the underlying structure may be reversibly broken down by flow. As a result their rheological behavior is of technological relevance to process design optimization, and can exhibit complex behaviors such as solid-like linear viscoelasticity, thixotropy, aging, yielding, hysteresis, and shear localization. Much is known about the fractal and fractal-like microstructure of low density gels under static conditions and the dissolution of the network as a result of flow, but less is known about concentrated systems. In this work, we explore the nanostructure, and rheological properties of concentrated silica nanoparticle gels (10 -50 vol%) formed by thermally quenching a model nanoparticle dispersion both at rest and under shear flows. The model system is composed of silica spheres which have a relatively thin grafted oligomeric surface layer that provides steric stability in a good solvent, but contributes to a reversible, short range attraction in poor solvents. Fiber optic quasi-elastic light scattering (FOQELS), small angle neutron scattering (SANS), and rheology (dynamic oscillatory, and steady shear) are used to probe the single particle properties, interaction potential, phase behavior, and structure, in relationship to rheological properties. Furthermore, the effects of shear flow on the gel formation kinetics and gel structure and mechanical properties are explored with flow-SANS, in which the fluid is sheared in a 1-2 plane shear cell. The goals of this study are to identify the hierarchical structures that quantitatively relate the state of the gel or glass, interparticle potential, and particle properties to the bulk rheology.

Wednesday 4:50 Meeting Rooms MNQR GG23

Contributions of dynamical heterogeneities to non-linear rheology of confined colloidal liquids under oscillatory shear

Prasad S. Sarangapani[1], Andrew Schofield[2], and Y. Elaine Zhu[1]
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We present a recent rheological study of confined colloidal liquids under oscillatory shear using a home-designed micron-gap rheometer interfaced with a confocal microscope. We simultaneously visualize the dynamics and measure viscoelasticity of "hard-sphere" poly-(methyl methacrylate) (PMMA) colloidal liquids of 1.2 µm in diameter to applied shear deformation of bulk volume fraction from 0.43-0.57, confined at gaps ranging from 80 µm to 1-2 µm. Significant non-universality in plastic behavior in the limit of large strain amplitudes is found. Non-affine motion, determined by subtracting the globally uniform strain from the bare particle coordinates reveal that highly mobile particles relax as cooperatively rearranging groups. We find that these regions typically approach the order of the confining dimension and are nearly isotropic in the bulk, yet exhibit strong anisotropy and coexist with long lived immobile regions at narrow gaps. We also quantify in detail the role of the observed gap dependent anisotropy on shear thickening observed in the limit of large strain amplitudes.

Wednesday 5:15 Meeting Rooms MNQR GG24

Computational study of rheology for colloidal suspensions and particulate gels

Michael D. Bybee and Jonathan L. Higdon
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The rheology of concentrated colloidal suspensions with attractive and repulsive particle interactions is studied using FLD (fast lubrication dynamics) simulations. The microstructure is determined from dynamic simulations with results presented for varying strengths of attraction, range of attraction and volume fraction. Rheology studies are conducted to evaluate the relaxation modulus for viscoelastic response as well as the frequency dependence of the storage and loss moduli. Step strain /relaxation and oscillatory shear simulations yield consistent results for the moduli. Ensemble averaging and novel noise reduction algorithms are introduced to dela with the extreme. Rheological parameters are computed for a range of strengths of attraction, repulsion, range of attraction and volume fractions from 10% to 40%. The introduction of repulsive forces reduces the storage modulus by more than order of magnitude compared to attractive gels.

Wednesday 5:40 Meeting Rooms MNQR GG25

Multiple glasses in colloidal star mixtures

Brian Erwin[1], Emanuel Stiakakis[2], Michel Cloitre[3], and Dimitris Vlassopoulos[4]
[1]FORTH and ESPCI and IBM-NY, Heraklion, Greece; [2]Weiche Materie, Forschungszentrum Juelich, Juelich, Germany; [3]Matiere Molle et Chimie, ESPCI, Paris, France; [4]Institute of Electronic Structure & Laser, FORTH, Heraklion, Crete, Greece

Recently it was shown that asymmetric mixtures of star polymers at different composition and size ratios can form multiple glassy states. Of particular interest is the possibility of glass melting due to depletion effects on adding the small component and the re-entrant glass formation upon further increasing its concentration. To elaborate these intriguing phenomena that were theoretically explained in the framework of mode coupling theory, we undertake a systematic experimental investigation involving dynamic light scattering and rheology. We discuss the interesting sensitivity of cooperative diffusion to the solid-fluid-solid transitions. We also analyze the linear rheology and discuss the extracted relaxation modes as functions of concentrations and size ratios. Our results support the generic picture emerging concerning the possible pathways for tailoring of the rheology of soft glasses. They are also suggestive of the role of interactions in these classes of hairy-particle colloids and their relaxation of aging and slow dynamics.

Symposium FM
Non-Newtonian Fluid Mechanics and Stability

Organizers: Radhakrishna Sureshkumar and Yong Joo

Wednesday 1:30 Hall of Ideas J FM6

Stability of elongational flow of the upper convected Maxwell fluid

Michael Renardy and Yuriko Renardy
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We prove that planar elongational flow of the upper convected Maxwell fluid is linearly stable and analyze the associated spectral problem.

Wednesday 1:55 Hall of Ideas J FM7

Thermal instabilities in melt spinning of viscoelastic fibers

Chunfeng Zhou and Satish Kumar

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Nonisothermal melt spinning of viscoelastic fibers where the viscosity varies in a step-like manner with respect to temperature is studied in this work. A set of one-dimensional equations based on the slender-jet approximation and the upper-convected Maxwell model is used to describe the melt spinning process. The process is characterized by the force required to pull the fiber, the strength of external heating, and the draw ratio, the square of the ratio of the fiber diameter at the spinneret to that at the take-up roller. For low levels of elasticity and sufficiently strong external heating, there can be three pulling forces consistent with the same draw ratio, similar to the Newtonian case studied by Wylie et al. [J. Fluid Mech. 570 (2007) 1-16]. For higher levels of elasticity, the process exhibits a draw ratio plateau where the draw ratio hardly changes with the pulling force, reflecting a competition between thermal and elastic effects. As in the Newtonian case, external heating introduces a new instability---termed thermal instability---that is absent in isothermal systems. Linear stability analysis reveals that external heating improves stability for low levels of elasticity, but can worsen stability for higher levels of elasticity, which is again a consequence of the interplay between thermal and elastic effects. Nonlinear simulations indicate that the predictions of linear stability analysis carry over to the nonlinear regime, and show that unstable systems exhibit limit-cycle behavior. The results of the present work demonstrate a possible mechanism through which external heating can stabilize the melt spinning of viscoelastic fibers.

Wednesday 2:20 Hall of Ideas J FM8

Probing instabilities in channel flow of entangled melts: A particle-tracking velocimetric study

Xiangyang Zhu and Shi-Qing Wang

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Well-entangled polymeric liquids exhibit various complicated flow patterns when forced to enter a narrow channel from a large reservoir. The connection between these instabilities and nonlinear polymer rheology has been largely elusive. The recent revelation of basic phenomenology behind simple shear and uniaxial extension of entangled polymers urges us to apply the effective particle-tracking velocimetric (PTV) technique to probe deformation and flow in different regions of a channel flow setup. Using polybutadiene and styrene-butadiene rubber as model entangled melts, we carry out PTV and rheometric observations beyond the interfacial stick-slip transition. By making PTV observations at both the channel entry and die land, we elucidate how entry material deformation and instability affect the subsequent channel flow in terms of molecular parameters such as molecular weight.

Wednesday 2:45 Hall of Ideas J FM9

Stability of plane Couette-Poiseuille flow of shear thinning fluid

Ian A. Frigaard[1] and Cherif Nouar[2]

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A linear stability analysis of the combined plane Couette and Poiseuille flow (PCPF) of shear-thinning fluid is investigated. The rheological behavior of the fluid is described using the Carreau model. The linearized stability equations and their boundary conditions result in an eigenvalue problem that is solved numerically using a Chebyshev collocation method. A parametric study is performed in order to assess the roles of viscosity stratification and the Couette component. First of all, it is shown that for shear thinning fluid, the critical Reynolds number for a two-dimensional perturbation is less than for three-dimensional. Therefore, it is sufficient to deal only with a modified Orr-Sommerfeld equation for the normal velocity component. The influence of the velocity of the moving wall on the critical conditions is qualitatively similar to that for a Newtonian fluid. Concerning the effect of the shear-thinning, the computational results indicate that this behavior leads to a decrease of the phase velocity of the traveling waves and an increase of stability, when an appropriate viscosity is used in the definition of the Reynolds number. Using a long-wave version of the Orr-Sommerfeld equation, the cut-off velocity is derived. The mechanisms responsible for the changes in the flow stability are discussed in terms of the location of the critical layers, Reynolds stress distribution, and the exchange of energy between the base flow and the disturbance.

Wednesday 3:10 Hall of Ideas J FM10

Multiple failure-mode transitions in transient polymer networks

Joris Sprakel[1], Johan T. Padding[2], and Wim J. Briels[2]

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Transient polymer networks are known to undergo a wide variety of viscoelastic flow instabilities. In this contribution we investigate two of these flow failure modes; shear banding and melt fracture. With particle-based simulations, in direct comparison to experiments, we show a transition from gradient banding to fracture in transient polymer networks with reversible associative nodes. It appears that banding leads to local weakening of the material from which fractures can ultimately propagate. Furthermore we illustrate that at higher deformation rates shear-induced ordering in these systems could be responsible for the transition to yet another type of flow instability, the so-called Weissenberg effect.

Wednesday 4:00 Hall of Ideas J FM11

Fluid mechanics of rinsing flows

Tienyi T. Hsu, Gerald G. Fuller, and Curtis W. Frank
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The fluid mechanics of "rinsing flows", describing the use of a jet of one liquid or air to push away a second, coating liquid on a rigid flat surface, has been investigated. This phenomenon is common to everyday life but despite this, few studies have considered the rinsing flow process in detail. The present study has investigated the effect of the viscoelasticity of the coating fluid in response to either water or air jets. One experimental challenge is that the timescale of the process is short and does not reach a steady state. Thus, this study has employed high speed imaging devices allowing the examination of the initial contact between the two fluids. Three classes of fluids with the same zero-shear viscosity have been investigated: glycerin-water Newtonian liquids, polymeric solutions, and worm-like surfactant solutions. Analyses of high speed videos reveal that the evolutions of the hydraulic jump circles have very different characteristics. For example, Newtonian liquids show an inverse exponential-like growth in circle size while polymeric solutions show a linear growth and for surfactant solutions, the circle size first increases then recoils due to the high elasticity of the fluid. It is also observed that Non-Newtonian liquids are able to suppress surface roughness in the hydraulic jump region due to a coupling of the extensional viscosities of these fluids and stagnation point flows in the vicinity of the hydraulic jump. Both the degree of roughness suppression and hydraulic jump circle size increase with the extensional viscosity of the solution. It is also found that these flows present interesting variations to the classic hydraulic jump with a variety of new phenomena due to the presence of the second, coating layer. For example, a Taylor-Saffman instability is revealed at the moving interface between fluid contacts. The wavelength of the instability is finer for the Non-Newtonian fluids compared to the Newtonian glycerin-water solutions.

Wednesday 4:25 Hall of Ideas J FM12

Relaxation times of CTAB/NaSal surfactant solutions

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Solutions of CTAB/NaSal are known from dynamic measurements to behave as Maxwell fluids for some concentrations and for low strain and strain rates. Outside of this regime, the fluids can undergo shear-induced structure changes. In this study, a variety of techniques were used to evaluate a solution's relaxation time, in both regimes and for several solutions. In the Maxwell regime, the relaxation time from G'-G" crossover agrees with the relaxation time determined from the cessation of steady shear. But the time determined from startup to steady shear decreases with shear rate, to a fraction of the other values. In the shear-induced structure change regime, measurements were made of startup and cessation of both shear stress and N1. Relaxation times were determined where possible, i.e., for exponential data. Also determined was the relaxation time from low-shear N1 values. The relaxation times based on the cessation of shear stress and of N1 agree, and depend on the shear rate. The times based on other measurements do not agree with these times and vary with each other, with differences as much as an order of magnitude. In contrast to startup shear stress data, the startup N1 data are not exponential and so do not yield a relaxation time; however, the time scale is much different from that for the shear stress. These wide variations in relaxation are related to micellar structure, particularly to changes in structure scale, both in the shear-independent and shear-induced structure change regimes.

Wednesday 4:50 Hall of Ideas J FM13

The dynamics of viscoelastic wormlike micelles in crossflow past a circular cylinder

Geoffrey R. Moss and Jonathan P. Rothstein
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Solutions of thermodynamically driven, self-assembled wormlike micelles are used with ever increasing frequency in a multitude of consumer products ranging from cosmetic to industrial applications. Owing to the wide range of applications, flows of interest are often complex in nature; exhibiting both extensional and shear regions that can make modeling and prediction both challenging and valuable. Adding to the complexity, the micellar dynamics are continually changing, resulting in a number of interesting phenomena, such as shear banding and extensional flow instabilities. We present the results of an investigation of the flow of several micellar solutions around a single circular cylinder. By systematically varying both the Deborah number of the test solution and the ratio of the cylinder's diameter to channel height, the flow kinematics, stability and pressure drop were measured. A combination of particle image velocimetry in conjunction with flush mount pressure transducers were used to characterize the flow, while flow induced birefringence measurements were used to determine the stresses leading to micelle deformation and alignment. The excess pressure drop was found to decrease initially due to the shear thinning of the test fluid at moderate Deborah numbers, but diverge at higher Deborah numbers as other elastic effects begin to dominate. Presented is evidence of the onset of an elastic instability in one of the test fluids above a critical Deborah number, manifest in fluctuating transient pressure drop measurements, asymmetric streamlines and localized failure, leading to relief of accumulated stress . We argue that this instability can be attributed to the measurable differences in the extensional rheology of the test fluids, and hypothesize that the stability may be tunable and predictable from that Rheology. Further, the dynamics of the cylinder in cross-flow are widely applicable in predicting and explaining the behavior of these solutions in other complex geometries.

Wednesday 5:15 Hall of Ideas J FM14

Capillary break-up, jetting and extensional rheology of associative polymer solutions

Vivek Sharma[1], James G. Serdy[2], Pradipto K. Bhattacharjee[1], and Gareth H. McKinley[1]
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Understanding the rheology and processing behavior of dispersions containing particles suspended in associative polymer solutions is relevant to a large variety of applications, including water-borne paints, food, inks, cosmetics, etc. These complex dispersions are processed over a broad range of shear and extensional rates. Commercially relevant formulations use dilute solutions of associative polymers, which have low viscosity and short relaxation times, and hence their non-Newtonian response is often not apparent in a conventional rheometer. In this talk, we explore several methods for systematically studying the linear and nonlinear rheology of associative polymer dispersions, including: high frequency oscillatory tests at frequencies up to 10 kHz, microfluidic shear rheometry at deformation rates up to 10^6 s^{-1} and the influence of transient extensional rheology in jet breakup. High deformation rates can be obtained in jetting flows; however inertial, elastic and viscous effects typically lead to complex dynamics, which preclude a simple capillary thinning analysis in a necking fluid thread. We show that by carefully controlling the excitation frequency, it is possible to drive the break-up in a particularly simple and symmetric mode, which can be used to extract extensional viscosity information. The growth and evolution of instability during jetting and break-up of these viscoelastic fluids shows the influence of both elasticity and extensibility. Finally we touch upon the effects of adding particles to these dispersions, which leads to formation of physical associations in solution and marked changes in the shear and extensional rheology.

Wednesday 5:40 Hall of Ideas J FM15

Characterization of a dilute polymer solution following preshear in microgravity

Johannes M. Soulages[1], Gareth H. McKinley[1], Nancy R. Hall[2], Kevin S. Magee[3], Gregory E. Chamitoff[4], and Michael E. Fincke[4]
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The Shear History Extensional Rheology Experiment (SHERE) is an International Space Station (ISS) experiment designed to study the effects of a pre-shear history on the transient extensional viscosity of a dilute polymer solution in a uniaxial stretching flow in the absence of gravity. Access to an extended microgravity environment allows us to measure the subsequent capillary thinning of the fluid filament after cessation of the extensional deformation without sagging under action of gravitational body forces. Understanding the deformation and thinning of fluid threads is particularly relevant in a wide variety of industries, including fiber-spinning, injection molding, food and consumer product processing, in addition to future "containerless processing" operations. In typical industrial polymer processing operations, viscoelastic polymer solutions experience a complex flow history with both shear and extensional kinematic characteristics. The SHERE hardware offers the ability to pre-shear the test samples before imposing a uniaxial deformation to explore the impact of this pre-shearing on the subsequent elastocapillary thinning. The SHERE main hardware experiment was launched to the ISS on board Shuttle Mission STS-120. Subsequently, two batches of 20 and 25 fluid samples were launched to the ISS on board Shuttle Missions STS-123 and STS-126, respectively. The SHERE experiments were performed by astronaut Gregory Chamitoff during Increment 17 between July and September 2008 and by astronaut Mike Fincke during Increment 18 between December 2008 and January 2009. In this talk, we will focus on the history of the SHERE project development as well as on the methodology used in this study. We will then discuss the main results obtained for a well-characterized dilute polymer solution and compare them to ground-based experiments. Finally, we will show potential applications of the current microgravity experimental findings.

Thursday Morning

Symposium SC
Suspensions and Colloids

Organizers: Jason Butler and Mike Solomon

Thursday 7:45 Lecture Hall SC41

Phase behavior and dynamics of colloidal microgels: Softness matters

Jae Kyu Cho and Victor Breedveld
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Colloidal microgels are sub-micron particles composed of a crosslinked polymer network swollen by solvent. Polymer-solvent interactions play a key role in these systems and the size of microgels often can be tuned via temperature and solvent composition. They show much more complex energetics and dynamics than hard sphere colloids, because of the complex interplay between solvent-polymer and interparticle interactions, including polymer solvation, network osmotic pressure and suspension entropy.

We have found that pNIPAm-co-AAc microgels can both swell and deswell in concentrated suspensions, relative to their size in dilute suspensions, depending on the subtle balance between attractive and repulsive forces. We will present the results of comprehensive phase behavior studies via particle tracking microscopy, including short-time studies in micro-dialysis cells and long-time studies in sealed capillaries. The dialysis cell enables rapid and reversible changes in solvent conditions, while monitoring the particle dynamics simultaneously. The sudden changes in particle volume fraction in these experiments cannot be achieved in hard sphere suspensions, and enable us to efficiently map out the phase diagram of the microgel suspensions.

The phase behavior studies emphasize the complexity of the interparticle interaction and suggest the existence of unusual, weakly attractive interactions at low pH. This hypothesis was confirmed by calculating the interaction potential from pair distribution functions in pseudo two-dimensional suspensions.

Finally, we studied the diffusion of both soft microgels and hard polystyrene particles under geometrical confinement between parallel plates, as a function of plate spacing. It was found that the mobility of the PS particles is in excellent agreement with models for hindered diffusion. Soft microgels, on the other hand, exhibit remarkably high mobility under confinement, even for plate spacings that are significantly smaller than the unperturbed microgel diameter.

Thursday 8:10 Lecture Hall SC42

Microviscosity, microdiffusivity, normal stresses?

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In active microrheology, the motion of a probe particle is tracked as it is driven by an external force through a colloidal dispersion. Most work in microrheology has focused on average probe motion, with the microviscosity determined by application of Stokes' drag law. But *fluctuations* in probe motion are also of interest; collisions between probe and bath particles cause velocity fluctuations, scattering it from its mean path. We have recently extended active microrheology theory to include probe fluctuations, and determined that the (long-time) probe scattering is indeed diffusive. The microdiffusivity, $\boldsymbol{D}^{\mathrm{micro}}$, is transversely anisotropic, scaling linearly in the volume fraction ϕ (for small ϕ) for all Péclet numbers Pe, which gives the strength of probe forcing compared to thermal forces. The notion that self-diffusion is driven by gradients in the particle-phase or osmotic pressure prompts investigation of normal stresses in active microrheology---the anisotropy of the microdiffusivity indicates the presence of normal stress differences. We take two approaches to determine normal stresses: First, via the relationship of the microdiffusivity to osmotic pressure gradients: $\boldsymbol{D}^{\mathrm{micro}} \sim \sigma / \phi$, where σ is the suspension stress. Second, we derive stresses from the deformed microstructure. The two approaches agree. Owing to the axisymmetry of the motion about a spherical probe, $N_2 = 0$, while N_1 is quadratic in Pe for $Pe << 1$, and linear in Pe for $Pe >> 1$. The agreement of the two approaches suggests that normal stress differences can be measured in active microrheological experiments if both the mean and the mean-square motion of the probe are monitored.

Thursday 8:35 Lecture Hall SC43

Two-point non-linear microrheology of a colloidal suspension

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Using optical tweezers, the forces acting on two micrometer-diameter probe particles are measured as they are driven at a fixed velocity through a quiescent suspension ("bath") of colloidal particles. Direct visualization of the suspension microstructure is achieved using concurrent high-speed confocal microscopy. Far from equilibrium (at a Peclet number, Pe >> 1), and in the limit in which the bath particles are nearly equal in diameter to the probe particles, a characteristic non-equilibrium bath microstructure develops around the probes, consisting of a boundary layer upstream of each probe, and a downstream wake depleted of bath particles. When the probe particles are oriented with their line of centers orthogonal to their velocity, an effective attraction is induced between them. This force is a function of probe separation and velocity. We will discuss the relationship between the attraction and the combined non-equilibrium bath microstructure for two probe particles in close proximity. Second, we compare the above case to measurements in which the probe particles are oriented with their line of centers parallel to the direction of motion through the bath suspension. Because the second probe follows in the wake of the first, this geometry potentially minimizes the contributions of the "direct" bath-probe collisions to the force exerted on the trailing probe particle, thus making the drag force measurement more sensitive to "indirect" bath-bath collisions. The latter result from the deformation of the suspension in the ?uid surrounding the probe, and are directly related to the suspension dynamics found in macrorheology that lead to shear-thinning.

Thursday 9:00 Lecture Hall SC44

Numerical prediction of the dynamics of nanoparticles embedded in a liquid crystalline solvent

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A hierarchical modeling approach has been adopted to examine the structure and dynamics of nanoparticle suspensions in confined liquid crystals. A molecular model and a combination of Monte Carlo and molecular dynamics simulations are used to investigate the defects that arise around the nanoparticles, both at rest and other imposed flow fields, and to explore how such defects influence the aggregation behavior of the particles. The continuum molecular model is solved by resorting to a radial basis function based technique. The validity of the model and our numerical results are established by direct comparison to results of molecular simulations and to experimental mobility data in both the isotropic and nematic phases. The model is then used to examine the response of different types of confinement, surface treatment, and flow field on the aggregation pathways of nanoparticles in liquid crystals.

Thursday 9:25 Lecture Hall SC45

An active microrheological technique to determine normal stress differences of complex fluids

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Passive microrheology is a popular technique for measuring the linear-response rheological properties of complex fluids, through the fluctuating motion of embedded colloidal probes. Active microrheology, in contrast, aims to infer nonlinear rheological information using actively driven probes. Presently, however, the focus of active microrheology has been limited to attempting to extract the material viscosity as a function of driving speed. In this talk, we propose a new active microrheological technique to determine both the first (N_1) and second (N_2) normal stress differences of a complex fluid, a task which is notoriously difficult in macroscopic mechanical rheometry. Specifically, we consider a two-point active microheology "experiment" in which a pair of colloidal probes are driven with constant velocity through a second order fluid --- the prototypical model for a large class of complex fluids in the limit of gentle deformations. We calculate the relative forces acting on the probes as they are pulled parallel and perpendicular to their line of centres, from which N_1 and N_2 are determined. Finally, we discuss the experimental feasability of the proposed technique.

Thursday 10:10 Lecture Hall SC46

Microstructure, orientation and rheology in suspensions of non-spherical dicolloidal particles

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The PME Stokesian dynamics technique has been extended to model hydrodynamic interactions in suspensions of dicolloidal particles in a Newtonian fluid. The dicolloids consist of two intersecting spheres of varying radii and center to center separation. Dynamic simulations on non-Brownian paticles show an interesting variation of the orientational order with volume fractions which is in contrast to high aspect ratio fibers. At low volume fractions, particles with fore-aft symmetry show a shift to higher Jeffery's orbit constant, i.e. a shift towards an orientation in flow-gradient plane. This leads to an enhanced orientational order parameter in the flow and gradient directions. On the other hand, particles without fore-aft symmetry show very little change in orientational order at low volume fractions compared to the corresponding infinite dilution values. At higher volume fractions, all particle shapes show a shift towards lower orbit constants, i.e. with particle axis toward the vorticity axis, which leads to an enhanced orientational order in the vorticity direction. It is shown that the orientation distribution in the concentrated suspension correlates well with the orientation probability of a single particle in a second order fluid with rheological coefficients giving the same normal-stress behavior as in the suspension.

Thursday 10:35 Lecture Hall SC47

Rheo-microscopy of semi-flexible fiber suspensions in shear flow

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The rheological behavior of fibers with different flexibilities suspended in a silicone oil in the semi-concentrated regime has been investigated by rotational rheometry and flow visualization. The microstructure evolution of the suspensions has been observed at different shear rates using two techniques: a Linkam Optical Shearing System (CSS450) and using a continuously-focusable InfiniVar® microscope placed under the lower plate of a rheometer, which has been replaced by a glass plate. Results from these two techniques show how the size of the visualization window and the number of fibers visualized influence the calculation of the second-order orientation tensor that is used to quantify the orientation state of the fibers. As expected it was observed that applying shear forces aligned fibers in the flow direction. However the extent of alignment was a function of shear rate, applied strain and fiber flexibility. The results showed that by increasing fiber flexibility, the orientation in the flow direction decreased. Rigid fibers oriented themselves more rapidly in the flow direction and the degree of orientation was higher than for flexible fibers. The second-order orientation tensor was represented graphically by ellipses to facilitate the observation of its evolution. Finally, a GENERIC model (General Equation for Non-equilibrium Reversible-Irreversible Coupling) has been used to predict the rheological behavior of the semi-flexible fiber suspensions as well as their microstructure. The model takes into account fiber-fiber interactions and also the semi-flexible nature of the fibers. The graphical representation of the second-order orientation tensor was confronted with model predictions and it was in good qualitative agreement.

Thursday 11:00 Lecture Hall SC48

Simulation of the rheological properties of suspensions of oblate spheroidal particles in a Newtonian fluid

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A simulation algorithm was developed to predict the rheological properties of oblate spheroidal suspensions. The motion of each particle is described by Jeffery's solution, which is then modified by the interactions between the particles. The interactions are considered to be short-range and are described by results from lubrication theory and by approximating locally the spheroid surface by an equivalent spherical surface. The simulation is first tested on a sphere suspension, results are compared with known experimental and numerical data and good agreement is found. Results are then presented for suspensions of oblate spheroids of two mean aspect ratios of 0.3 and 0.2. Results for the relative viscosity η_r, normal stress differences N_1 and N_2 are reported and compared with the few available results on oblate particle suspensions in a hydrodynamic regime. Evolution of the orientation of the particles is also observed and a clear alignment with the flow is found to occur after a transient period. A change of sign of N_1 from negative to positive as the particle concentration is increased is observed. This phenomenon is more significant as the particle aspect ratio increases. It is believed to arise from a change in the suspension microstructure as the particle alignment increases.

Thursday 11:25 Lecture Hall SC49

Dynamic simulation of non-spherical suspensions

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Rheology of non-colloidal non-spherical suspensions in simple shear flow has been investigated by particle-level simulation. A simple approach to modelling a non-spherical particle in a Newtonian fluid is made by considering the particle to be composed of spheres connected by Hookean constraint forces acting along the line-of-center direction. Bending and twisting forces can be ignored due to the three-dimensional cluster structure. Hydrodynamic interactions are evaluated by pair-wise summation of Rotne-Prager disturbance velocity of spheres. An isolated rod-like particle in simple shear exhibits periodic closed orbit which is commonly referred to as Jeffery orbit. The orbit period of rod-like particle as a function of aspect ratio is consistent with literature results. Short-range repulsive force is included to model non-spherical particulate suspensions. Dynamic simulations of rod-like and plate-like suspensions have been conducted. In both cases, particle orientation distributions from the model are found to be in reasonable agreement with literature results. Also, rheological properties have been evaluated by two different approaches: orientation distribution and direct computation of particle stress.

Thursday 11:50 Lecture Hall SC50

Performance of various moment closures in simple and periodic shear and turbulent channel flow of fiber suspensions

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The dynamics of a dilute Brownian fiber suspension can be described by the moments of the orientation distribution function. In this approach, a closure model expressing the fourth moment in terms of the second moment is needed. On the other hand, a direct computation is also possible by solving the Fokker-Planck equation describing the fibers dynamics, e.g. by a Monte-Carlo method. We investigate the accuracy of different closure models against the results obtained by a Monte-Carlo method in simple shear, periodic shear and turbulent channel flows. Normalization, quadratic, hybrid, Hinch and Leal's, natural and IBOF closure models are considered here. In simple shear flow, the IBOF model

gives the highest accuracy at the highest computational cost. As the Peclet number (Pe) decreases, the accuracy of the different models gets closer. For periodic shear, the results are close to each other except for the normalization and the quadratic models. For non-Brownian fibers (Pe at infinity) only the IBOF model gives very good results and the other models perform equally badly. In turbulent channel flow, only at small Pe the IBOF is more accurate, and at high Peclet numbers all models yield almost the same accuracy. In the non-Brownian case, all closures including the IBOF lead to peak errors of about 10% in the second moments. It means that in turbulent drag reduction at high Pe, one can use less sophisticated and computationally cheaper models such as normalization, quadratic and hybrid instead of the IBOF model which is computationally much more expensive than the others.

Symposium SM
Polymer Solutions and Melts

Organizers: Ralph Colby, Jules J. Magda and Lynden Archer

Thursday 7:45 Meeting Rooms KLOP SM31

Increasing polyelectrolyte viscosity by addition of salt

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High molecular weight polyelectrolytes are commonly used as drag reducers, viscosity enhancers in food and other applications, and as drilling fluids in enhanced oil recovery. An understanding of the rheology of polyelectrolyte solutions under various solvent conditions is critical to their efficient use in industry. Polyelectrolyte concentrations ranging from dilute to concentrated in both water and salt solution are studied using oscillatory and shear rheology. In salt free solution, the scaling of xanthan viscosity is found to agree well with predictions. Three critical concentrations (c^*, c_e, and c_D) marking changes in the viscosity scaling behavior in water are determined. In 50 mM NaCl, the viscosity scaling is well described by theory for a neutral polymer in a theta solvent and two critical concentrations (c^*, c_e) are observed.

As expected for polyelectrolytes, the viscosity of xanthan is observed to decrease significantly upon addition of NaCl for concentrations in the semidilute unentangled regime. The decrease in viscosity is accompanied by a decrease in the magnitude of both the storage and loss moduli. The crossover frequency shifts to a higher frequency corresponding to a shorter relaxation time. However, for xanthan concentrations above c_D, the zero shear rate viscosity increases by a factor of four in the presence of 50 mM NaCl. The magnitude of both the storage and loss modulus also increases significantly in the presence of NaCl. The crossover frequency shifts to lower frequencies corresponding to longer relaxation times. Similar increases in viscosity upon addition of salt are measured for several other high molecular weight polyelectrolytes (HPAM, PAA, Carrageenan, Welan).

The effects of the size and charge of added salt molecules on both the shear and oscillatory rheology of polyelectrolyte solutions are also examined.

Thursday 8:10 Meeting Rooms KLOP SM32

AC-polarization and conformational transition of single weak polyelectrolyte in uniform AC-electric fields

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Despite the emerging interest in employing AC-electrokinetics to effectively manipulate and assemble supramolecular aggregates, such as AC-field induced protein crystallization and DNA hybridization, the detailed AC-polarization mechanism of biomacromolecules remains little understood. In this work, we examine the conformational dynamics of synthetic polyelectrolytes under AC-electric fields of varied frequencies (10-1000 kHz) and amplitudes (1-20 V) by using fluorescence correlation spectroscopy (FCS) at a single molecular level. We focus on poly(vinyl pyridine) (PVP) as a model weak polyelectrolyte whose coil-to-globule conformation in the bulk solution can be tuned by adjusting the pH and ionic strength. To avoid the conformational change due to the imposed dielectrophoretic (DEP) force on PVP in a nonuniform AC-field, PVP is placed between two parallel quartz plates coated with ITO to achieve a uniform AC-field, where the PVP concentration is kept constant without polymer assembly at varied AC-frequencies across two plates. Surprisingly, we observe the abrupt collapse of a PVP coil to form a globule when AC-frequency is applied below 200 kHz; furthermore, the critical AC-amplitude to induce the coil-to-globule transition shows a strong correlation with critical AC-frequency and solution pH. A picture that the counterion redistribution near a PVP chain results in a cyclic compression force on the polyelectrolyte coil is accounted for the AC-induced conformational transition and further examined with varied pH and medium conductivity.

Thursday 8:35 Meeting Rooms KLOP SM33

The viscoelastic behavior of polymer/oligomer solutions

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The viscoelastic properties of poly(a-methyl styrene), its hexamer, and their athermal solutions at various concentrations are studied. Master curves for the dynamic shear responses, G' and G", are successfully constructed for both the pure materials and the solutions, indicating the validity of the time-temperature superposition principle. The temperature dependence of the shift factor follows the Vogel Fulcher behavior over the temperature range studied. The segmental dynamics appear unchanged by concentration, which is different from the calorimetrical studies where solutions show obviously broadened glass transitions. We suggest that the broadening of calorimetric transition for our mixtures is due to the change in temperature dependence of the segmental dynamics rather than a broadening of the dynamic spectrum. The rubbery plateau decreases linearly with the square of the polymer concentration. The length of the plateau increases with increasing polymer concentration. The influence of the instrument compliance on the results is also discussed.

Thursday 9:00 Meeting Rooms KLOP SM34

Thermo-thickening in solutions of telechelic associating polymers and cyclodextrins

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Telechelic associating polymers (hydrophilic ethoxylated backbone, hydrophobic n-alkyl end-groups) form viscous solutions in water due to associations between the hydrophobes. The addition of a, b, or g-cyclodextrin (CD) substantially reduces the solution viscosity because the CD molecules envelop and sequester the hydrophobes. The present paper explores the variation in polymer-CD solution viscosity with temperature. We find that, in the case of a-CD alone, the solutions show "thermo-thickening", i.e., the viscosity increases from 25 to ca. 60°C whereupon it reaches a peak value and then drops. In contrast, solutions with b- and g-CD show monotonic drops in viscosity upon heating. At a fixed polymer content, the thermo-thickening is higher for higher a-CD concentrations. We have also studied how surfactants and lipids impact the thermo-thickening. Addition of single-tailed micelle-forming surfactants causes the viscosity to revert to the more typical decreasing trend with temperature. However, addition of double-tailed lipids to a polymer/a-CD solution accentuates the thermo-thickening behavior. The thermo-thickening is explained by the propensity of a-CDs to unbind from the hydrophobes and thread onto the polymer backbone when temperature is raised.

Thursday 9:25 Meeting Rooms KLOP SM35

Development of a comprehensive rheological property database for EOR polymers

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One of the most important factors in chemical enhanced oil recovery (EOR) is mobility control, for which partially hydrolyzed polyacrylamide (HPAM) and other polymers are extensively used. Rheological properties of the EOR polymer solutions depend sensitively on the polymer's molecular properties and concentration, salinity and temperature, as well as shear rate. To develop a comprehensive database that quantifies the dependence on above variables, rheological measurements with many commonly employed EOR polymers were made, and the parameters in the rheological models that correlate polymer viscosity with the variables were obtained. Accurate description of polymer viscosity as the polymer flows in the reservoir is critically important in modeling the EOR process behavior and field performance by simulation. Because the data and the correlations obtained cover a wide range of reservoir conditions, this work can be conveniently employed for laboratory process design and scale-up simulations. In addition to the steady shear viscosities, the oscillatory rheological properties have also been measured to better understand the polymer behavior during flow in porous media. In view of the recent EOR applications to recover viscous oils and to offshore fields, the data were obtained for wider ranges of the polymer molecular weight and concentration, and salinity, than those reported in the literature. The rheological properties for commonly used EOR polymers under wide range of conditions have been systematically measured. This is a first comprehensive compilation of the rheological data and their correlation parameters for the recent polymer products whose properties may be different from the similar polymers used during the earlier period of active chemical EOR research.

Thursday 10:10 Meeting Rooms KLOP SM36

Coarse graining at various scales for dilute polymer solutions

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In an earlier work [Jain, S. and Larson, R. G., Macromolecules (2008) 41, 3692], simulations of an atomistic polymer chain showed that the bending and torsional potentials suppress fast modes of relaxation. Our present work probes several new aspects associated with the atomistic polymer chain model. We compare the behavior of the same atomistic chain with its corresponding coarse-grained counterpart in extensional and shear flows. The unraveling dynamics in extensional flows and the mean stretch for shear flows are in good agreement with each other, suggesting the success of the coarse-grained representation. We also study the static and dynamic properties of a polystyrene chain using explicit-solvent molecular dynamics (MD) simulations with benzene as solvent. A methodology is proposed to develop force field for implicit-solvent MD simulations for the above system. Finally, we compare the relaxation dynamics of polystyrene chain predicted by the implicit- and explicit-solvent MD simulations.

Thursday 10:35 Meeting Rooms KLOP SM37

Time-composition superpositioning in the rheological behavior of triblock copolymer/selective co-solvent blends

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Thermoplastic elastomers composed of styrenic triblock copolymers are of great importance in applications such as adhesives and vibration dampening due to their resilience and facile processing. The swelling of these polymers by adding midblock selective solvents or oligomers provides an easy route to modify the morphology and mechanical behavior of these systems. In this study we consider a ternary blend of a poly[styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymer and mixtures of two midblock selective co-solvents: a mineral oil that is liquid at ambient temperature and a glassy oligomeric tackifier resin that exhibits complete solubility in the midblock matrix. We use dynamic rheology to study the viscoelastic response of a wide variety of systems under oscillatory shear. The copolymer concentration is varied between 15 and 35 wt% while the resin/oil ratio in the midblock-solvent matrix is independently varied. Small angle x-ray scattering spectra reveal the formation of spherical polystyrene micelles. Tensile oscillatory tests performed at low temperatures confirm that the tackifier resin and oil are completely miscible with the midblock. Frequency spectra acquired at ambient temperature show that increase of the resin/oil ratio serves to increase the glass transition temperature (Tg) of the midblock and slow down midblock relaxation. The viscoelastic behavior obtained shifts in the frequency domain depending on the resin/oil ratio. For each copolymer concentration, all frequency data can be shifted by time-composition superpositioning (tCS) to yield a single master-curve with horizontal shift factors that can be correlated to the Tg of the co-solvent. tCS fails at large time scales due to relaxation processes associated with the pullout of polystyrene endblocks from micelles. The extent of tCS failure depends on endblock length and co-solvent quality with respect to polystyrene, which can be discerned by dynamic temperature sweep experiments.

Thursday 11:00 Meeting Rooms KLOP SM38

Mechanical hole burning spectroscopy in polymer solutions: Is the hole related to the length scale?

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We have been using Mechanical Spectral Hole Burning (MSHB) in our labs to investigate dynamic heterogeneity for polymeric materials, which exhibit relatively weak dielectric responses. The dielectric hole burning has been interpreted to occur because of spatial and dynamic heterogeneity in complex fluids. In the prior work, MSHB was applied to a densely entangled block copolymer and successfully distinguishes the heterogeneous from the homogeneous states (below and above the ODT). In the current work, a series of polystyrene (PS) solutions was chosen to investigate the effect of different types of heterogeneity on mechanical spectral hole burning and in particular to evidence a length scale associated with the hole burning response. Three types of heterogeneity can be investigated by using polymer solutions: the entanglement spacing; the entanglement density (or number of entanglements per chain); and the chain end density. The length scale was varied by changing either solution concentration or molecular weight of the PS. Different types of dynamics from close to the Rouse regime into the terminal region were also examined. Our results are consistent with a heterogeneous dynamics over the time scales from close to the Rouse regime into the rubbery plateau regime and the rubbery plateau-to-terminal flow transition regime. Terminal relaxation dynamics, on the other hand, were found to be homogeneous for the PS/diethyl phthalate solutions investigated. The results also indicate the properties of the burned hole are dominated by the type of dynamics rather than the length scale of heterogeneity.

Thursday 11:25 Meeting Rooms KLOP SM39

Tracking of phase separation kinetics in copolymer solutions using rheological measurements

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The rate of solvent removal during the film casting of block copolymer solutions is known to have a significant effect on the performance of the film in such processes as proton transport and desalination. The performance is related to the morphology which is believed to be related to the rate of solvent removal through phase separation kinetics. Rheological methods are being investigated as a way to monitor phase separation kinetics of block copolymer solutions at order-order transitions while removing solvent at various drying rates and temperatures. The Avrami equation is being used to model the time-dependence of phase separation by using measurements of G' and G" to fit the Avrami exponent and rate constant. Polystyrene-block-polybutadiene and polystyrene-block-polyisoprene of varying compositions in numerous solvents are being used initially in this work. Preliminary work involves identifying order-disorder transitions and order-order transitions and studying the kinetics about the order-disorder transitions to validate the techniques. Further, the ability to use the Avrami equation relies on the system undergoing a process that is comparable to crystallization. Studies are being performed to verify that the method remains valid while changing between ordered structures. TEM images along with SAXS can be used to obtain information on the morphological transitions occurring support the predictions of the Avrami equation based on growth dimensions. Isothermal tracking of phase separation kinetics at various constant concentrations is also underway. Results show distinct changes in the time-dependence of G' and G" at various concentrations and for different polymer compositions. However, the order-order transitions must be determined before more meaningful interpretations of the observations can be made.

Thursday 11:50 Meeting Rooms KLOP SM40

Thin film lubrication based on PDMS networks

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This study investigates on the interfacial friction and wear properties of surface-tethered cross-linked polymer thin films. Thin, two-tiered films produced by covalently tethering polydimethylsiloxane (PDMS) networks to self-assembled monolayers manifest the lowest friction coefficient (mu = 0.0039) recorded for a dry lubricant film. To determine the origin of this result, we introduce controlled amounts of pendent and free PDMS chains into optimal PDMS network films and explore their effects on interfacial friction, wear, and film modulus. Using a combination of atomic force microscopy, nanoindentation, and rheology measurements we determine the molecular-scale processes responsible for lubrication properties of thin PDMS films.

Symposium IC
Industrial and Complex Systems Rheology

Organizers: Matt Liberatore and Jim Oberhauser

Thursday 7:45 Hall of Ideas G IC6

Capillary rheometry of bread dough: Experimental and conceptual issues

Christopher I. Hicks and Howard See

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An Australian hard wheat flour-water dough has been characterised using parallel plate and capillary rheometers over an extensive range of apparent shear rates (10-3-103s-1) relevant to process conditions. Shear rates up to 104s-1 were explored. Torsional measurements showed that the shear viscosity of dough increased with strain to a maximum value then decreased, suggesting a breakdown of the dough structure. This was consistent with other published data on doughs. Both torsional and capillary experiments revealed the shear-thinning behaviour of dough, which was described by a power-law viscosity model. Pressure fluctuation was observed in the capillary data and increased with shear rate, suggesting the velocity profile of the material changes as it flows down the capillary which could be collectively due to sample heterogeneity, surface fracture, or release of entrapped gas. The wall slip behaviour of dough was investigated and found to be diameter dependent and occur at a critical shear stress of approximately 10 kPa. A two regime power law viscosity model was proposed, as the power law index changed from approximately 0.3 in the low shear rate range to 0.67 in the high shear rate range. Current results demonstrate that capillary rheometry is a viable means of rheologically testing dough at high shear rates provided pressure fluctuation is carefully considered and capillary rheometry corrections, namely wall slip, are accounted for.

Thursday 8:10 Hall of Ideas G IC7

Rheology and phase behavior of nanovesicle-polymer mixtures

Basavaraj M. Gurappa[1], Naa Larteokor McFarlane[1], Matthew L. Lynch[2], and Norman J. Wagner[1]

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Polymer-surfactant mixtures are commonly used in a number of industrial formulations. The processing and exploitation of these complex systems requires a fundamental understanding of polymer-vesicle interactions, phase behavior and flow properties. Theoretical predictions for the behavior of these mixtures are particularly challenging because the vesicles are 'semi-soft' with a radius comparable to the Rg of the polymer and even polymer with similar charge as the vesicles exhibit finite absorption on the vesicles, meaning these systems lie at the fringe of conventional theories. This work was undertaken to bring some predictability to the behavior of these mixtures. To this end, nano-sized vesicles were prepared by agitation of a concentrated paste of cationic surfactant and characterized by dynamic light scattering. The polymer-surfactant interactions were studied by isothermal titration calorimetry, allowing quantitative determination of absorption isotherms of polymer on the vesicles. The phase behavior was studied by visual inspection of mixtures prepared by varying vesicle volume fraction, polymer concentration and polymer size, while using high- and low-molecular weight PEO and PVP. These studies provided strong evidence that polymer (absorbed or soluble) drives the observed phase behavior. The flow properties measured by shear rheology (capillary and stress-controlled measurements) unambiguously distinguishing between bridging and depletion as the mechanism of polymer-induced phase separation. These results are discussed in context on AO and PRISM theories.

Thursday 8:35 Hall of Ideas G IC8

Vibrational effects on particle sedimentation in complex fluids

Patrick T. Spicer and Marco Caggioni

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Particle sedimentation in complex fluid products is rarely desirable and rheological modification is frequently used to guard against such instabilities. However, a fluid rheology that prevents sedimentation under static conditions may not be useful during transport when a wide range of vibrational frequencies is encountered. This work studies the vibration-induced sedimentation of particles suspended in yield-stress

fluids using video observations. Comparisons are made with theoretical predictions and national transport guidelines, while the effects of thixotropy are also examined.

Thursday 9:00 Hall of Ideas G IC9

High shear rate rheometry using narrow gap rotating parallel plates

David W. Giles[1], Thomas E. Briese[1], Ethan B. Secor[2], Christopher W. Macosko[1], and Robert B. Secor[3]

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Industrial coating processes often use narrow gaps, high shear rates, and non-Newtonian liquids. In rotational rheometers with parallel plate geometry, the shear rate is inversely proportional to the gap, and gaps and shear rates comparable to those used in industrial coating processes seem possible, but measurements with such small gaps require special care. Connelly and Greener (1985) showed that two artifacts occur with this narrow-gap geometry: a gap error and a shear heating error (at high rates). With narrow gaps, less than 100 microns, the gap error can be the same order of magnitude as the assumed gap, but they showed for Newtonian liquids how this error can be accounted for, and how shear heating can be detected and avoided using fast shear rate ramps. Dontula et al. (1999) reported additional analysis of shear heating in narrow gap viscometry. Recently, Davies and Stokes (2008) reported that accurate high shear rate rheometry is achievable with commercial parallel plate rheometers and narrow gaps, 5 (!) to 100 µm, even with non-Newtonian liquids. They did not report the same difficulty with shear heating, but used the procedures of Connelly and Greener to correct for the gap error. We assess the accuracy of data obtained with narrow gap parallel plate rheometry using Newtonian and non-Newtonian liquids, and determine reasons why shear heating is or is not a problem.

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Thursday 9:25 Hall of Ideas G IC10

Consideration of elongation effects for both fiber reinforced and unfilled fluids by means of an invariant constitutive model

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In polymer engineering a constitutive model based on Stokes' law of friction is widely used for modeling the flow behavior of so-called generalized Newtonian fluids. Stokes' law of friction treats the rheology of generalized Newtonian fluids. Generalized Newtonian fluids incorporate the idea of deformation-rate-dependent viscosities and are considered as non-memory continua. In contrast to such generalized Newtonian or Stokesian continua, fluids showing deformation history dependent - memory - effects are termed non-Newtonian. The established interpretation of the Stokes' law of friction for generalized Newtonian fluids is in effect a restrictive simplification of the Stokesian stress tensor. According to this commonly used rheological model, the shear viscosity represents the scalar proportionality factor coupling the deviatoric stress tensor and the rate-of-deformation tensor. As a result, strain rates in the Navier-Stokes equation are evenly scaled as shear rates. In process simulation programs, strain rates are either neglected or scalarly multiplied by extensional viscosities or implicitly considered by utilizing a representative quantity of the real deformation state, the magnitude of the rate-of-deformation tensor. In view of the increasing anisotropy of today's applied polymer systems and the ongoing micro- and nanofluidics developments, the formulation of invariant constitutive models for both filled and unfilled continuum fluids becomes indispensable. Based on the derivation of Stokes' law of friction and Gibson's proposal for transversally isotropic fluid elements, a novel universal constitutive formulation for the deviatoric stress tensor is developed. For this purpose, the assumptions and postulates of Stokes are reviewed and the derivation of the Navier-Stokes equation is discussed. Due to the invariant and effect segregated proposed constitutive formulation, the model's employment in differential viscoelasticity models is further discussed.

Thursday 10:10 Hall of Ideas G IC11

Bulk and surface molecular orientation distribution in injection molded liquid crystalline polymers: Experiment and simulation

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Bulk and surface distributions of molecular orientation in injection molded plaques of thermotropic liquid crystalline polymers have been studied using a combination of analytical techniques, coordinated with process simulations using the Larson-Doi 'polydomain' model. Two-dimensional wide-angle x-ray scattering (2-D WAXS) in transmission was used to map out the detailed bulk orientation distribution. Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) were utilized to probe the molecular orientation states to about ~5 µm and ~2 nm, respectively, below the sample surface. These noninvasive, surface-sensitive techniques yield results that agree with each other fairly well, thus providing complementary validation of the robustness of these methods. A nearly exact analogy between Larson-Doi and fiber orientation models has allowed the first simulations of LCP injection molding, using commercially available process simulation tools. The simulations successfully predict many fine details in the bulk orientation distribution across the sample plaque. Direct simulation of surface orientation at the level probed by FTIR-ATR and NEXAFS was not possible due to the limited resolution of finite element mesh. However, simulation results extracted from shear-dominant skin region (~0.4 mm) are found to provide a qualitatively accurate indicator of near surface orientation. Finally, the simulations capture the relative relation of bulk and surface orientation states across the different regions of the sample plaque.

Thursday 10:35 Hall of Ideas G IC12

On-line shear stress measurement during the injection molding process using a novel rheo-dielectric sensor

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This paper presents the development and experimental results of a novel rheo-dielectric sensing technique, based on dielectrostriction measurement, for on-line shear stress measurement during the injection molding process. Dielectrostriction is a rheo-dielectric effect, which is defined as a variation of dielectric properties of material under deformation or during flow. The dielectrostriction effect resembles the well-known birefringence phenomenon. As birefringence in liquid polymers is described by the stress-optical relationship, a stress-dielectric relationship exists for and is applicable to dielectrostriction. In addition, dielectrostriction measurements can be performed on both transparent and opaque materials with a much simpler data acquisition technique and can be implemented for on-line stress measurement for polymer processing. In this study, we employed the dielectrostriction technique to perform shear stress measurement during the injection molding process. A planar capacitor sensor rosette has been developed and attached to the surface of an injection mold to obtain the dielectrostriction signal under various injection speeds for shear stress analysis of polymer melts. The experimental data in terms of shear stresses compared well with simulation results, suggesting that on-line dielectrostriction measurement for polymer processing applications is a feasible option.

Thursday 11:00 Hall of Ideas G IC13

Planar extensional flow resistance of a foaming plastic

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Extrusion of a foaming plastic generally involves strong planar extensional flow in the die. As a result, both shear and extensional viscosities affect the nucleation of gas bubbles and their growth. In this study, a novel technique is developed to determine both viscosities for a polymer melt or a polymer/gas solution. The technique depends on a die consisting of a straight rectangular channel with a high aspect ratio, followed by a thin planar hyperbolic channel. The hyperbolic shape induces flow with a nearly constant extensional rate. The shear viscosity is determined from the pressure drop along the straight channel, and the extensional viscosity is determined from the pressure drop along the hyperbolic channel, taking shearing and the exit pressure into account. Analysis of flow in the hyperbolic channel assumes that the extensional viscosity depends on the strain as well as the extensional rate.

Two dies were made with the same shape but different thicknesses, and the first measurements were made with the polymer alone, a foaming-grade polystyrene. Shear viscosity measurements from the straight channels compare well with data from commercial rheometers. The corresponding comparison for the extensional viscosity measurements is reasonable, with differences attributed to pre-shearing and the approximated flow field. A polystyrene/CO_2 solution was then tested, with pressure in the die maintained sufficiently high that the gas stayed in solution. Both viscosities were significantly reduced by addition of the CO_2 to the polymer, an effect similar to an increase in temperature.

Thursday 11:25 Hall of Ideas G IC14

Sag in thermoforming

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Thermoforming processes flat plastics sheeting into complex shapes by first melting the sheet, and then by shaping it. While melting, the sheet can extend under its own weight, bringing the middle of the sheet closer to the lower bank of radiative heaters. Called sag, this causes the underside of the sheet to be hotter. To suppress such sag, practitioners stretch the sheet laterally, employing cambered transfer rails to keep the sheet taut. In this paper, we model sag analytically, employing a transport phenomena approach for a long thin rectangular Newtonian sheet in cylindrical coordinates. We uncover a universal dimensionless relation between sag and time, and a useful dimensionless group that we call sagability. We find that, unsuppressed, to leading order, the middle of the sagging sheet descends with the cube root of time. Also, we discover a particular time at which sag increases rapidly, without bound, and we call this sag runaway. We also show how to use sag measured in a laboratory former to deduce the Newtonian viscosity of a thermoforming resin at its softening point. We then test this deduction with our new experimental measurements. For practitioners, we provide a design inequality for rail cambering, and supplement this with a worked example.

Thursday 11:50 Hall of Ideas G IC15

Flow properties and extrudate swell of monodisperse polymer melt composites

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Rheological properties of multiphase systems like polymer composites and their prediction using constitutive equations are of high interest for understanding the processing performance of thermoplastics. In the literature many publications deal with commercial polymeric materials as a visco-elastic matrix while for the case of monodisperse polymers not much data have been published. In the present study the complex flow behaviour of monodisperse polyisoprene melts filled with micrometer-sized spherical glass bead particles has been investigated.

The pure matrix and composites with different volume fractions of glass beads have been investigated by uniaxial elongational, capillary and rotational shear rheometry. The effects of filler addition are discussed with respect to the linear and non-linear flow behaviour as well as extrudate swelling and melt fracture behaviour at isothermal conditions. The rheo-optical analysis shows that the wave length of the major surface distortions increases with flow rate while the magnitude of the melt fracture and surface instabilities is reduced with increasing glass-bead concentration.

Symposium GG
Gels, Glasses and Jammed Systems

Organizers: Corey O’Hern and Subramanian Ramakrishnan

Thursday 7:45 Meeting Rooms MNQR GG26

Jamming in systems composed of frictionless ellipse-shaped particles

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We study the structural and mechanical properties of jammed ellipse packings, and find that the nature of the jamming transition in these systems is fundamentally different from that for spherical particles. Ellipse packings are generically hypostatic with more degrees of freedom than constraints. The spectra of low energy excitations possess two gaps and three distinct branches over a range of aspect ratios. In the zero compression limit, the energy of the modes in the lowest branch increases quartically with deformation amplitude, and the density of states possesses a delta-function at zero frequency. We identify scaling relations that collapse the low-frequency part of the spectra for different aspect ratios. Finally, we find that the degree of hypostaticity is determined by the number of quartic modes of the packing.

Thursday 8:10 Meeting Rooms MNQR GG27

Signatures of jamming in flowing and static granular materials

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The study of jamming of static packings of frictionless spheres has revealed many interesting features that signal the approach of the jamming transition as the packing fraction is varied. This has motivated recent efforts to investigate how jamming occurs under the influence of other parameters such as shearing and thermal agitation. Using granular dynamics simulations we compare and contrast how signatures of jamming in frictionless and frictional systems depend on how the jamming transition is approached. In static systems the packing fraction is varied as previously studied in purely frictionless systems. This method provides a suitable method to identify the random loose packed state. In the other case, structural and dynamical features are studied in granular flows down an inclined plane as the inclination angle is reduced towards the angle of repose.

Thursday 8:35 Meeting Rooms MNQR GG28

Testing the Edwards' hypothesis in small granular systems

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Statistical methods modeled on equilibrium statistical mechanics are often applied to describe properties of static granular packings. These approaches are based on the Edwards' hypothesis stating that all mechanically-stable static configurations of a granular system, satisfying given macroscopic constraints, are equally probable. Since these methods successfully describe certain properties of granular packings, this fact is used to justify the Edwards' assumption, in the absence of a direct proof of validity of this hypothesis.

We use a combination of coordinated numerical simulations and a novel experimental technique to directly measure probability distribution of mechanically stable packings in small systems of frictionless granular disks. We find that packings occur as discrete points in the

configurational space, and, contrary to the Edwards' assumption, have highly nonuniform probabilities. Moreover, the packing probabilities are robust with respect to the packing-generation procedure. Our results suggest that the most frequent MS packings may dominate the structural and mechanical properties of granular systems. This observation is a crucial first-step in constructing a statistical description for large granular systems.

Thursday 9:00 Meeting Rooms MNQR GG29

Anisotropic power law strain correlations in sheared amorphous jammed materials.

Craig E. Maloney[1] and Mark O. Robbins[2]
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The local deformation of steadily sheared two-dimensional Lennard-Jones glasses is studied via computer simulations at zero temperature. In the quasistatic limit, spatial correlations in the incremental strain field are highly anisotropic. The data show power law behavior with a strong angular dependence of the scaling exponent, and the strongest correlations along the directions of maximal shear stress. These results support the notion that the jamming transition at the onset of flow is critical, but suggest unusual critical behavior. The predicted behavior is testable through experiments on sheared amorphous materials such as bubble rafts, foams, emulsions, granular packings and other systems where particle displacements can be tracked.

Thursday 9:25 Meeting Rooms MNQR GG30

Soft glassy rheology in the hard sphere limit

Thomas K. Haxton and Andrea J. Liu
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We conduct nonequilibrium molecular dynamics simulations to measure the steady state shear stress σ and packing fraction φ as a function of temperature T, pressure p, shear strain rate $d\gamma/dt$, and interaction potential for a fluid of bidisperse, finite-range, soft disks in two dimensions ($d = 2$). We find that the rheology and the packing fraction smoothly approach scaling functions as temperature, pressure, and strain rate are lowered while keeping the dimensionless parameters $kT/a^d p$ and $a(d\gamma/dt)(m/a^d p)^{1/2}$ fixed. Our results point to a common explanation for the glass transition and the colloidal glass transition. Both the temperature-driven glass transition and the density-driven colloidal glass transition can be understood in terms of the sensitive dependence of the rheology of hard spheres on the ratio $kT/a^d p$.

Thursday 10:10 Meeting Rooms MNQR GG31

An empirical constitutive law for concentrated colloidal suspensions in the approach of the glass transition

H. Henning Winter[1], Miriam Siebenburger[2], Matthias Ballauff[2], and Matthias Fuchs[3]
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Concentrated, non-crystallizing colloidal suspensions in their approach of the glass state exhibit distinct dynamics patterns. These patterns suggest a powerlaw rheological constitutive model for near-glass dynamics as presented here. The empirical rheological constitutive equation differs significantly from previous models of near-glass dynamics, but it does not require any new parameters. Parameters and their respective values are identical with the known parameters of MCT. No new parameter was added and none was removed. The new finding as reported here concern the interrelation of these parameters for glass forming materials in the approach of their glass state. The distinct features of the near-glass dynamics allow a clear differentiation between glass transition and gelation in soft matter.

Thursday 10:35 Meeting Rooms MNQR GG32

Complex yielding transition from an attractive glass to a colloidal gel

Nick N. Koumakis and George Petekidis
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Simple hard sphere glasses show a single yielding process that corresponds to the breaking of nearest neighbour cages. The addition of short range depletion attractions causes the system to exhibit a two step yielding process that has been proposed to correspond to an initial particle bond breaking and a subsequent cage breaking process [1]. This work provides rheological experimental evidence and elucidates the origin of the two step yielding process by examining a range of hard sphere colloid concentrations, while keeping the interparticle depletion attractions constant. We examine the linear and non-linear properties of high volume fraction attractive glass to low volume fraction gels with oscillatory and steady rheology. We find that the transition from a highly concentrated attractive glass to a low volume fraction colloid-polymer gel appears to take place gradually with the cage breaking process being substituted by a cluster dominated process as the volume fraction is decreased. Brownian dynamics simulations are used to gain insight on the microscopic rearrangements and structure changes that occur during yield. Different ranges of attraction are also implemented both experimentally and in simulations to solidify our conclusions.

[1] K. Pham et al. J Rheology (2008).

Thursday 11:00 Meeting Rooms MNQR GG33

Scaling of free energy barriers to flow events with applied stress

Daniel Lacks

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Rheological responses depend on both the temperature and the stress loading rate. As described by Eyring, mechanical stress lowers free energy barriers, thus facilitating progress over the barrier by random thermal fluctuations. The Eyring model, which approximates the stress dependence of the barrier height as linear -- this is simply the first term in the Taylor expansion of the barrier height as a function of load, and is appropriate when the barrier height changes only slightly before the system escapes the local free energy minimum (e.g., at high temperatures). However, as the temperature decreases, larger changes in the barrier height occur before the system escapes the free energy minimum, and the linear dependence of the barrier height on stress is not necessarily appropriate. In our work, we calculate the free energy profiles of model polymers as a function of their end-to-end distances, and histogram reweighting method are used to determine the free energy of the protein as a function of its end-to-end distance. In this way we determine how the height of the barrier to unfolding changes when an external force pulls on the molecule. Furthermore, we investigate the relevance of catastrophe theory to these changes in the height of free energy barriers.

Thursday 11:25 Meeting Rooms MNQR GG34

Structure and dynamics of coarsening emulsions

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We investigate the structure and dynamics of a non-aqueous coarsening emulsion. The experiment is performed on an index and density matched emulsion prepared by homogenization with droplets occupying approximately 80% of the volume fraction. Three dimensional visualizations of the droplets are obtained by fluorescent confocal microscopy at different time intervals as the emulsion coarsens. We find that the droplet size distribution matches a Weibull distribution. The pair coordination function as a function of droplet core size shows a peculiar liquid structure where small droplets fill the interstices between big ones. While we observe self similar behavior in droplet growth, the evolution of the droplet size distribution departs from that predicted by mean field theory.

Thursday 11:50 Meeting Rooms MNQR GG35

Controlled jamming of particle-laden interfaces using a spinning drop tensiometer

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Partially-wettable particles often adsorb nearly irreversibly at liquid/liquid interfaces. Under conditions when the interface is crowded with a particle monolayer, "2D jamming" can occur, i.e. the interface loses mobility and displays solid-like characteristics. We studied the jamming of iron oxyhydroxide (FeOOH) particles adsorbed at the interface between ethylene glycol and mineral oil using a spinning drop tensiometer (SDT). With decreasing rotational rate, the cylindrical drop retracted due to interfacial tension, thus reducing the interfacial area and increasing interfacial particle concentration. Accordingly, when the specific interfacial area became comparable to that for a close packing of particles, interfacial jamming occurred and drop retraction was arrested. Fast interfacial contraction or low capillary pressures led to less compact jammed monolayers, i.e. with a larger specific interfacial area. There was also significant hysteresis between compressing vs. expanding the jammed monolayer, suggesting that a certain minimum force is required for unjamming. Limited experiments with the same particles at a mineral oil/ silicone oil interface showed altogether different behavior: a particle-free portion of the interface coexisted with a particle-covered portion, suggesting that the monolayer behavior at this non-polar/non-polar interface is dominated by interparticle attraction.

Symposium FM
Non-Newtonian Fluid Mechanics and Stability

Organizers: Radhakrishna Sureshkumar and Yong Joo

Thursday 7:45 Hall of Ideas J FM16

Viscoelastic flow simulation using the Radial Basis Function Method (RFM)

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For two decades, researchers have been working to model viscoelastic flows in 3D geometries. Although some complex flows have been successfully simulated, they are still limited to low Weissenberg number (We) values while requiring high computational times. RFM offers a novel, simplified approach which has the potential to solve for geometries with a high degree of complexity. The cost benefit of RFM is to use as few nodes as possible while continuing to increase We. 3D geometries with highly non-linear problems, low power law indices and convective diffusion systems have been successfully implemented and compared to analytical solutions. The Giesekus and Phan-Thien Tanner models are implemented into a radial basis functions method simulation to model the flow through non-circular tubes. RFM, also referred to as radial basis functions collocation method is a meshless technique that does not require homogeneous grid points. The method has shown higher accuracy compared to other numerical techniques, even when using a relatively small number of collocation points for a given geometry. The

technique successfully modeled the flow through square tubes, presenting the secondary flows observed experimentally by other researchers. Furthermore, the results are in agreement with Finite Element and Finite Volume numerical approaches. Simulation and experimentation, thus far, have shown that for some materials, such as polystyrene, secondary flow velocities in non-circular geometries are as high as 1% of the main flow velocity. When considering the High Weissenberg Number, meshless grid techniques avoid the limitations presented by typical methods using meshes, such as capturing steep stress gradients at sudden changes in geometry.

Thursday 8:10 Hall of Ideas J FM17

On the limitations of elastic dumbbell based constitutive equations in simulation of flow of dilute polymeric solutions with stagnation points

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Chemical & Biomolecular Engineering, University of Tennessee in Knoxville, Knoxville, TN 37996-2200, United States

In recent years, a number of studies have focused their attention on continuum level computations of dilute polymeric solutions in mixed kinematics flows with stagnation points. Examples include two benchmark flow problems, namely, flow past a cylinder in a channel and sedimentation of a sphere in a tube. These studies have demonstrated that the use of the Oldroyd-B model (Hookean dumbbell) in the computations will lead to divergent normal stresses in the wake of the cylinder/sphere at Weissenberg numbers of order 1. This divergence of the stresses is a direct consequence of occurrence of coil to stretch transition and an unbounded extensional viscosity in the uniaxial extensional flow region of the wake. We have recently performed extensive continuum and multiscale flow simulations in these benchmarks flow problems utilizing the FENE-P constitutive equation and the FENE dumbbell model. These studies have demonstrated that even in the case of a non-linear entropic spring (bounded extensional viscosity) the gradient of normal stresses in FENE-P computations also diverge in the wake region at Wi˜O(1) for polymer chains with large finite extensibilities. The occurrence of this phenomena has been directly correlated with the large stress gradients that arise from presence of highly over extended states (dumbbell lengths > the maximum chain extensibility, i.e., violated states). However, at lower finite extensibilities, the stress gradients in the wake can be resolved in the FENE-P computations even in presence of significant number of violated states. Hence, computations can be pursued to much higher Wi. However, the accuracy of interesting flow dynamic predictions such as recirculation in the wake of the sphere at high Wi is questionable due to the large contribution to the total polymer stress arising from violated states. A direct comparison of the FENE-P and FENE computations reveals that the closure approximation used in the FENE-P model is not appropriate for complex kinematics flows with stagnation points.

Thursday 8:35 Hall of Ideas J FM18

Measurement technique and data analysis of extensional viscosity for polymer melts by Sentmanat Extensional Rheometer (SER)

Johanna Aho[1], Victor H. Rolón-Garrido[2], Seppo Syrjälä[1], and Manfred H. Wagner[2]
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Sentmanat Extensional Rheometer (SER) is a device used for characterizing the extensional flow properties of various substances, for example polymer melts. We measured the transient extensional viscosity of low-density polyethylene at different temperatures using SER in combination with MCR301 rheometer (Anton Paar) and compared the results with the ones obtained with Rheometrics Melt Extensiometer (RME) and Münstedt Tensile Rheometer (MTR). Moreover, we compared the experimental data to the theoretical approach by Molecular Stress Function (MSF) model.

The main purpose of this work was to pay attention to the possible errors and inaccuracies related to measurement of extensional viscosity and to bring up the different issues that should be considered in experiments and calculation in order to get reliable results. We achieved the best results performing the measurements using long pre-tempering time of the device, mounting the temperature sensor tight next to the SER frame, and fixing the sample without clamps. In addition, we corrected the experimental data taking into account the changes of the sample dimensions due to thermal expansion and pre-stretching. The corrected results were well in accordance with RME and MTR; although the maximum values achieved in transient tests were lower. The MSF model was able to describe the strain hardening behavior at all three temperatures by the same two non-linear parameters.

Thursday 9:00 Hall of Ideas J FM19

A smoothed-particle-hydrodynamics-based fluid model with a local shear-rate dependent viscosity: Application to flow of a suspension with a non-Newtonian fluid matrix

Nicos S. Martys[1], William L. George[1], Steven G. Satterfield[1], Didier Lootens[2], Pascal Hebraud[3], and John G. Hagedorn[1]
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A smoothed particle hydrodynamics (SPH) based approach is utilized to obtain a set of numerical equations for approximating a non-Newtonian fluid with spatially dependent viscosity. To test this approach, flow fields obtained by direct numerical solution of the general Naver-Strokes equation using the 'regularized' Bingham model of Papanastasious, which has a shear rate dependent viscosity, are compared to those obtained by the SPH model. Very good agreement is obtained for the case of simple pipe flows. As an application of this model, the effect of having a non-Newtonian fluid matrix, with a shear rate dependent viscosity in a moderately dense suspension is examined. Simulation results are compared to experimental data of mono-sized silica particles in a shear thinning fluid matrix. The evolution of the local shear rates, viscosity and stress fields under application of a constant rate of strain is described for such systems. We also consider the case of non-spherical particles. Here simulation results are compared with experiments on sand particles in a calcium carbonate paste.

Thursday 9:25 Hall of Ideas J FM20

An eXtended Finite Element Method (XFEM) for the simulation of the flow of viscoelastic fluids with suspended particles

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We present an eXtended Finite Element Method (XFEM) combined with DEVSS-G/SUPG formulations for the direct numerical simulation of the flow of viscoelastic fluids with suspended rigid particles. In this method, the finite element shape functions are extended through the partition of unity method (PUM) by using virtual degrees of freedom as the enrichment for the description of discontinuities across interface. For the whole computational domain including both the fluid and particles, we use a regular mesh which is not boundary-fitted. Then, the fluid domain and the particle domain are fully decoupled by using XFEM enrichment procedures. The interaction of the fluid and particles is considered as a boundary condition on the interface by using constraints implemented with Lagrange multipliers. For moving particle problems, we incorporate temporal arbitrary Lagrangian-Eulerian (ALE) scheme without any re-meshing. Furthermore, local mesh refinements around the interface are achieved using grid deformation methods, in which the number of elements is not increased. For a validation of the proposed method, we show numerical results for the flow around a stationary particle using the Oldroyd-B model, which is a well known benchmark problem. The accuracy and convergence have been verified by comparing with boundary fitted mesh problems. The results are also compared with fictitious domain methods. Our method shows a significant improvement of local accuracy around the particle compared to the fictitious domain method. We are able to obtain similar solutions compared with boundary fitted mesh problems. We also show the results of a freely moving particle suspended in a fluid between two rotating cylinders. When XFEM is combined with the grid deformation method, we can obtain converged solutions with significantly reduced computation time.

Poster Session

Symposium PO
Poster Session

Organizers: Chinedum Osuji and Danilo Pozzo

Wednesday 6:10 Grand Terrace PO1

Optically actuated micromanipulation of silicon nanomembranes

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We present progress in manipulating silicon nanomembranes using a functionalized bead attachment mechanism based on holographic optical tweezers. This approach provides a non-contact means of directing motion of the nanomembranes while limiting the risk of damage to the silicon due to optical absorption and laser heating. The attached functionalized bead acts as a trappable microscopic handle and allows nanomembranes to be controlled and translated in a solution. These forces are controlled using a near-infrared (1067 nm) holographic optical tweezers system with total beam powers on the order of 500 mW, allowing nanomembranes to be transported distances well into the millimeter range. The silicon nanomembranes are macroscopic free-standing sheets of single-crystal silicon which can be as thin as 10 nm or less. The thinness of the membranes imparts unique electronic, optical and mechanical properties. This characteristic, combined with the ability to precisely engineer their dimensions, makes silicon nanomembranes ideal candidates for use in new electronic and photonic devices. The nanomembranes utilized for this work have controlled thicknesses of 220 nm and areas reaching up to 200x200 microns. Other methods for directed motion of silicon nanomembranes will be discussed along with an outline of potential new techniques and applications for three dimensional optical manipulation and assembly.

Wednesday 6:10 Grand Terrace PO2

Creep properties of cell wall layers and compound corner middle lamellae in wood

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Bulk wood properties are derived from an ensemble of processes taking place at the micron-scale, and at this level the properties differ dramatically in going from cell wall layers to the middle lamella. To better understand the properties of these micron-scaled regions of wood, we have developed a unique set of nanoindentation tools that allow us to measure local elastic modulus and hardness creep properties. The creep measurement entails a technique called broadband nanoindentation creep (BNC), which is able to probe the flow behavior across 4 decades of strain rate. Because conventional nanoindentation techniques are poorly suited for testing highly heterogeneous specimens, such as wood cells, we have developed a special method for removing artifacts caused by heterogeneities. After these artifacts are removed, the elastic modulus can be determined in the usual way. In loblolly pine, we measure the properties of cell wall layers and compound corner middle lamellae (CCML) of both untreated and ethylene glycol treated wood. The ethylene glycol plasticizes both the cell wall layers and CCML.

Wednesday 6:10 Grand Terrace PO3

Improved solubility of drug molecules by means of the development of polymeric cocrystals: A structural and rheological study

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Polymeric cocrystals can be formed by introducing small molecules into pockets of free space in polysaccharide matrices. Our research demonstrates that iota-carrageenan is a suitable system to prepare polymeric cocrystals by encapsulating a variety of drug and nutraceutical compounds. X-ray structural analyses of iota-carrageenan clearly show the presence of cavities in between a pair of polymer double helices. These free spaces have the potential to bind small molecules, and results show marked changes in the lattice dimensions upon their encapsulation. Rheological measurements provide distinct differences between viscosities of iota-carrageenan (IC) and those of polymeric cocrystals (PCs) at similar concentrations. The viscosity of IC is several orders of magnitude higher compared to PCs at low shear rates. Shear thinning is seen for IC while PCs exhibit shear thinning at low shear rates followed by Newtonian behavior at higher rates. The effect of temperature, strain, and frequency has also been explored. Further, differential scanning calorimetry (DSC) points out the thermal protection of drug molecules by carrageenan matrix up to elevated temperatures. Overall, the study demonstrates that drug molecules incorporated polymeric cocrystals have significantly higher solubility than iota-carrageenan.

Wednesday 6:10 Grand Terrace PO4

Effect of ultra-high pressure homogenization (UHPH) on viscosity and shear stress of fermented milky beverage

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In this study, the milk base, constituted of a mixture of skimmed raw milk and reconstituted whey in the same proportions that guaranteed 9% of total solids, was pressurized by ultra high pressure homogenized (UHPH) with pressures of 150, 200 and 250 MPa and inlet temperatures of 15, 20 and 25oC following a factorial design 22 with central points. After cooling, pasteurized pineapple pulp, previously sweetened with sugar or aspartame was added to the mixture. Three kinds of products were elaborated: fermented milk drink (BL), fermented milk drink with pineapple pulp and sugar (BLA) and fermented milk drink with pineapple pulp and aspartame (BLL). The study aimed to evaluate the rheological properties of such products taking into account the inlet temperature and UHPH pressure levels, compared to corresponding control, which was thermally treated (90oC/60s). The sensory evaluation using the Quantitative Descriptive Analysis (QDA) was very important to identify the most suitable formulation to be used in the rheological parameter studies. The results have shown that the highest whey content formulations (F50 and L50) presented the highest averages for the characteristic milky beverage sensory attributes and they were used in subsequent studies. Results allowed one to conclude that the UHPH process at 150MPa and inlet temperature of 15oC was similar to the thermal treatment. All samples showed viscoelastic behavior and tixotropy when treated with two cycles of shear rate from 0-300 s-1 in 600 s and return to 0 in 300s.

Wednesday 6:10 Grand Terrace PO5

Red blood cell deformation in an extensional flow microfluidic device

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Changes in rheological properties of blood, caused at least in part by alterations of the mechanical properties of red blood cells (RBCs), can provide valuable information for the diagnosis and understanding of various pathologies including cardiovascular disease, diabetes, sepsis, and mechanical blood trauma caused by blood contacting medical devices. A decrease in the deformability of the RBC, caused by stiffening of the membrane, is an indicator of many of these conditions. Using microfluidic methods for measuring RBC deformability requires a very small sample volume and probes the deformation of a large number of cells while providing data on individual cells. Another benefit of microfluidic methods is their ability to be used to test the cells quickly after their trauma or damage.

In order to quantify RBC deformation and characterize the viscoelastic properties of the RBC membranes, microfluidic devices were fabricated containing a constricted region to produce extensional flow. The width of the constricted region was chosen to be large enough that all RBCs, even those with reduced deformability, could pass through the channel, but small enough so that sufficient strain rate occurs at flow velocities compatible with imaging constraints (i.e. less than 2 mm/s) and single cells could be easily identified for analysis. A series of images were recorded for individual RBCs flowing through the constriction and subsequent expansion, and deformation, velocity, and extension rate were calculated as the RBC passed through the constricted region. Both normal cells and those with reduced deformability to mimic pathological RBCs were characterized.

This microfluidic technique provides a tool which can be used to characterize the rheological properties of individual RBCs quickly while using small sample volumes necessary when dealing with patient blood. This system can be used to detect alterations in these cell properties.

Wednesday 6:10 Grand Terrace PO6

Modeling the rheological properties of cheeses of different fat content

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The physical properties of most cheeses allow them to be modeled from the perspective of soft condensed matter physics. Cheddar, like most cheeses, consists of a fairly homogeneous gel phase with imbedded fat particles and can be represented as a particle-filled gel. In this study, the rheological properties of Cheddar cheese containing different amounts of fat globules were fitted to twelve theoretical models for suspensions and particle-filled gels. The advantages and limitations of the theoretical models were compared. Four models containing a maximum filler volume fraction of 0.64 best described the data and were selected to fit the storage modulus (G') of cheeses at 10, 15, 20 and 25^{o}C after aging the cheeses for 2 to 24 weeks. The four models predict similar results of the storage modulus of the fat globule (G_f') and the protein gel matrix (G_m'). The estimated G_f' is much larger than the G_m' at 10^{o}C; however, it decreased in a faster rate than G_m' with increasing temperature and reached an almost equal value as G_m' at 25^{o}C. Therefore, the strengthening effect of the fat content to the cheese G' becomes less significant as temperature increases because the fat globules transform from relatively rigid fillers at $T < 20^{o}$C to soft fillers at $T > 20^{o}$C. The estimated G_f' is always larger than zero, suggesting that the fat globule behaviors as an active filler in the cheeses. The effect of aging time on the cheese G' is only detected at 20 and 25^{o}C, where the cheese G' and the G_m' slightly decrease after aging cheeses for a longer time but the G_f' does not change much. The quantitative results from theoretical models suggest that the cheese rheological properties are determined by the solid fat content at $T < 20^{o}$C and dominated by the protein gel matrix at $T > 20^{o}$C.

Wednesday 6:10 Grand Terrace PO7

Nonlinear response of the vocal fold lamina propria under large-amplitude oscillatory shear

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Viscoelastic properties of the vocal fold lamina propria have been quantified well into the nonlinear range for describing tissue response under uniaxial tensile stretch, but nonlinear vocal fold response under large-amplitude shear deformation is poorly understood, which is more relevant for understanding the mechanics of mucosal wave propagation for phonatory situations other than voice onset and offset. Previous studies reporting the viscoelastic shear properties of vocal fold tissues have been limited to characterization of the small-amplitude viscoelastic response in the linear viscoelastic region, because of the lack of a coherent framework for describing any nonlinearities beyond the linear region, and also because of the fact that the definitions of viscoelastic functions (such as elastic shear modulus G' and viscous shear modulus G") are based on the assumption of linearity. Based on a recently proposed rheological framework for quantifying such nonlinearities, this study examined the viscoelastic response of human vocal fold cover specimens subjected to large-amplitude oscillatory shear, up to a shear strain amplitude of around 1.0. Results indicated that the linear viscoelastic moduli cannot adequately describe the tissue response under large-strain shear deformation, whereas geometrical interpretations of Lissajous-Bowditch curves could unveil nonlinearities that are obscured by the use of G' and G", such as the phenomenon of strain stiffening.

Wednesday 6:10 Grand Terrace PO8

A novel gelling system comprising corn arabinoxylan and locust bean gum

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Polysaccharides and their binary mixtures are used extensively in several food and non-food applications as thickeners, stabilizers, gelling agents, viscosifiers and emulsifiers. Arabinoxylans constitute an important set in the polysaccharides domain. These are cell-wall non-starch polysaccharides and present in many cereals such as corn, wheat, rye, oat, rice and sorghum. However, they are underutilized mainly due to their low-viscosity behavior, when they are in solutions. In this regard, we have developed a novel gelling agent consisting of corn arabinoxylan (CAX), an extract of corn fiber, and locust bean gum (LBG), a high viscous leguminous seed polysaccharide. The methodology involves mixing CAX and LBG using microwave heating. The binary mixture displays strong gelling behavior with storage modulus G' greater than the loss modulus G". In contrast, a hotplate heating of the mixture exhibits liquid like behavior. Further the gel is stable up to 30 °C and at higher temperatures it undergoes a gel-sol transition. Results clearly demonstrate the enhanced utility of a low-value byproduct from corn fiber towards a valued added product with potential applications for the food, pharmaceutical and medicinal areas. This blend has the potential for generating novel textural characteristics by using reduced level of polysaccharides in the formulations. Further, due to the intrinsic property of arabinoxylan as a dietary fiber these blends can be exploited for incorporating increased level of fiber in food applications.

Wednesday 6:10 Grand Terrace PO9

Gelation of iota-carrageenan at dilute concentrations: Roles of urea and salt

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Carrageenans represent a family of sulfated polysaccharides extracted from marine algae. Their intrinsic gelation provides many applications in foods as thickeners, gelling agents, syneresis inhibitors and binders. These hydrocolloids are made up of a disaccharide galactan backbone with variable amount of sulfation at different hydroxyl positions. Depending on their source of extraction, presence or absence of a sulfate ester as well as anhydro group, fifteen carrageenans are known to date. However, only kappa, lambda and iota -carrageenans have so far been exploited industrially and are subjected to extensive x-ray and rheological studies towards understanding their structure-function relationships. Molecular structure of iota-carrageenan has been well characterized and precise atomic information is now well established. The three-dimensional structure shows that irrespective of cation type, the core structure is a rigid double helical arrangement stabilized by strong inter-chain hydrogen bonds. Water molecules mediate hydrogen bonding network, which along with sulfate group ionic interactions promote carrageenan-carrageenan interactions leading to junction zones. It is known that urea breaks hydrogen bonds whilst salt promotes biopolymers gelation. In order to gain a better understanding about the molecular level mechanisms of such processes we have undertaken a systematic investigation about the effect of urea and salt on the viscoelastic properties of iota-carrageenan at dilute concentrations (0.5, 1.0 and 1.5 w/w). Our results demonstrate that, for higher iota-carrageenan content addition of urea marginally improved the gel properties, and for lower amounts the effect is negligible. On the other hand, salt addition yielded higher gel strength and thermal stability. These findings highlight the roles of additives on the iota-carrageenan dilute solution behavior.

Wednesday 6:10 Grand Terrace PO10

Metastability effects on complex fluids rheology: Concentrated monoclonal antibody solutions

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Understanding antibody (protein) solution rheology is critical for implementing the use of pre-filled syringes for sub-cutaneous administration. Many therapeutically active biologic products are high concentration protein solutions that are thermodynamically non-ideal, which often show temperature-dependent opalescence (turbidity). Because these high concentration protein solutions may be developed for pre-filled syringe (PFS) delivery, it is important to determine whether turbidity can affect formulation rheology, and hence PFS performance. Protein therapeutic drugs are exposed to a broad temperature range between storage (5 ^oC) and administration (25 ^oC). Over this temperature range different phase transitions are observed in globular protein solutions, which may exhibit complex phase behavior[1]. Phase transitions such as liquid-liquid phase separation (LLPS) and crystallization may yield supra-molecular structures (phase-separated droplets and crystals, respectively). Structures with sizes smaller than or comparable to the wavelength of visible light can cause scattering of light and hence turbidity. Because protein solutions are characterized by colloidal interactions, their rheology is a function of their thermodynamics and supra-molecular structure[2]. The physical phenomenon underlying opalescence could hence affect the rheology of these protein formulations. We therefore perform light transmission measurements (350 nm wavelength) of the temperature-dependent turbidity of four monoclonal antibodies (mAbs) formulated in different buffers. Formulations of all mAbs reveal increasing turbidity upon cooling from 25 ^oC to 0 ^oC. Because the increasing turbidity observed on cooling can depend upon concentration, the mAb concentration in these experiments was constant. Formulations of two different mAbs show two co-existing liquid layers upon centrifugation at 3500 g for 2.5 hrs at 0 ^oC, confirming LLPS. These mAb formulations also reveal characteristic rheological signatures of LLPS in the two phase region (at 5 ^oC) resulting in an increase in the shear storage modulus, G', at low frequencies in oscillatory shear (due to interfacial elasticity) and also a time dependent viscosity/modulus in the two phase region (due to morphological growth). In formulations of two other mAbs, no LLPS is detected, because no interface forms even after centrifugation at 3500 g for 7.5 hrs at 0 ^oC. Nevertheless, the formulations of the latter two mAbs do show a time-dependent but slower growth in G' at 5 ^oC, indicating structure build-up (greater than molecular length scales). The structural/thermodynamic origins of the time dependence in the rheology of the formulations of the two mAbs that do not show LLPS are being confirmed by static light scattering and by calorimetry, and will be presented along with their implications for PFS performance.

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[2] R. G. Larson "The Structure and Rheology of Complex Fluids" Oxford Univ. Press, NY (1999).

Wednesday 6:10 Grand Terrace PO11

Temperature and frequency dependence of viscoelastic behavior of barium titanate ceramic

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The classical bounds for composite properties can be exceeded if the inclusion has negative-stiffness. Recent study of a particulate composite of polycrystalline BaTiO3 in Sn reveals an extremely large Young's modulus (even larger than that of diamond) within the temperature window where inclusions undergo ferroelastic transformation, which entails negative bulk modulus for the inclusions. With the aim of directly observing the softening of bulk modulus hypothesized in the design of the above composite, we have studied the viscoelastic properties (modulus and mechanical damping) of polycrystalline BaTiO3 by means of Broadband Viscoelastic Spectroscopy (BVS). A peak in mechanical damping has been observed near the Curie point 130oC corresponding to the "tetragonal-cubic" ferroelastic transformation. The height and the width of the peak increase with rate of temperature change and the inverse of frequency. Anomalous responses in mechanical damping and modulus were observed outside the normal transition temperature region. These anomalous may be associated with the absorption and dissipation of stored elastic energy between constrained domains and their surroundings under the external oscillation stress. The observations of such anomalies above the Curie point indicate the existence of domain structure at cubic phase. Isothermal frequency scans (10-3 Hz to 103 Hz) reveal a hump on the mechanical loss curve below 1 Hz near the Curie point, outside of which, such a hump tends to be flat. Both Young's modulus and shear modulus soften with decreasing frequency, Young's modulus softens more than shear modulus. Quasi-isothermal measurement reveals a significant softening in bulk modulus (a factor of four) and a transient negative Poisson's ratio (-0.25) during the ferroelastic transformation.

Wednesday 6:10 Grand Terrace PO12

The rheological effect of non-inertial shear induced migration of rigid polymers and nanorods at high Peclet numbers

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Mechanisms of net migration for rigid, Brownian rods sheared at high rates are explored. At these large, yet finite, values of the Peclet number, the competition between the randomization caused by Brownian rotation and tendency of the shearing flow to align the rods breaks the symmetry about the flow direction of the orientation distribution. The asymmetric distribution of the rod's orientation can then couple with inhomogeneous shear flows to generate a net migration. Examples include the migration away from bounding walls in simple shear flow and Poiseuille flow, where the inhomogeneous field is produced by hydrodynamic interactions with the walls, as well as the net migration of rods toward the axis of rotation in torsional flows. These effects are not inertial, as the studies are performed under the conditions of Stokes flow and each mechanism is analogous with similar phenomena for flexible polymers, though the rigid rods require a much higher value of the Peclet number before the migration becomes significant. Rheological impacts of the migration mechanism are slight for the case of simple shear flow, but can be significant for torsional flows.

Wednesday 6:10 Grand Terrace PO13

Dynamic properties of imidazolium based ionic liquids studied by mechanical spectroscopy

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Ionic liquids are intensely studied as a replacement solvent for reactions and separations since they exhibit negligible vapor pressure and they can be designed to be environmentally benign. Therefore, investigation of dynamic properties of ionic liquids is vital for design and evaluation of their application. In this study we determined the dynamic mechanical responses of three ionic liquids of the imidazolium family using an advanced rheometric expansion system (ARES, TA Instruments). We investigated the shear modulus and steady shear viscosity of 1-ethyl 3-methylimidazolium ethylsulfate ([Emim][EtSO$_4$]), 1-butyl 3-methylimidazolium tetrafluoroborate [bmim][BF$_4$] and 1-butyl 3-methylimidazolium hexafluorophosphate [bmim][PF$_6$] near their respective glass transition temperatures. The frequency dependent response function was analyzed to investigate the temperature dependency of shear modulus and the result showed that these materials follow the time temperature superposition. We also found that the shear rate dependence of the steady state viscosity is significantly different from the frequency dependence of the complex viscosity. That is the Cox-Merz rule does not hold for these ionic liquids.

Wednesday 6:10 Grand Terrace PO14

Magnetorheology of viscous ferrofluids

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Ferrofluids are suspensions of magnetic nanoparticles in Newtonian carrier fluids. The nanoparticles, typically an iron oxide such as magnetite, are single domain magnets with dipole moments which align with externally imposed magnetic fields due to magnetic torque. When the dipole moment is rigidly locked to the particle the magnetic torque results in relative slip between the particle angular velocity and the local flow vorticity. Such slip induces increased viscous dissipation and hence a magnetic field dependent suspension scale viscosity. Previous theoretical work indicates that the rheology of dilute suspensions of magnetic nanoparticles is governed by two parameters: the magnetic field amplitude and the shear rate. Although there have been numerous reports of magnetic field and shear dependent viscosity of ferrofluids, direct comparison with theory is prevented by limitations in the studied experimental systems. The use of magnetite introduces a complication as the dipole moment of this material simultaneously aligns with imposed magnetic fields through rigid body rotation and through the so-called Néel mechanism, in a way which depends on the diameter of the nanoparticle, making quantitative comparison with existing theories difficult. Furthermore, because most ferrofluids consist of suspensions in low-viscosity fluids, it is impossible to fully characterize the predicted shear rate dependence of their rheology. Here we present a detailed investigation of the magnetic field and shear rate dependent rheology of ferrofluids consisting of narrowly dispersed cobalt ferrite nanoparticles suspended in highly viscous fluids. The cobalt ferrite nanoparticles can only respond to the applied magnetic field through rigid body rotation, making them ideal in testing theoretical predictions of ferrofluid behavior. The experiments illustrate many of the expected features, in addition to behavior induced by chain formation, such as shear thinning in zero field and thixotropy.

Wednesday 6:10 Grand Terrace PO15

Rheo-SALS investigation of shear and temperature induced phase separation in coacervate systems

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A quantitative study of the shear-induced phase separation of three different polycation/mixed micelle coacervates is presented. Simultaneous rheology and small-angle light scattering (Rheo-SALS) measurements allow the investigation of micron scale phase separation under flow in the coacervate solutions. At temperatures below 18^{o}C, all three of the coacervate solutions are clear Newtonian fluids across the entire range of shear rates investigated. Once a critical temperature and/or shear rate are achieved, phase separation is observed in the small-angle light scattering images and the fluid begins to exhibit shear thinning behavior. Two definitive SALS images demonstrate the appearance of circular droplets at low shear rates near the critical temperature which become ellipsoidal droplets at higher shear rates. The shear-induced droplets range in size from 1 to 4.2 µm. The ellipsoidal droplets have aspect ratios as high at 4.2. A conceptual picture is proposed in which shear flow extends the polyelectrolyte chains of the clear coacervate solution. The extended chains create interpolyelectrolyte-micelle interactions, promote expulsion of small ions from the complex, and result in the formation of micron scale phase separated droplets.

Wednesday 6:10 Grand Terrace PO16

Turbulence structures in turbulent boundary layer flow of homogeneous aqueous surfactant solution at large and small drag reduction ratios

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In our quite recent work [Tamano et al., Phys. Fluids, Vol.21, No.045101 (2009)], we systematically investigated the influence of the drag-reducing surfactant on the velocity fields of the turbulent boundary layer at various momentum-thickness Reynolds numbers Re from 301 to 1,437 and the drag reduction ratio DR from 8 to 74% under different streamwise locations and concentration and temperature of solutions using a LDV system. We verified the existence of the additional maximum of the streamwise turbulence intensity near the center of the boundary layer. At almost the same Re, however, we could not compare turbulence structures between at the large and small DR. In this study, turbulence structures of the drag-reducing turbulent boundary layer flow in the surfactant solution at the Re around 800 were compared between at the large and small DR. Turbulence statistics and structures were obtained by the two-component LDV system and the PIV system for the streamwise and wall-normal (x-y) section and the streamwise and spanwise (x-z) section. The surfactant solution used here was a mixture of cetyltrimethyl ammonium chloride (CTAC) with sodium salicylate as counterion, which was dissolved in tap water. The concentration of CTAC was 65 ppm, and the molar ratio of counterion to CTAC was two. The drag reduction ratios DR=78% and 34% were obtained at the solution temperature T=30 and 35 degree Celsius, respectively. The quadrant analysis of streamwise and wall-normal velocity fluctuations revealed that at DR=78%, the positive contribution of the sweep and ejection events to the Reynolds shear stress was comparable with the negative contribution of the inward-interaction and outward-interaction events, so that the Reynolds shear stress was almost zero. At DR=78%, both streamwise and spanwise velocity fluctuations were attenuated largely across the turbulent boundary layer. On the other hand, at DR=34%, turbulence structures were similar to those of water as a whole, although the scale was larger compared to the water.

Wednesday 6:10 Grand Terrace PO17

Strain-rate frequency superposition in large-amplitude oscillatory shear

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In a recent work, Wyss, *et.al.* [Phys. Rev. Lett., **98**, 238303 (2007)] have noted a universal property of 'soft solids' under oscillatory shear, the so-called strain-rate frequency superposition (SRFS). We extend this study to the case of soft solids under large-amplitude oscillatory shear (LAOS). We exhibit results from LAOS studies in a commercially available aqueous gel, a monodisperse soft-sphere suspension, and a biopolymer suspension, and show that constant strain-rate frequency sweep measurements in soft solids can be shifted onto a single master curve for higher harmonic moduli, with the *same* shift factors as for the case of linear viscoelastic moduli, reported in Wyss, *et.al.*

Wednesday 6:10 Grand Terrace PO18

Use of a microfluidics chip to obtain viscosity results over a wide shear rate range for solutions of peptide-modified hyaluronic acid chains or actin protein fibers

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Several biopolymers play important functions in cells and tissues in the human body as a result of their viscoelastic properties. We will present viscosity results over a wide shear rate (500-20,000 sec-1) for aqueous solutions containing one of two biopolymers: peptide-modified hyaluronic acid (HA) or actin protein. The results were obtained by conventional rheometry and by use of the VROCTM microfluidics chip (RheoSense Inc., San Ramon, CA). Native HA was chemically-modified with polypeptide chains containing self-assembling hydrophobic residues. Due to this modification shorter HA chains (or low HA content) can potentially be used to obtain an equivalent boost in viscoelastic properties for biomedical applications. The physical properties of this material elucidated from dynamic light scattering (DLS) and viscometry will be presented in the poster. Shear thinning experiments performed on the modified HA at high shear rates using VROCTM will also be presented. Actin is a globular protein with a molecular weight of 43kDa with the unique ability to polymerize reversibly into double helical filamentous structures under physiological salt conditions. This polymerization, which is essential for several cell functions, can be achieved in vitro by controlling the ionic condition of actin solutions. DLS and microviscometry were carried out on actin monomer and actin polymer solutions. The shear thinning behavior of actin studied using VROCTM at high shear rates will be presented in the poster.

Wednesday 6:10 Grand Terrace PO19

Direct visualization of strain-induced yielding in colloidal gels

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Colloidal depletion gels undergo yielding when a critical stress or strain is applied to them. This phenomenon is a poorly understood function of interparticle interactions and the underlying gel microstructure. We aim to identify and quantify the relationship between an applied strain and the structural evolution of a gel network using the direct visualization technique of confocal microscopy. We synthesized siloxane-stabilized poly(methyl methacrylate) (PMMA) colloids of various diameters and created gels ($f = 0.20$, $c/c^* = 1.1$) by inducing a depletion interaction with non-adsorbing polystyrene ($R_g = 21.7$ nm). We performed three types of rheological measurements on the gels: oscillatory strain sweep, start-up of steady-shear, and creep flow, and deduced the yield strain of the gel to be 0.06 ± 0.01. We used confocal laser scanning microscopy to visualize gel microstructure under quiescent and shear flow conditions. We compare the short- and long-range structure of the gel before and after executing step strains of various magnitudes.

Wednesday 6:10 Grand Terrace PO20

Rheological characterization of oxide surface films on liquid metals

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Oxidizing liquid metals in air, such as Gallium, exhibit a combination of liquid-like and solid-like effects that make them useful for microfluidics and for micro-electronics. Despite the usefulness of these materials, little is known about how to characterize their rheological properties. We present experiments performed with parallel plate geometries of different sizes that demonstrate that yield stress behavior originates from the oxide film on the outer surface of the liquid metals. Our measurements also demonstrate that the oxide film exhibits a complicated, yet reversible, dependence on shear history, including thixotropic effects. We rationalize our observations in terms of surface oxidation.

Wednesday 6:10 Grand Terrace PO21

Shear thickening, jamming, and dilation in suspensions

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Cornstarch suspended in water has the remarkable mechanical property of shear thickening. Using rheometry measurements we find shear thickening to be a generic property of suspensions of non-attractive particles. The severity of shear thickening, characterized by the slope of the viscosity curve, is found to diverge at a critical packing fraction corresponding to the jamming point. Video microscopy measurements show the shear thickening regime is a phase transition from a low stress phase where the particles remain unsheared to a high stress phase with fully developed shear. The onset of shear thickening occurs when the shear stress is sufficient to pull particles apart; for example against gravity for large particles, and can be tuned by inducing electric or magnetic attractions. Dilation can be observed as particles penetrate the fluid surface in the high stress regime. The maximum stress of the shear thickening regime is shown to match, for a wide range of suspensions, the ratio of surface tension divided by a radius of curvature comparable to the particle size. This suggests the large stress associated with shear thickening comes from capillary forces as a consequence of dilation.

Wednesday 6:10 Grand Terrace PO22

Stress activated dynamics during structural arrest of a colloidal glass

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We study the dynamics of a repulsive colloidal glass in the presence of a mean field stress, σ_m, applied to the system via parallel superposition rheology. The system ages in a manner dependent on the magnitude of the stress. For small stresses, the storage and loss moduli evolve with weak power laws, with $G' > G''$ as commonly observed in soft glassy materials. At large σ_m, the system is completely fluid and presents a relatively time invariant viscous response. At intermediate stresses, the loss modulus exceeds the storage modulus at short times but develops a peak concomitant with a crossover between the two as the system ages. Stress is thus seen to activate the dynamics of the system, permitting the observation of the structural relaxation of the material in reverse, i.e. vitrification, as the system ages and progressively slows down. We have drawn parallels between our experiments and flow arrest in viscosity bifurcation experiments. We observe that the characteristic time for flow arrest in viscosity bifurcation experiments show an exponential dependence on the applied stress. These results qualitatively highlight the activating role of stress on the dynamics as has been advanced in recent theoretical frameworks.

Wednesday 6:10 Grand Terrace PO23

Particles feel the squeeze: Rheology of squishy particle glasses

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In this poster presentation we discuss our recent efforts in understanding the effects of particle compressibility on the mechanics of colloidal glasses. Using rheometry, confocal rheometry and light scattering we investigate how squishy microgel particles reach a jammed state. Our ultimate motivation is to bridge length scales between single-particle mechanics, microscopic dynamics and macroscopic rheology.

Wednesday 6:10 Grand Terrace PO24

Acrylamide gelation in the presence of montmorillonite particles

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Acrylamide advancement has been probed in 15% aqueous solutions at room temperature incorporating montmorillonite at concentrations up to 2w/w% and crosslinking using ammonium persulfate using parallel plate rheology. The initial viscosity determinations used an oscillatory variable shear rate between 1 and 15 rad/sec at a shear strain of 200% devoid of persulfate as a curing agent. The cure profiles were performed at a constant 1 rad/sec with 5% strain at ambient temperature. Viscosity advancement profiles show a marked sigmoidal behavior in dynamic viscosity with a plateau viscosity of the gels associated with a rheometer torque well below its limit. The presence of montmorillonite lowered the initial viscosity and led to longer induction times required to trigger gelation, as identified by analytical determinations of the gel point using the power law and the sigmoidal model compared to neat resins without filler. There seemed to be little difference in the viscosity of the composite in the gel condition. Observational studies of the gel following formation showed an unusual pooling of clay particulates at the edges of the parallel plate, at a rotational angle of 30o from each other at 200% strain. Altering the strain also altered the number of observed pools. Clearly there is both a gravity driving force for particulates to settle during gel cure and a separate centrifugal force pushing the particles away from the center of the plate. The sedimentation front triggers this angular symmetry. We will present our rheological results, mathematical analyses, and the corresponding microscopy of the particulate pooling during gelation at the meeting.

Wednesday 6:10 Grand Terrace PO25

Concentration dependent micellization of Pluronic F127 solutions and the kinetics of ordering by both rheology and DSC

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Researchers have harnessed the reverse-thermal gelation behavior of PEO/PPO/PEO triblock copolymer solutions (commercially known as Pluronics) as drug-delivery vehicles or as formulated injectables. The gelation mechanism has been determined to be the close packing and ordering of Pluronic micelles[1,2]. While the phase behavior has been studied extensively in the past, the kinetics of the gel transition has not been thoroughly studied. Barba *et al.* have recently published an empirical model for the micellization and gelation of Pluronic F127 based on differential scanning calorimetry (DSC) and dielectric constant measurements[3]. Here we have measured the rheology of F127 solutions with both temperature (15-65°C) and concentration (10-30% w/v), using ramp rates of 0.1-10°C/min to study the kinetics of gelation. DSC analysis was also performed on the same Pluronic formulations and same ramp rates as the rheology experiments. Using the power law analysis method of determining gelation temperature (T_{gel}), our results indicate that T_{gel} increases at higher temperature ramp rates as compared to the equilibrium or near-equilibrium ramp condition (defined as the results obtained with a ramp rate of 0.1°C/min through the gel transition region). Qualitatively, the time associated with dynamic viscosity rise as micellization occurs is inversely proportional to the temperature ramp rate and F127 concentration. Sigmoidal analysis will be carried out on the rheology data to quantitatively analyze the gelation time intervals and couple that to the DSC results. At the conference the rheology data we've collected and analyzed will be directly compared with that by Barba *et al.*[3] and their model predictions.

1. Wanka et al. Macromolecules (1994) vol. 27 (15) pp. 4145-4159
2. Lau et al. J Polym Sci Pol Phys (2004) vol. 42 (10) pp. 2014-2025
3. Barba et al. J Appl Polym Sci (2009) vol. 114 pp. 688-695

Wednesday 6:10 Grand Terrace PO26

Imaging the effects of peptide surfactant on droplet deformation in a Taylor-Couette cell using rotationally compensated RARE (ROTACOR)

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Controlling the properties of fluid-fluid interfaces is important in many fields including oil recovery, waste water treatment, food processing and pharmaceutical formulation. A fascinating new group of peptide surfactants (AM1 & AFD4) have recently received attention because of their ability for controlled change between a cohesive "film state" and a mobile "detergent state" due to a stimuli [1-3]. We investigate the effects of these surfactants on the deformation of a single droplet (34%wt Toluene, 66%wt Chloroform) suspended in a glycerol solution inside a wide gap Taylor-Couette cell rotated from 0 to 2.0 rps. These deformations were studied using a novel rapid nuclear magnetic resonance imaging method (ROTACOR [4]) which compensates for the rotation of the droplet inside the Taylor-Couette cell. While in the "film state" the peptide surfactants reduced the deformation of the droplets when compared with the deformations of the system without any surfactant present, while by comparison a droplet with 2%wt Tween60 surfactant present showed increased deformation. When a small amount of EDTA was added to the peptide surfactant system causing a change to the "detergent state" the deformation of the droplet increased when compared with the "film state" deformation, demonstrating that the altered nature of the fluid-fluid interface leads to a change in the droplet deformation.

[1] A.F. Dexter, A.S. Malcolm, A.P.J. Middelberg, Nat. Mater. 5 (2006) 502-506.
[2] A.F. Dexter, A.P.J. Middelberg, J. Phys. Chem. C 111 (2007) 10484-10492.
[3] A.P.J. Middelberg, L. He, L.F. Dexter, H.-H. Shen, S.A. Holt, R.K. Thomas, J.R. Soc. Interface 5 (2008) 47-54.
[4] A.J. Sederman, K.G. Hollingsworth, M.L. Johns, L.F. Gladden J. Magn. Reson. 171 (2004) 118-123.

Wednesday 6:10 Grand Terrace PO27

Jamming of solid-stabilized emulsions

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A significant amount of work has focused on studying the mechanical properties of surfactant-stabilized emulsions - that is, suspensions of one fluid dispersed within another, stabilized by surfactant molecules at the interface. We are investigating the rheology of dense solid-stabilized (versus surfactant-stabilized) emulsions.

Wednesday 6:10 Grand Terrace PO28

Yield stress and viscosity of ice suspensions formed from water-in-oil emulsions

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Clathrate hydrates are molecular inclusion compounds are a common concern in oil and gas pipelines as they can cause blockages to pipelines resulting in disruption to production. These crystalline compounds are composed of over 80 mole% water and are typically stable at high pressures and low temperatures. To understand the rheology of clathrate hydrates, we first investigated ice slurries in crude oil as a simple analogy to clathrate hydrates, thus allowing studies at atmospheric pressure. While the study of ice as an analogy to clathrate hydrates is important, it is not the only application. Substantial work with ice slurries has been done in refrigeration, where plugging of pipes is also a major concern. For this work a series of water-in-oil emulsions were prepared at different volume fractions of water, ranging from 0.10 to 0.70. In addition, the effect of the addition of salt was studied (3.5 wt% NaCl, the same concentration as sea water). The emulsions were cooled to -10°C and the yield stress was analyzed as a function of time after nucleation. No yield stress was observed for water volume fractions below 0.10 and 0.20 for the fresh and salt water samples, respectively. For the systems with fresh water at higher volume fractions yield stress was observed to fall into two distinct regimes: volume fraction of 0.25-0.55 where yield stress was on the order of 300 Pa and 0.6-0.7 where yield stress quickly increased to an unmeasurable value (greater than 4000 Pa, the instrument's limit). For the salt water samples, yield stress was found to increase exponentially but at values lower than those with fresh water. An annealing time after nucleation for both samples was applied and showed a peak in the yield stress at 2 hours for the fresh water sample and at 8 hours for the salt water samples.

Wednesday 6:10 Grand Terrace PO29

Effect of particle size on the nanostructure, phase behavior, and dynamic oscillatory rheology of a model nanoparticle gel

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Colloidal suspensions can undergo an abrupt transition between a fluid and solid state when either the volume fraction of particles or the inter-particle potential is varied. For dispersion containing particles that repel one another, a repulsive-driven glass can form nears the maximum packing. Conversely, particles with attractive interactions can percolate to form a space-filling network termed gels or attractive-driven glasses. Gels are technologically relevant as they are commonly encountered in the manufacturing of many industrial and commercial products. In many cases the processing of these materials relies on the fact that the structure can be reversibly broken down by flow. Hence, the rheology of such suspensions can display complex behaviors such as yielding, aging, shear thickening, shear banding, thixotropy, etc. Our overall research deals with understanding the effect of particle potential, size, and shape on the structure and mechanical properties (shear rheology) of attractive systems. In this work we present experimental results on the effect of particle size on the structure, thermodynamic phase behavior, and dynamic oscillatory rheology of a model thermoreversible system. The model system consists of a silica core in which octadecane has been grafted to the surface. When suspended in tetradecane, the particles are sterically stabilized at high temperatures and aggregate at low temperatures; a behavior that has been linked to the phase behavior of the molecular grafting. At high enough volume fraction of particles this results in a thermoreversible gel termed "sticky spheres" in literature. We study the effect of particle size by changing the core diameter from ~30 to ~120 nm. Dynamic light scattering (DLS), fiber optics quasi-elastic light scattering (FOQELS), small angle neutron scattering (SANS), and dynamic oscillatory and steady shear rheology are utilized to probe the single particle properties, interaction potential, phase behavior, and structure, in relationship to rheological properties.

Wednesday 6:10 Grand Terrace PO30

Low molecular weight polymers addition effect in bauxite slurry viscosity

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The rheological behavior of mineral slurries is related to suspension microstructure and flow force nature and magnitude. It is well known that the apparent viscosity of colloidal particles suspensions, as kaolin slurries, is greatly modified by surface active compounds addition, in such manner that interaction between particles can be manipulated to promote viscosity levels suitable to application or process requirements. Despite of this kind of effect, we understand better in case of colloidal particles, which inertial forces are meaningless, some surface active compounds, as polyelectrolytes and non-ionic hydrosoluble polymers, may also promote apparent viscosity reduction of non-colloidal concentrated suspension, what could decrease pumping energy requirements or make other operational steps easier. In this work, it was carried out a study about the effect of different polymer additive types - cationic, anionic and non-ionic - in an apparent viscosity of bauxite slurries. Bauxites ores, the raw material of aluminum production, are processed as grinded particles in aqueous media. The bauxite ore is a heterogeneous mixture of minerals mainly composed by aluminum and iron oxides, but the presence of clay minerals is common and frequently induces a viscosity rise. The crystalline phases of a Brazilian bauxite ore grinded sample were determined by X-ray diffraction analysis (XRD) and the particle size distribution was achieved by screen analysis. Suspensions of 50 and 60 % (w/w) with two different particle size distributions were prepared and the rheological tests were performed in simple shear mode, using a Searle type rheometer. It was observed that the non-ionic additives promoted slurry viscosity reduction whereas the other additive types acted as suspension coagulants. As it was expected, the non-ionic additive with both hydrophilic and hydrophobic groups in the chain, the poly(vinyl alcohol) (PVOH) with acetate groups, showed a better performance when compared to PVOH fully hydrolyzed.

Wednesday 6:10 Grand Terrace PO31

Alignment of micellar hydrogels through steady shear and oscillatory flow

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Poly(ethylene oxide)$_n$-poly(propylene oxide)$_m$-poly(ethylene oxide)$_n$ block copolymers (trade name Pluronic) self assemble into individual micelles at low temperatures and form ordered micelle hydrogels at higher temperatures. These ordered phases exhibit the property of thermoreversibility, which allows the block copolymer to easily transition between isotropic and ordered micelle phases. Monodisperse nanoparticles on the order of 10 nm can be templated inside the interstitial spaces of the pluronic micelle hydrogels to form nanocomposites. Contrast matching small angle neutron scattering (SANS) experiments have verified these nanoparticles are templated in the interstitial sites of cubic packed pluronic micelle hydrogels.

These micellar hydrogels have been shown previously to align to a uniform micelle hydrogel crystal with shear. A powder fraction can be calculated to estimate the fraction of the hydrogel that is not oriented with the shear field. It is shown in this work that these micellar hydrogrels can also be aligned with oscillatory flow in addition to shear. The alignment of the micellar hydrogels increases as either the frequency or the strain percentage of the oscillation is increased. For the nanocomposite systems, an increased order of alignment is shown through oscillatory flow than through shear flow. The powder fraction of shear aligned nanocomposites is higher than the micelle hydrogel system whereas the powder fraction of the oscillatory aligned nanocomposites is lower than the micelle hydrogel system. The static nanostructures and alignment will be discussed and quantified.

Wednesday 6:10 Grand Terrace PO32

Microstructure and rheology of dilute Carbopol dispersions

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Carbopol is a commercial polymer microgel used as a thickener in many products. pH- neutralized, aqueous dispersions of Carbopol have a yield stress for Carbopol mass fractions as low as 0.0005. We investigate the bulk rheology and the micron-scale properties and structure of dilute suspensions of Carbopol using shear rheometry, microrheology, and small-angle light scattering. Our results indicate that the Carbopol particles expand by a factor of 10 in radius when the pH is neutralized, and that the onset of the yield stress is associated with jamming of these highly expanded particles.

Wednesday 6:10 Grand Terrace PO33

Jetting and capillary break-up of viscoelastic fluids

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The surface tension driven instability leading to atomization of an axisymmetric jet of non-Newtonian fluids is the basis of many applications including spray paints, inkjet printing and agricultural spraying, say for dispersing insecticides. The addition of polymers affects the capillary instability and break-up, by modifying both the break-up length of the jet as well as the formation of drops. In this study, we combine experiments and nonlinear theory to determine the influence of both elasticity and extensibility on the growth and evolution of instability during jetting and break-up of model associative polymer solutions. The presence of polymers affects the transient extensional rheology, which stabilizes jet against breakup, where the presence of elasticity acts to destabilize the jet more compared to the Newtonian fluid of same viscosity. Jetting flows involve inertial, elastic and viscous effects, which typically lead to complex dynamics, precluding a simple capillary thinning analysis in a necking fluid thread. We show that by carefully controlling the excitation frequency, it is possible to drive the break-up in a particularly simple and symmetric mode, which can be used to extract extensional viscosity information.

Wednesday 6:10 Grand Terrace PO34

Particle self-assembly and chaining in flows of viscoelastic fluid

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The overall objective of this work is to understand aggregation and chaining of small particles in flows of viscoelastic polymer solutions. It is well known that although particles remain dispersed in Newtonian fluids they often demonstrate chaining and self-assembly aggregation behavior in viscoelastic fluids. Particle image velocimetry (PIV) relies on particle motion to reflect the motion of the carrier fluid. For this to be true, it is important that (1) particles have sufficiently small Stokes number to follow the fluid motion with acceptable accuracy, and (2) particles not interact with each other. The former assumption is well-understood, but the latter assumption may not hold for the case of viscoelastic fluids in which tracer particles aggregate. In all the previous PIV works, it is tacitly assumed that particles do not interact. In this work we explore and quantify this assumption by establishing some understanding of the conditions (e.g., dilution, particle specific gravity, and particle size) leading to particle aggregation and inaccurate PIV. The experiment comprises two concentric cylinders, with the inner cylinder rotating, a small Nd:YAG laser with sheet forming optics, and a high-speed (1000 fps) video camera. By creating a laser sheet across the gap between the cylinders and collecting images from below, we perform PIV of the cylinder driven flow. To separate the effect of shear thinning and elasticity, a Boger fluid (PIB in PB) and a shear thinning solution (Polyethylene Oxide in water) are used. We vary the particle size and particle volume fraction and observe the differences in PIV results. By comparing the results to similar experiments in Newtonian fluid (where the uncertainty is less than 5%), we identify the deviations resulting from particle interaction. Our results show, for example, particle chaining in 2% Polyethylene Oxide solution with concomitant effects on the PIV results.

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Wednesday 6:10 Grand Terrace PO35

Experimental investigation on the breakup of an emulsion jet

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In this work, the breakup of a jet of both water-in-oil and oil-in-water emulsions is studied and compared with the breakup of pure water and pure oil jets. The injection of water/oil emulsions in combustion systems has been shown to produce a variety of benefits, including reduced pollutant emissions and particulate. This work initiates the development of a more fundamental understanding of the processes associated with atomization of emulsions. The experimental setup includes a droplet generator (a piezoelectric for an actuator and a 200 micron nozzle) which sends the jet into the air (at 15 m/s) and breaks it into droplets. We demonstrate how the distribution and sizes of droplets of the dispersed liquid inside the emulsion affect the breakup behavior. The water-in-oil emulsion consists of 15% water in 85% diesel fuel. Oil surfactant (span 80) and water surfactant (tween 85) are used to stabilize the emulsion. The emulsion is a fine distribution of water droplets in the oil, and the zero shear viscosity is 100 Pa.s as measured by a rheometer. The breakup length is longer and more randomness is shown compared to pure water or oil, however, it remains sensitive to the disturbance provided by the actuator. This shows that the breakup of a well-distributed mixture of a stable emulsion can be controlled. For the oil-in-water emulsion, 25% oil is mixed with 75% water and a surfactant is added to stabilize the emulsion. The emulsion is shear thinning and the zero shear viscosity is 35Pa.s. In contrast to the highly-dispersed case, the jet breaks into droplets randomly without being responsive to disturbances. Interestingly, when the emulsion droplets are collected to reuse, the collected emulsion is less viscous (3 Pa.s) and includes larger drops of oil poorly distributed in water, resulting in the formation of long ligaments. The experimental investigations lead to the conclusion that the distribution and sizes of the dispersed liquid not only influence the viscosity, but also strongly affect the breakup behavior.

Wednesday 6:10 Grand Terrace PO36

Validation of the linear viscoelastic region of a silicone polymer and a worm-like micellar solution using normal force to determine the onset of non-linearity

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It is well established that a non-Newtonian sample being measured outside of the linear viscoelastic region will create stresses perpendicular (normal) to the direction of shear (Ferry). These stresses should be measurable, and could, therefore be used to verify whether any particular oscillatory measurement has been made within the sample's linear viscoelastic region. Measurements using high speed collection of torque, position and normal force data were made to determine whether a meaningful normal force signal could be resolved from within the linear viscoelastic region, during the transition from linear to non-linear behaviour, or in the non-linear region. The results were subjected to Fourier analyses to detect the presence of harmonics in the signal, and these analyses were compared with the more traditional method of determining the linear viscoelastic region.

Wednesday 6:10 Grand Terrace PO37

Viscoelastic properties of associating polymers having multiple associative groups

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We have developed a theory and a Brownian dynamics simulation method based on a single-chain approach to describe dynamics of associating polymer chains in the transient network formed by themselves, and studied viscoelastic properties of this network. Excluded volume interaction and hydrodynamic interaction are disregarded for simplicity. If the number of associative groups N_a per chain is small, the dynamic shear moduli are well described in terms of the Maxwell model with a single relaxation time τ_X corresponding to the lifetime of the association in the moderate and lower frequency regimes. If N_a is larger and the association rate of associative groups is much larger than the dissociation rate (i.e., the network is fully developed), a longer relaxation time τ_A exists that is proportional to $\tau_X N_a^2$, and the moduli are well described in terms of the Rouse model with the longest relaxation time τ_A in the frequency regime $\omega < 1/ \tau_X$. The origin of this associative Rouse behavior is the association/dissociation processes among associative groups and is different from that of the Rouse behavior observed in the higher frequency regime that stems from thermal motion of polymer segments between bound associative groups.

Wednesday 6:10 Grand Terrace PO38

Polypropylene / polyaniline-grafted-short glass fiber composites: Microstructure and thermal transitions

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The microstructure, thermal and dynamic mechanical properties of isotactic polypropylene (iPP) reinforced with polyaniline grafted short glass fibers (PAn-g-SGF) have been investigated. Composites containing 10, 20 and 30 wt% of PAn-g-SGF were studied. Additionally, a composite of iPP blended with 5 wt % PP-grafted-maleic anhydride (PP-gMA) and 30 wt% of PAn-g-SGF was also investigated. iPP recrystallizes into a spherulitic morphology giving rise to a four lobe small-angle light scattering (SALS) pattern. The microfiller promotes transcrystallization with a slightly larger spherulite size. The overall degree of crystallinity, however, decreases as the concentration of microfiller increases. Dynamic mechanical measurements around the melting and crystallization transitions showed that the melting (crystallization) temperature first decreased, reaching a minimum at ca. 20wt%, and then increased as the concentration of microfiller increased. On the other hand, the activation energy for melting was found to be an increasing function of concentration of microfiller. The blend containing maleic anhydride copolymer showed the higher shear modulus and activation energy and negligible change in transition temperatures. The increase in transition temperatures above 20wt% concentration of microfiller coincides with electric conductivity measurements previously reported suggesting that the percolation threshold is responsible for these results.

Wednesday 6:10 Grand Terrace PO39

Transient rheology of a polypropylene melt reinforced with long glass fibers

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The purpose of this research is to understand fiber orientation of long glass fibers(> 1mm) in polymer melts and the associated rheology in well-defined simple shear flow. Specifically, we are interested in associating the rheological behavior of glass fiber reinforced polypropylene with the transient evolution of fiber orientation in simple shear in an effort to model fiber orientation in complex flow. A sliding plate rheometer was designed to measure stress growth in the startup and cessation of steady shear flow. Results were confirmed by independent measurements on another sliding plate rheometer. A fiber orientation model that accounts for the flexibility of long fibers, as opposed to rigid rod models commonly used for short fibers, was investigated and results are compared with experimentally measured values of orientation. The accuracy of this model, when used with the stress tensor predictions of Lipscomb and Dinh-Armstrong, is evaluated by comparing against experimental stress growth data. Samples were prepared with different initial orientations including random, perpendicular to the flow, and parallel with the flow. Results show that fiber flexibility has the effect of retarding transient fiber orientation evolution. Additionally, it is shown that the stress growth measurements provide results that are not fully explained by the chosen models. The concept of using the Goddard-Huang mobility tensor to account for fiber interactions is considered.

Wednesday 6:10 Grand Terrace PO40

Rheological characterization of intelligent hydrogels prepared via γ-ray induced polymerization of micellar monomer solutions and microemulsions

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Intelligent hydrogels are prepared in a one-step reaction using gamma-ray induced polymerization of micellar aqueous comonomer solutions and microemulsions containing polymerizable surfactants and N isopropylacrylamide (NIPAM). A chemically and physically cross-linked network structure is formed consisting of blocks of Poly NIPAM and polymerized surfmer (Poly-surfmer). The Poly surfmer blocks act as physical cross-linking units improving the mechanical stability of the gel.

Depending on the structure of the surfmer and the chemical composition of the hydrogel different mechanical stabilities were obtained. The addition of 11-acryloylundecyltrimethylammonium bromide leads to a significant increase of the mechanical stability compared with pure NIPAM hydrogels, while 11 methacryloylundecyltrimethylammonium bromide has a much smaller positive effect on the stability of the systems. Typically a compression strain around 75 % is necessary to induce microscopic fracture, while 80 - 90 % are necessary to induce macroscopic failure (breaking apart of the samples in sub-mm-size pieces).

The system has a lower critical solution temperature (LCST) around 35 °C. Temperature cycling tests between 20 °C and 50 °C show a good reversibility of the rheological behavior above and below LCST. Below the LCST a phase angle δ lower than 30°, in some cases lower than 5° is found, which was confirmed by the very high to complete reversibility of the deformation in creep and creep recovery tests.

Hydrogels were subjected to swelling tests. Depending on the composition different water uptakes were observed. In some cases water contents of more than 99 % are possible while still retaining a decent mechanical stability. The mechanical stability in compression of the gels decreases with increasing water content.

Wednesday 6:10 Grand Terrace PO41

Molecular stiffening and surface tension in ultrathin polymer films

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The mechanical properties of ultra-thin poly (n-butyl methacrylate) (PBMA) films were investigated by the novel bubble inflation technique developed in our lab. Creep experiments were performed at temperatures above the glass transition temperature (Tg) of bulk PBMA. Using both an energy balance approach and a stress-strain analysis, we found that the observed increase of rubbery modulus can be attributed to a mixture of molecular stiffening and to surface tension effects. The molecular stiffening is the major contribution, while the macroscopic surface tension is unchanged or only modestly changed. PBMA shows quite different behavior from PVAc or PS, including a pressure-dependent compliance that does not reach a plateau value, higher surface energy contributions to the total energy (resistance to deformation), less increase of modulus with decreasing film thickness (30 fold vs 1000 fold), lower thickness dependence of the modulus (scales as power of -1.6 vs -2) . This observation indicates that the molecular stiffening in ultrathin films is a universal phenomenon, but its magnitude depends on the polymer repeat unit structure.

Wednesday 6:10 Grand Terrace PO42

Rheological detection of very low levels of long chain branching in commercial polymers

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Here we explore the limits of detectability of long-chain branching by blending commercial long-chain branched polyethylenes, including Dow polymers PL1840 and PL1880 with polyethylenes of very similar molecular weight and molecular weight distribution, but lacking long-chain branching (LCB). The concentration of long-chain branched polyethylene is varied down to as low as 2%, to obtain ultra-low levels of long-chain branching, as low as 0.355 long chain branches per million backbone carbons atoms. We find that the presence of LCB can be detected through its effect on the linear rheology, even in the samples with only 0.355 long-chain branches per million backbone carbon atoms. We use a generalized "tube" model for predicting the linear rheology of these polymers (the "Hierarchical Model") to show theoretically that such ultra-low concentrations of LCB is indeed theoretically detectable using linear rheology.

Wednesday 6:10 Grand Terrace PO43

X-ray scattering studies of flow-induced alignment in model polymer-clay nanocomposites

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We report the average orientation state of clay nanoparticles in steady and transient shear flows. These studies were performed on model suspension based on a Newtonian polymer matrix with a clay loading of 2wt%, prepared by methods previously reported by (Mobuchon et. al., Rheol Acta 46: 1045, 2007); the Newtonian matrix used here helps simplify the system greatly by removing complexities due to high polymer elasticity. Extensive rheology of the system was conducted on a stress controlled rheometer (ARES, Rheometric Scientific) showing yield stress-like behavior in steady shear testing. Time dependent growth of modulus was observed in flow cessation experiments. Flow-induced structural measurements were done in the flow-gradient (1-2) plane of simple shear flow using a custom made cone and plate shear cell via both small-angle and wide-angle x-ray scattering (SAXS and WAXS). Steady state measurements using both SAXS and WAXS show shear dependent orientation of the nanoparticles, with the particles getting increasingly oriented towards the flow direction as the shear rate increases. Time dependent behavior during transient flows was made possible due to the high flux synchrotron radiation, revealing partial relaxation of nanoparticles orientation during flow cessation. Other transient tests like step down and flow reversal showed interesting changes in particle orientation providing greater insight to bulk rheological behavior. Most of the SAXS and WAXS results were qualitatively the same; however some quantitative differences are seen because of the differences length scale probed using both the techniques.

Wednesday 6:10 Grand Terrace PO44

Molecular sequence segregation in molten thermotropic random copolyesteramide

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Rheo-X-ray, the use of X-ray scattering to monitor the behavior of polymeric melts subjected to shear, is here applied to study the microscopic response to shear of main-chain thermotropic random copolyesteramide. The copolyesteramide is based on 60% 2,6-hydroxynaphthoic acid, 20% terephthalic acid and 20% diaminophenol. This polymer is marketed as VECTRA B950. The molecular weight is ca. 30,000 g/mol, and it has a melting point of 285 °C, as determined by DSC scanning at 20°C/min. A parallel rotating disks cell designed to operate on a conventional X-ray generator has been used. The experimental setup allowed for the observation of the 002 (meridional) reflection in the melt. This reflection provide information about the periodicity (or otherwise) along the axes of the polymer chains and the degree to which neighboring chains are in longitudinal register. In this work we also report on the influence of shear rate and temperature on the 002 meridional reflection. The results showed that increasing shear rate disrupted the longitudinal register among polymer chains.

Wednesday 6:10 Grand Terrace PO45

Particle tracking velocimetry studies of polymer-polymer interfaces

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Particle Tracking Velocimetry (PTV) [1] was used in conjunction with rheological measurements to investigate slip at polymer-polymer interfaces in simple shear geometry using a sliding plate rheometer. Polymer pairs include narrow molecular weight styrene butadiene rubber (SBR) and polyisoprene (PIP). The samples were found to eventually undergo interfacial failure. However, the interfaces were able to withstand strains as large as 1 at high Weissenberg numbers. In some cases, arrested interfacial slip was also observed after shear cessation. These new results may shed light on the nature of A/B polymer interfaces in terms of the interfacial width and state of interfacial chain entanglement.

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Wednesday 6:10 Grand Terrace PO46

Study on slip phenomena in mold cavity of microcellular injection molding

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Microcellular injection molding with supercritical fluid (SCF) is able to produce lightweight, dimensionally stable plastic parts while using less material and energy. However, the molded parts of this technique are often unacceptable due to surface quality problems, such as surface roughness, streaks or swirl marks. Our work presents the function of slip phenomena to improve the surface quality of low density polyethylene (LDPE) microcellular injection molded parts. The samples were characterized by 2D surface roughness tester and Zygo® light interferometer, and then subjected to differential scanning calorimetry and dynamic rheological behavior analyses. It was found that an appropriate external lubricant addictive, injection speed and mold temperature had significant impacts on the parts surface quality. Surface roughness improved more than 30% compared to standard microcellular injection molded parts under the same processing conditions (low mold temperature, 25 and 45?). Most importantly, the dynamic mechanical properties, thermal properties and parts weight reduction of the samples with addictives showed little change. Melt slip theory is discussed to explain these reasons.

Wednesday 6:10 Grand Terrace PO47

Structural recovery and physical aging of epoxy film subjected to CO_2 jump

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This group has previously investigated the impact of structural recovery and physical aging on thermodynamic and mechanical properties of polymers after temperature jumps and compared with plasticizer jumps (1). Increasing plasticizer content depresses the glass transition temperature (Tg) in glassy polymers and this results in changes in the mechanical, optical and dielectric properties. Plasticizer jumps using a strong polar molecule have been previously studied by our group and have shown qualitatively similar behavior to temperature jump experiments (2). In the current work, we report the results on plasticization effects using a weakly polar molecule (CO_2) on the structural recovery and physical aging of glassy polymers after plasticization jumps and compare the behavior with temperature formed glasses.

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Wednesday 6:10 Grand Terrace PO48

Electrical conductivity and rheology of carbon-filled polypropylene-based resins

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Varying amounts of three different carbons (carbon black, carbon nanotubes, and synthetic graphite particles) were added to polypropylene and the resulting single filler composites were tested for electrical conductivity (1/electrical resistivity) and rheological properties. The percolation threshold was 1.4 vol% for carbon black composites, 2.1 vol% for carbon nanotube composites, and 13 vol% for synthetic graphite composites. The electrical resistivity at the highest loading level for each filler was 1.2 ohm-cm for 15 wt% (8.1 vol%) carbon black in polypropylene, 0.4 ohm-cm for 15 wt% (7.4 vol%) carbon nanotubes in polypropylene, and 0.1 ohm-cm for 80 wt% (61.6 vol%) synthetic graphite. For synthetic graphite/polypropylene composites, the viscosity increase was due to a volume filling effect. Composites containing carbon nanotubes and/or carbon black exhibited viscosity increases above those containing only synthetic graphite particles.

Wednesday 6:10 Grand Terrace PO49

Magnetic microrheometry of polymer coatings

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Polymer coatings are prepared by depositing a polymer solution or reactive monomer onto a substrate and then drying or curing to for a solid coating. During solidification, the viscosity of the coating increases dramatically. The local viscosity can also vary through the coating thickness due to gradients in solvent concentration or chemical reaction rates. Information about the changes and spatial gradients in the viscosity of coatings during solidification would aid in process design and formulation, and also to avoid solidification defects. Since conventional bulk rheometry cannot easily be used to follow viscosity changes of coated layers during solidification, a new method is required for nondestructive real-time monitoring of the local viscosity and its change over time. In this study, we used magnetic microrheometry to investigate local rheological properties of polymer coatings. A new apparatus was designed for coating rheology studies. NdFeB magnets, mounted on micropositioners, were used to produce a strong and uniform force on Fe-oxide microparticles dispersed within coatings. Particle motions were tracked with an optical microscopy the data was used to find local viscosity and its change during solidification. Validation studies were carried out with coating liquids of known bulk rheological characteristics: aqueous 5.08 wt % poly(vinyl alcohol) (PVA) and 13.5 wt % polyimide precursor in NMP (PI). The viscosity from the microrheometry was determined to be 0.13 Pa•s for PVA and 19.3 Pa•s for PI. These results were close to the results from the bulk rheometry (0.11 Pa•s for PVA and 12.7 Pa•s for PI). The bulk measurements also showed that the liquids are Newtonian in the low shear rate range used in the microrheometry. The PVA coating viscosity was characterized during drying. Its viscosity increased from 0.13 to 5.2 Pa•s over the course of 65 minutes. The effect of particle position relative to the substrate was also studied and conditions were found to avoid artifacts related to position.

Wednesday 6:10 Grand Terrace PO50

Direct measurement of deformation-induced molecular mobility in polystyrene

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Using an optical photobleaching technique we are able to simultaneously measure creep and molecular mobility in polymer glasses. In previous experiments on poly(methyl methacrylate) using this technique, a factor of 2000 mobility enhancement was observed during deformation. Here we extend the previous work in several directions. We show that similar results are obtained on lightly cross-linked polystyrene glasses. We have also utilized multiple probe molecules to show that the distribution of relaxation times in polymer glasses narrows significantly during plastic flow. Finally we explore the effect of cross-linking density in polystyrene on these relationships.

Wednesday 6:10 Grand Terrace PO51

Effects of shear forces on the conductive network formation in multiwalled carbon nanotube/epoxy composites

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In this study, carbon nanotube based polymer nanocomposites are produced by dispersing multi-wall carbon nanotubes in an epoxy system containing bisphenol-A resin and an amine hardener. The effects of processing conditions on the electrical conductivities and percolation thresholds are discussed. By a rheometer which can monitor CNT/Epoxy suspensions rheologically, optically and electrically at the same time, it is shown that shear forces have great influence on the conductive network formation and on the electrical conductivities of the suspensions. The formation and destruction of agglomerates are observed by evaluating their mean sizes as a function of time. The agglomerate size decreases with growing shear rate, however, if the shear rate is reduced to the previous level, agglomerates start reforming. This shows that the agglomeration process is reversible and every shear rate value can produce a certain size of agglomerate. Temperature effect on the destruction and formation of agglomerates are also investigated and it was seen that, with increasing temperature, the speed of destruction and formation of agglomerates increases. The effects of processing steps regarding the network formation in the suspensions are discussed. In some of the suspensions, pre-shearing steps at high shear rates are needed in order to obtain a conductive network. As a future work, fiber level simulations developed by [1] will be used to simulate network formation of CNTs in polymer composites.

References: 1. Emilio J. Tozzi, Hydrodynamics, Rheology and Conduction in Suspensions of Arbitrarily Shaped Fibers, Ph.D. Thesis, University of Wisconsin-Madison, 2008.

Wednesday 6:10 Grand Terrace PO52

Gelation of drilling fluids in deepwater wells

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During drilling operations, many fluids must present gelation properties to maintain in suspension particle solids generated by the driller when the pumping is interrupted. However, excessive gelation can cause undesirable pressure peaks when the circulation is retaken, what promotes operational risks. Well drilling in deep and ultra deepwater presents an additional challenge as the fluid will be submitted to high pressure and temperature variations during its circulation from the surface to the bottom of the well. This work is aimed to evaluate the application of several rheological experiments in order to represent the gelation of the fluids in deep water conditions. Thus, we can obtain a better understanding of the phenomenon in order to develop a methodology to be used in fields to prevent the emergence of huge pressure peaks when the circulation is retaken. Once the procedures are established, it was evaluated the gelation of the fluid system in different stop times (corresponding to connections, short and complete maneuvers). The results have shown a great influence of the temperature on the gel formation process and the viscosity peaks. Besides, the resting time also influences the viscosity peaks. Repeatability of the viscosity versus shear rate curves was obtained before and after gelation, indicating that the fluids properties are recovered.

Wednesday 6:10 Grand Terrace PO53

Dynamic rheological properties of binetworked gels

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1,3:2,4-dibenzylidene sorbitol (DBS), a low-molar-mass organic gelator (LMOG), is a crystalline solid that can, upon dissolution in a wide variety of organic solvents and polymers, self-assemble via intermolecular hydrogen bonding into nanofibrils with a primary unit diameter of ~10 nm which form a continuous, load-bearing network at low concentrations (< 1 wt%) that is temperature- and shear-sensitive. Another network-forming molecule is an ABA triblock copolymer with microphase-separated glassy endblocks in the presence of a midblock-selective solvent. At sufficiently high solvent concentrations, the copolymer molecules self-assemble into a network stabilized by micelles that are solid at ambient temperature. Unlike the DBS networks, the copolymer networks tend to exhibit considerable elasticity and resilience. We investigate the binetwork generated when DBS and an ABA triblock copolymer are added together and permitted to gel concurrently. We employ dynamic rheology to probe the effect of DBS on poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) triblock copolymer network development in a midblock-selective solvent. Frequency sweeps conducted at ambient temperature confirm that, within the linear viscoelastic limit, the materials examined behave as physically-crosslinked gels at all loadings of DBS (0 to 5 wt%). The storage modulus of the material increases significantly with increasing DBS concentration and provides an enhancement of more than an order of magnitude at 1 wt% DBS. Isochronal temperature sweeps are performed to discern the interaction between DBS and SEBS micelles. At low DBS concentrations, the nanofibrils reinforce the micelles and shift the order-disorder transition (ODT) of the copolymer to higher temperatures, as evidenced by a precipitous fall in G'. Beyond a loading of 1 wt% DBS, however, the nanofibrillar network saturates, and additional DBS further contributes to the formation of spherulitic structures. The rheological tests conducted here are complemented by microscopy analysis.

Wednesday 6:10 Grand Terrace PO54

Early stages in polymer crystal growth for isotactic poly-1-butene: Spherulite jamming or network percolation?

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Isothermal crystallization experiments were performed on isotactic poly-1-butene. Optical microscopy, DSC, SALS, and rheology, at early stages of spherulite growth, provide quantitative information about nucleation density, volume fraction of spherulites and their crystallinity, and the mechanism of connecting into a sample spanning structure. An understanding of the kinetics of nucleation helps predicting the crystal growth, in particular for early stages of crystallization. An attempt is made to connect the crystal fraction inside spherulites with the average crystallinity of the entire sample. The crystal fraction inside spherulites is very small initially but increases with time and catches up with the sample crystallinity later on. Optical microscopy near the fluid-to-solid transition suggests that the transition, as determined by rheology, is not caused by packing/jamming of spherulites but by the formation of a percolating structure. Impingement of pairs of spherulites occurs already much before percolation. This makes it difficult to predict crystal growth and define spherulitic impingement for the whole sample. At percolation, the absolute crystallinity is about 7-8 vol%. This shows that spherulites are mostly amorphous before impingement.

Wednesday 6:10 Grand Terrace PO55

Processing of PLA/clay/wood nanocomposites: Thermal-mechanical properties

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Poly (lactic acid) (PLA) has suitable mechanical properties for a wide-range of applications. However, there are also problems associated with cost, brittleness, distortion temperature, gas permeability and melt viscosity. Adding inorganic or organic fillers to the polymer matrix to form composites improves its properties. Wood is a renewable material of low density and cost, higher resistance to breakage and less abrasion to processing equipment. Wood/biopolymer composites (WBPCs) also provide environmental incentives. Wood/PLA composites with 20-40 wt. % wood flour exhibit improved flexural and tensile moduli, increased heat deflection temperature (HDT), and higher temperature of thermal decomposition. Wood/PLA composites still have several deficiencies, such as relatively low flexural and tensile strength, low notched impact strength, low dimensional stability, creep and large thermal expansion. A concentration of less than 5 wt. % nanoclay can result in remarkable improvements of the mechanical and thermal properties of PLA based materials. Hence, compounding nanoclay with wood flour/PLA composites should result in greatly improved clay wood biopolymer composite materials. There are three main factors that are believed to affect the properties of clay wood biopolymer composites (CWBPCs). One is the poor interfacial adhesion between the polymer matrix and the filler surface. A second is the dispersion of nanoclay (intercalated or exfoliated) and wood fibers in the polymer matrix. The latter relates to the brittleness of PLA. Hence, compatibilization should be used to improve interfacial interactions. Effective compounding and processing conditions also play an important role in controlling filler dispersion as well as controlling crystallization conditions used to modify the PLA matrix.

Wednesday 6:10 Grand Terrace PO56

Stiffening, fracture, and friction of physically associating networks by shear rheometry

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The aim of the present work is to employ shear rheometry as a tool to simultaneously study the mechanical strength, toughness, and frictional properties of soft viscoelastic networks. A physically associating acrylic triblock copolymer solution is utilized as a model system. At elevated temperatures these solutions are viscoelastic liquids with near Maxwellian relaxation. The relaxation time increases dramatically as temperature is reduced, such that at room temperature the solutions become viscoelastic networks. When deformed over a range of shear rates, these networks demonstrate elastically driven behavior that can be quantified via rheometry. During fast deformation (i.e.,Weissenberg number, Wi, greater than unity), strain stiffening followed by softening is observed, reminiscent of fluid fracture.[1] At decreased rates (Wi less than unity), evidence of viscoelastic- and liquid-like instabilities is observed.

Compared to previous studies of extreme nonlinearity, the work performed here benefits from studying solutions with well-defined molecular structures, tailorable chain architectures, and a wide range of accessible relaxation times. Connections can also be established between the shear geometry used here and conventional mechanical analysis in tension and compression. For example, the linear and nonlinear behavior of the networks prior to fracture can be modeled by an empirical strain energy function that has been used previously to capture strain stiffening of acrylic triblock copolymer gels in biaxial compression.[2] Additionally, the post-fracture stress response during shear deformation at a constant rate is found to be consistent with previous results obtained for the frictional sliding of gels.[3]

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[2] M. E. Seitz, D. Martina, et al., *Soft Matter* **5** (2), 447 (2009).
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Wednesday 6:10 Grand Terrace PO57

Characterization of shape-memory polymers on DMA

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Shape-memory polymers (SMP) have received increasing attention because of their scientific and technological significance. These kinds of materials have the capability of changing their shape in response to an external stimulus, such as temperature or light. The ability of shape memory polymers to spontaneously recover large deformations in restricted environments has been exploited in numerous applications, such as heat-shrink tubing, deployable aerospace structures, microsystems, and biomedical devices. It is important to develop a quantitative mechanical analysis technique for better understanding the performance of this kind of material. In this paper, the thermo-mechanical response of a polyurethane based shape-memory polymer material was analyzed using a TA Instruments DMA Q800. A detailed procedure was developed for quantitative measurement of the properties in cyclic mechanical tests.

Wednesday 6:10 Grand Terrace PO58

Electrospinning of highly sulfonated polystyrene nanofibers and the influence of rheological behavior of the solution on electrospinnability

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Nanofibers of highly sulfonated polystyrene (IEC ~ 4.5 meq/g) were successfully electrospun and the process of electrospinning this difficult-to-spin material was studied in detail. Of particular interest were the relationship between rheological properties and spinnability. To this end, the solution viscosity and complex dynamic modulus of SPS in DMF were measured using an AR-G2, controlled-stress rheometer equipped with a concentric-cylinder fixture. A change in scaling of the viscosity-concentration relationship occurred at a critical concentration, Ce, where the scaling exponents changed from 0.36 ± 0.15 to 4.57 ± 1.13 at low and high concentration, respectively. As the solution concentration increased, the morphology changed from beads to bead-on-string fibers to continuous cylindrical fibers. Beaded fibers and continuous bead-free fibers of SPS (500 kDa) in DMF could be spun at ~ 2 Ce and 3.5 Ce, respectively, where Ce is the entanglement concentration measured from solution viscosity measurements. This value is somewhat lower than the 8 Ce for poly(2-(dimethylamino)ethyl methacrylate hydrochloride) in 80/20 w/w deionized water/MeOH reported by McKee et al. (Macromolecules 2006, 39, 575-583). The onset of formation of beaded fibers, as opposed to isolated beads, coincided with a sharp transition in the scaling of the storage modulus-concentration relationship.

Wednesday 6:10 Grand Terrace PO59

Crystallization kinetics and properties of annealed electrospun PLA and nylon fibers

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In this study, electrospinning experiments have been carried out to investigate the effect of annealing on the crystallization kinetics and physical properties of two polymeric electrospun fibers. Submicron scale Nylon 6 and PLA fibers with different crystallization rate have been obtained using several solvents under the optimal conditions for a stable flowing jet. From the rheological, thermal, morphological, and structural analyses, the crystallization kinetics of both as-spun fibers and annealed fibers has been explored. It has turned out that crystalline structural patterns of two fibers as annealing time evolves are totally different each other, caused by the degree of the flow-induced crystallization acting on the spinline. Also, we have tried to scrutinize the effect of solvent evaporation on the crystallization and compare the results by solution and melt electrospinnings.

Wednesday 6:10 Grand Terrace PO60

Rheo-dielectric and velocity field analysis of entangled polyisoprene solution under shear flow

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Rheo-dielectric and particle tracking measurements are conducted to examine the chain dynamics under homogeneous shear flow for entangled solutions of linear cis-polyisoprene (PI) in oligo butadiene. The PI chains have type-A dipoles parallel along their backbones, and the dielectric response corresponds to the relaxation of end-to-end vector of the chains. Watanabe et al. (Macromolecules, 35, 2339, (2002)) reported that the dielectrically detected terminal relaxation time of the PI chains is insensitive to the shear rate even under fast shear where shear thinning is observed. To analyze such dielectric relaxation data, usually homogeneous flow profiles are assumed. However, S. Q. Wang et al. have recently reported that entangled polymer melts and solutions show inhomogeneous velocity profiles if shear rate is much larger than terminal relaxation time. Hence observation of the flow velocity profiles of the sample will be important to consider the mechanism of dielectric behavior. We utilized particle tracking velocimetry (S. Q. Wang, Macromol. Mater. Eng. 292, 15, (2007)) to observe velocity profiles in the PI solution. Homogeneous flow profiles were observed in the PI solution under shear with the shear rate slightly larger than terminal relaxation time but smaller than Rouse time of the PI chains. We will report the dielectric property measured in this shear rate region and discuss chain dynamics.

Wednesday 6:10 Grand Terrace PO61

Further examination of elastic driven failure of entangled melts after step uniaxial extension

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Recent particle tracking velocimetric observations of step shear uncovered new features concerning the elastic yielding of entangled polymer melts [1]. Specifically, it was found that macroscopic motions still take place after cessation of a slow shear with rates below the reciprocal of the Rouse relaxation time. Under this condition, no chain stretching is possible due to the fast chain retraction, and therefore no mechanism for instability is feasible during stress relaxation, according to the Doi-Edward type tube model. We propose to further compare experiment with the tube model by investigating characteristic behavior of entangled melts during and after step extension. In particular, we are interested in finding out whether a step-stretched specimen of non-crosslinked styrene-butadiene rubber would be stable against necking during relaxation at both fast and slow Hencky strain rates. [1] P. E. Boukany, S. Q. Wang, and X. Wang, Macromolecules, web published (2009).

Wednesday 6:10 Grand Terrace PO62

Molecular imaging of wall slip and shear banding in entangled DNA solutions

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Recent experimental observation based on particle-tracking velocimetric measurements revealed that entangled fluids may suffer wall slip or shear banding when flow rates are faster than the terminal relaxation rate. These findings raised several issues in rheometric measurements and challenged available theoretical pictures of entangled polymer fluids under large deformation. Here, we used confocal microscope and stained DNA to visualize the conformation of long chains in entangled media during shear and channel flow. Several important features like apparent slip, true slip and shear banding is observed during startup shear directly through the stained DNA molecules without introducing any tracking particles. These new experimental findings may elucidate the molecular origin of flow inhomogeneity in entangled polymeric fluids.

Wednesday 6:10 Grand Terrace PO63

Effect of interfacial crosslinking, compatibilizer concentration and volume fraction on reactively compatibilized model immiscible blends

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In the polymer blend industry is it common to generate at compatibilizer using an interfacial chemical reaction between polymers in different phases. This method, known as reactive compatibilization, typically involves an end-functional polymer in one phase reacting with a multifunctional polymer in the other phase to form a graft copolymer. In this paper we explore immiscible polymer blends in which **both** reactive species are multifunctional, and thus form a crosslinked network at the interface.

We first explore the effects of the crosslinked interface by comparing two model blends, a "reference" blend compatibilized by a diblock copolymer, and a reactive blend compatibilized by an interfacial crosslinked network. While the diblock-containing blend forms a typical droplet matrix morphology, the reactive blend shows a droplet-matrix morphology with non-spherical drops, sometimes with wrinkled interfaces, that are joined together in a space-spanning network. These features are attributable to the interfacial crosslinking in the reactive blend and depend on compatibilizer concentration.

The rheological properties (creep, recovery, and dynamic oscillatory) of the diblock-containing blend are similar to those of compatibilized droplet-matrix blends studied previously. Conversely, at adequately high compatibilizer concentrations, the reactive blend exhibits gel-like behavior due to the space-spanning network, coalescence is suppressed, and large viscosity and creep recovery are observed. At lower compatibilizer concentrations, these properties are not observed. Varying the volume fraction results in a sharp increase in the viscosity and creep recovery near the phase inversion point. Interestingly, when PDMS is the majority phase, no gel-like behavior is observed, even at high compatibilizer concentrations.

Wednesday 6:10 Grand Terrace PO64

Determination of the distribution of orientation angles of glass fibers suspended in Newtonian and Boger fluids

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A determination of the distribution of orientation angles of glass fibers suspended in a Newtonian and a Boger fluids was performed in this work. For this purpose, a flow visualization of the suspensions in the semidilute and concentrated regime was carried out in a parallel plate rheometer at 25 ºC. Images of the flow region were obtained and analyzed by using fast Fourier transforms. The distribution of orientation of fibers was isotropic at rest for the range of concentrations studied, but became anisotropic with increasing the shear rate up to reach a fully orientated state in the flow direction. The orientation states were properly described by a second order tensor considering that the initially isotropic distribution becomes orthotropic as soon as the flow is started. Finally, it was observed that the elasticity of the matrix retards the fiber orientation, this is probably due enhancement of hydrodynamic interactions.

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Wednesday 6:10 Grand Terrace PO65

Description of the kinematics of the stick-slip capillary flow of high-density polyethylene by using PIV measurements

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A study of the kinematics of the stick-slip capillary flow of high-density polyethylene has been carried out in this work by using particle image velocimetry (PIV). The experiments covered a wide shear rate range and the velocity maps and profiles across the die were obtained for the different regimes of the discontinuous flow curve. In the low shear rate region, the melt exhibited shear thinning without slip. In the unstable stick-slip regime, an alternating behavior between full adhesion and slip was observed, whereas both, the maximum velocity and the slip velocity of the melt, changed continuously during pressure oscillations. In addition, non-homogenous slip, characterized by regions with and without slip at the die wall, was occasionally observed during the oscillations. A steep rise of the slip velocity took place from the onset of the stick-slip regime and reached values higher than 70% of the maximum velocity for the profiles in the high shear rate branch. However, a true plug flow was never observed due to shear thinning of the melt. Finally, a direct proof of the Mooney theory for slip in polymer melts is given on the basis of the comparison of velocity profiles measured in the low and high shear branch.

This work was supported by CONACYT (51837 K) and SIP-IPN (20082313). F. R-G and B. M. M-S had CONACYT and PIFI-IPN scholarships to carry out this work. J. P-G and L. de V. are COFAA-EDI fellows.

Wednesday 6:10 Grand Terrace PO67

Continuum based rheological modeling of polymer/layered silicate nanocomposites

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The aim of this work was to propose a modified constitutive equation in order to model the melt rheological behavior of nanoclay plettlets containing polymers. In the first attempt an upper-convected structural model, which has been used for suspensions with strong inter-particle interactions, in which the structural parameters was considered to be a function of organoclay plettlets alignment was adopted. While this model was able to qualitatively describe the shear stress behavior in simple shear flow experiments, its predicted results were not in quantitative agreement with experimental results in different shear rates. Therefore in the second attempt the total force (stress) was assumed to be the summation of hydrodynamic and interparticle forces. For modeling hydrodynamic stress contribution, Lipscomb constitutive equation was employed and for inter-particle contribution a yield stress based and a structural constitutive model was adopted. The results predicted from this model were found to be in satisfactory agreement with experimental results obtained at different shear rates and organoclay contents. The melt linear and nonlinear rheological data required for modeling were obtained via experiments performed on polypropylene/organoclay nanocomposites samples by using a rheometric mechanical spectrometer (RMS).

Wednesday 6:10 Grand Terrace PO68

Probing dough rheology using sliding plate rheometry

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Dough is a multi-component complex fluid consisting of water and swollen starch particles suspended in hydrated elastic gluten matrix. Rheological properties of dough play an important role in the agricultural and the food processing industries. However, rheological characterization of dough is proving to be difficult due to a range of testing issues and anomalies in flow behavior. For example, in a cone-plate or parallel-disk rotational rheometer, we get dough rollout from the gap before steady state viscosities can be established. Free boundary errors due to edge effects become pronounced in rotational rheometers since they employ total torque measurement. In this work, we exploit the benefits of using local shear stress transduction in addressing these difficulties in the rheological testing of dough. Steady shear, large amplitude oscillatory shear (LAOS) and exponential shearing will be carried out using sliding plate rheometry incorporating local shear stress transduction.

Wednesday 6:10 Grand Terrace PO69

Development of wall boundary model for primitive chain network simulations

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In condensed polymeric liquids confined in slit channels, the movement of chains is constrained by two factors: entanglement among the chains and the excluded volume between the chains and the wall. In this study, we propose a wall boundary (WB) model for the primitive chain network (PCN) model, which describes the dynamics of polymer chains in bulk based on coarse-graining upon the characteristic molecular weight of the entanglement. The proposed WB model is based on the assumptions that (i) polymers are not stuck but simply reflected randomly by the wall, and (ii) subchains below the entanglement length scale behave like those in bulk even near the wall. Using the WB model, we simulate the dynamics of entangled polymer chains confined in slit channels. The results show that as the slit narrows, the chains are compressed in the direction normal to the wall, while they are expanded in the parallel direction. In addition, the relaxation time of the end-to-end vector increases, and the diffusivity of the center of mass decreases. The compression in the normal direction is a natural effect of confinement, while the expansion is introduced by a hooking process near the wall. The trends revealed that the relaxation time and diffusivity depend on the increase in friction due to an increased number of entanglements near the wall, which is also associated with the hooking process in the PCN model. These results are expected within the assumptions of the PCN model. Thus, the proposed WB model can successfully reproduce the effects of wall confinement on chains.

Wednesday 6:10 Grand Terrace PO70

Brownian dynamics simulations of rheology of magnetic fluids in magnetic fields

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Magnetic fluids, or so-called ferrofluids, are suspensions of magnetic nanoparticles which respond to imposed magnetic fields by changing their viscosity without losing their fluidity. Because the particles possess a magnetic dipole, an externally imposed magnetic field induces a body couple on the suspension and hence a state of asymmetric stress is possible. Prior work on modeling the behavior of magnetic fluids has focused on using phenomenological suspension scale continuum equations. A disadvantage of this approach is that one such equation, the so-called Shliomis magnetization relaxation equation [Soviet Physics JETP, 34, 1972], is subject of debate as its derivation is based on ad hoc arguments. An alternate expression (MRSh), due to Martsenyuk et al. [Soviet Physics JETP, 38, 1974] is available, but its complexity prevents analytical solutions except in the simplest flow and magnetic field configurations. Particle-scale simulations are emerging as an important tool in describing flows of magnetic fluids. Simulations present an alternative to study the applicability and limitations of suspension scale phenomenological equations in describing the flow of magnetic fluids under imposed magnetic fields. The rheology of dilute suspensions of spherical magnetic nanoparticles suspended in a Newtonian fluid and under applied shear and constant magnetic fields was studied through rotational Brownian dynamics simulations. Simulation results were compared with the predictions of suspension-scale models based on the two magnetization relaxation equations. Excellent agreement was observed between simulation results and the predictions of the MRSh equation. Good qualitative agreement was observed with predictions of the Shliomis equation, although this model fails to predict the magnitude of the magnetic field dependent effective viscosity.

Wednesday 6:10 Grand Terrace PO71

Application of the discrete slip-link model to bidisperse linear systems

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In contradiction with tube models the discrete slip-link model (DSM) shows that the contribution of chain sliding dynamics (SD) to the relaxation modulus has a shape significantly different from the contribution by constraint dynamics (CD) for monodisperse linear chains. However, the product of these two contributions are nearly identical for the two models, so no real difference is observable between the two theories. On the other hand, this observation suggests that tube models and slip-link models might yield different predictions for the observable relaxation modulus of bidisperse blends. Tube models essentially predict double reptation for blends. However, better agreement with data is obtained by using a phenomenological exponent of 2.2, which was proposed by Marrucci and also recommended by Rubinstein et al. and by Ruymbeke et al. The exponent is hypothesized to be an effect either of non-binary entanglements or tube dilation.

The adjustable parameters of the DSM are fitted to a single-molecular-weight, monodisperse experimental dataset and held fixed for bidisperse blend predictions of the same chemistry and temperature. No additional physics or mathematics are added to the theory. We find that the DSM with binary entanglements predicts data at least as well as double reptation with the phenomenological exponent of 2.2. We conclude that the assumption of binary events for entanglements is sufficient. We use the DSM to then explore the source of the ad hoc exponent 2.2. For example, the DSM showed that the presence of CD influences relaxation by SD, which is neglected in tube models.

Wednesday 6:10 Grand Terrace PO72

Coarse projective integration circumvents the closure problem for FENE dumbbells

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Coarse projective integration is a computational procedure that performs simulations at a macroscopic, coarse level of description, using only appropriately initialized simulations with a more microscopic, fine-scale model. We present a coarse projective integration method for FENE dumbbells. At the fine-scale, we use a stochastic simulation of an ensemble of FENE dumbbells; a closed evolution law at the coarse level is assumed to exist (but unavailable!) in terms of the mean square displacement and the stress tensor. The procedure consists of three steps: (1) lifting, i.e. initialization of the ensemble, consistently with the coarse variables; (2) fine-scale simulation; and (3) restriction, i.e. computation of the coarse variables from the ensemble, after which an extrapolation (projection) is done forward in time. The approach avoids the need for approximate closure relations, while being more efficient than a full fine-scale simulation. We discuss the lifting procedure and variance reduction, and illustrate the potential of the approach on a simple model problem.

Wednesday 6:10 Grand Terrace PO74

Extensional flow of viscoelastic fluids

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In this paper, we consider viscoelastic stresses arising in the extensional flow of a Oldroyd and Giesekus model, We present exact solutions to partial differential equations describing the viscoelastic stresses. Also we present singular solutions for a range of values of the Weissenberg number and deduce the results of Renardy (J. Non-Newtonian Fluid Mech. 138 (2006) 204-205), and Becherer et al. (J. Non-Newtonian Fluid Mech. 153 (2008) 183-190) for the case of upper convected Maxwell (UCM) fluid and one independent spatial variable. As we considered the viscoelastic stresses over two spatial variables, we are able to study the effect of variable boundary data at the inflow. As such, our results are applicable to a wider range of fluid flow problems. Keywords: Extensional flow, stagnation point flow, Oldroyd and Giesekus model, upper convected Maxwell fluid, exact solution.

Wednesday 6:10 Grand Terrace PO75

Numerical solution of the start-up of well drilling fluid flows

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Many oil well drilling fluids are designed to gel when it is not submitted to shear stress. The purpose is to avoid cuttings to lie over the bit during the circulation stoppage. When circulation resumes the pumping pressure rises above the circulation pressure in order to overcome the gel strength. Due to its thyxotropic effect, the gel viscosity remains high for a while after the circulation restarts. The gelation may have significant importance, specially, in deep waters where high pressures and low temperatures take place. The current work presents a compressible transient flow model of the start-up flow of drilling fluids, in order to predict borehole pressures. The model comprises one dimensional conservation equations of mass and momentum. A thixotropic fluid model is fitted to rheometer data and it is used to characterize the time dependent rheology of gel breaking. The viscous effect is modeled by employing the friction factor approach. The results of the transient flow model are corroborated with the literature data. Case studies are conducted to evaluate the effect of fluid flow properties, well geometry and pumping pressure on borehole pressures.

Wednesday 6:10 Grand Terrace PO76

Spontaneous flow and rheological properties of active liquid crystals

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We report analytical results and hybrid lattice Boltzmann (HLB) simulations of the hydrodynamics of an active nematic liquid crystal sandwiched between confining walls. When no external forces are applied to the extensile fluid in 1D, we observe a linear instability leading to a spontaneous flow, while for the contractile fluid the transition is subcritical. In 2D and 3D both instabilities are linear leading to a chaotic flow close to the onset of the linear instability. The observed flow patterns resemble "bacterial turbulence" often seen in dense bacterial suspensions.

Under applied steady shear, for extensile fluids we have found 1D flows with negative viscosities which are linearly unstable in 2D. Similarly, under oscillatory shear, there exist regions where either G' or G", or both become negative. Again, these 1D flows are shown to be unstable and we calculate the nominal rheological response of the resulting 2D vortex flow.

Wednesday 6:10 Grand Terrace PO77

A new jamming critical point controls the glassy dynamics of ellipsoidal particles

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Using numerical simulations, we study glassy dynamics in systems composed of bidisperse soft repulsive ellipse-shaped particles as a function of temperature (T), volume fraction (v), and aspect ratio (a). We find a critical aspect ratio (a* = 1.5), which separates two qualitatively different dynamical regimes. Below a*, rotational degrees of freedom (RDOF) relax faster than translational degrees of freedom (TDOF), and above a*, TDOF relax faster than RDOF. At a=a*, both TDOF and RDOF relax logarithmically with time, suggesting that a=a* is a critical point in the T-v-a plane. Particle rearrangement events are qualitatively different in these two regimes: relaxation occurs via cage breaking events for a < a* versus large collective fluctuations for a > a*. The collective fluctuations for a > a* give rise to anomalous $t^{1/2}$ behavior in the mean-square displacement. These results suggest deep connections between glassy dynamics and the jamming transition. We believe that the critical point at a = a* and the anomalous collective fluctuations found in glassy systems of ellipses have their origin in the peak in the jammed packing fraction at a* and the hypostaticity of static ellipse packings.

Wednesday 6:10 Grand Terrace PO78

Molecular hydrodynamics in nanoparticle suspensions

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Recent developments in the field of micro- and nanofluidics have renewed interests in the study of molecular hydrodynamics in confined geometries. In our previous work we had studied the friction force experienced by a nanoparticle that was translating in a confined fluid.[1] The nanoparticle had a smooth surface. That work was focused on studying the effect of various factors such as velocity slip at nanoparticle surface, presence of nanochannel surfaces and cooperative hydrodynamic effects on the friction force experienced by the smooth nanoparticle and showed deviations from the Stokes law predicted bulk value for the friction force. In this work we have studied a nanoparticle with rough surface in a nanoconfined fluid. The rough nanoparticle provides a more realistic representation of the experimental system and enables us to study the effect of nanoparticle surface characteristics on the hydrodynamic behavior. We use molecular dynamics (MD) simulations to study the friction force experienced by a nanoparticle that is translating through the channel and also the torque experienced by nanoparticle that is rotating and compare these with the continuum predictions. It was observed that the surface roughness significantly reduces the velocity slip at the nanoparticle surface resulting in friction force values that are higher than those for a smooth nanoparticle; these values are in better agreement with the continuum predictions. The torque experienced by the rotating nanoparticle was observed to be smaller than the Stokes law predicted value.

[1] S. C. Kohale and R. Khare, J. Chem. Phys. 129, 164706 (2008).

Wednesday 6:10 Grand Terrace PO79

Laser microrheology for soft materials

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This work present the application of the microrheology technique for the study of the visco-elastic properties of fluids like colloids, polymers, gels, emulsions. Microrheology is based on the Diffusing Wave Spectroscopy (DWS) method that relates the particle dynamics to the speckle field dynamics, and further the visco-elastic moduli G' and G" at the micron scale with respect to frequency. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. We show that the robust measurement of speckle correlation using the inter image distance can bring useful information for industry on viscoelasticity variations over a wide range of frequency without additional parameter (for instance comparison between products with different concentrations of polymer, structure recovery of one product after shearing, evolution of the mesh size of a polymer during gelation, variation of viscoelastic properties versus temperature, pH, stability of emulsion, suspension...).

Wednesday 6:10 Grand Terrace PO81

MEMs parallel plate rheometer for small amplitude oscillatory shear micro rheology measurements

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Growing numbers of applications including proteomics, cosmetics, and thin film coatings use novel viscoelastic materials that derive their rheological properties from micro scale structure created by the inclusion of long chain molecules, nano particles and dispersed fluids. These applications also often involve flow through confined geometries which deform the micro structure, altering the materials' rheology and limiting their effectiveness. Characterization of these novel materials is often difficult due to the small volumes initially formulated. Therefore, "micro rheology" and thin film rheology techniques have been employed to characterize these materials. Micro rheology commonly refers to analyzing the motion of micro probe particles to measure fluid response at small length scales. This method examines a small area around the probe particle, ignoring a fluid's micro structure. A number of methods exist to study thin films, but they rely on complex modeling of probe geometry, contact area and material properties to extract anything more than the elastic modulus of a film.

We propose a MEMs parallel plate rheometer for micro rheology that will confine viscoelastic materials to length scales on the O(1) um, but probe the entire material response to dynamic oscillatory shear. The MEMs Parallel Plate rheometer uses a 1 mm square nano positioner stage to apply a controlled sinusoidal strain. Through physical modeling of the system, both storage and loss moduli can be extracted for a wide range of frequencies. The confinement of the fluid is set by adjusting the gap between the stage and a transparent cover plate that allows optical observation. By decreasing this gap, the increasing effects of confinement can be observed. Because the strain is applied to the entire fluid body, this device examines the effects of confinement on the entire micro structure. Furthermore, this device uses less than 1 nL of material, which is beneficial for these types of novel experimental materials.

Wednesday 6:10 Grand Terrace PO82

Dynamic self-assembly of non-colloidal particles in Couette flow

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Numerical simulations, using the force-coupling method, demonstrate that the dynamic self-assembly of concentrated, non-colloidal suspensions into order states may occur in Couette flow significantly below the freezing transition for homogeneous suspensions. At a volume fraction as low as &phi = 0.48, particles near the wall assemble into strings which are organized as a simple hexagonal array by hydrodynamic interactions. The suspension exhibits a complex behavior depending on the ratio of the channel-height to the particle radius, H/a. Increasing H/a from a base value of 10, ordering transitions are observed, from disorder to hexagonal order and then to disorder-order coexistence. Only in a narrow range of H/a, the whole channel is in a hexagonally ordered state, while the disorder-order coexistence is prevalent for a wide range of H/a. It is shown that, in the small channel H/a = 10, the transition to hexagonal order is significantly hindered. The application of external torques on the particles can further modify the order-disorder transitions. The hexagonal order of the particles is weakened bythe negative torque, leading to the increase of the shear viscosity. On the other hand, the positive torque has a favorable effect on the ordered state. At a lower volume fraction (&phi = 0.40), where the hexagonal order is not developed, the external torques do not have a significant effect on the suspension rheology.

Wednesday 6:10 Grand Terrace PO83

Self-consistent particle simulation of shear banding of anisotropic particulate suspensions in rotating Couette flow

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Shear banding of particulate suspensions in rotating Couette flow has been studied by a self-consistent particle simulation. Hydrodynamic interaction is taken into account by combining the microscopic particle dynamics and the macroscopic flow simulation. The flow field and the particle motion are coupled and solved self-consistently. We analyze three-dimensional microstructures of repulsive particulate suspensions using DLVO-type potentials under disturbed rotating Couette flow. Anisotropic particulate suspensions are modeled by bonding particles as a cluster. Non-homogeneous tangential velocity profiles and discontinuous shear rates clearly indicate the shear banding in particulate suspensions. Flow induced microstructures are analyzed to find out the effect of interparticle potential force, rotating velocity, particle volume fraction, and cluster anisotropy on shear banding. Vorticity directional instabilities in microstructures are also investigated to understand vorticity banding in shear experiments. We expect this study provide a deep understanding on dynamics of particulate suspensions in complex flow field.

Wednesday 6:10 Grand Terrace PO84

Field-induced motion of a ferrofluid droplet: A testbed for treatment of retinal detachment

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Recent developments in the synthesis and characterization of ferrofluids are motivated by biomedical applications, where the treatment of retinal detachment is one example. A small amount of ferrofluid is injected into the vitreous cavity of the eye and guided by a permanent magnet inserted outside the scleral wall of the eye. The drop travels toward the side of the eye, until it can seal a retinal hole. The time taken for the drop to migrate is an important quantity which needs to be predicted, and which must be relatively short for the feasibility of this procedure. The motion of a hydrophobic ferrofluid droplet under an externally applied magnetic field is investigated numerically. A viscous medium models the vitreous material. The time taken by the droplet to travel through the medium and the deformations in drop shape are investigated and found to compare well with an experimental study on a simplified model.

Wednesday 6:10 Grand Terrace PO85

Static length scales in overcompressed, jammed packings of soft grains in 2D

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We study mechanically stable, disordered packings of soft disks above jamming, and use a form of the point-to-set correlation function to describe a length scale that diverges as the packing fraction approaches the critical jammed packing fraction from the over compressed regime. We will present a method for sampling mechanically stable force networks for a given disordered packing geometry, and measure the point-to-set correlation function for the sampled networks, averaged over many underlying packing geometries. This correlation function exhibits multiple length scales. We will also discuss the critical nature of mechanically stable, overcompressed ellipse packings with respect to the point-to-set correlation function.

Wednesday 6:10 Grand Terrace PO86

Viscoelastic stress wakes for Newtonian drop in a viscoelastic matrix

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We numerically study the influence of viscoelastic "wakes" that emanate from the drop tips. A recent experimental study of a Newtonian drop suspended in a viscoelastic matrix undergoing simple shear displays a transient overshoot in drop deformation, which is absent in fully 3D simulations. We therefore study the effects of viscoelastic stresses on Newtonian drop deformation in a viscoelastic matrix under shear. During drop evolution, the less deformed drop is found to be aligned more with the flow direction. As the drop to matrix viscosity ratio increases from 1 to past 3, drop rotation is promoted, with accompanying retraction when the capillary number is sufficiently high. Thus, an overshoot in deformation is promoted with increasing viscosity ratio.

Wednesday 6:10 Grand Terrace PO87

Particle collision in viscoelastic fluids

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Particle-particle and particle-wall collision occurs in many natural and industrial applications such as sedimentation, crystal growth, suspension rheology, and microfluidic devices such as those used in mechanical cell lysis. To accurately predict the behavior of particulate flows, fundamental knowledge of the mechanisms of single collision is required. Whereas several experimental studies have been conducted on the influence of the Newtonian fluid on the collision process, few numerical studies address this issue and the effect of viscoelasticity of the liquid yet to be discovered. In this work, particle-wall collision in Newtonian and viscoelastic fluids is numerically and experimentally studied. The effect of Stokes number, surface roughness, and Deborah number on the rebound velocity of a colliding spherical particle on a wall is considered. The experimental study of particle-wall collision in poly(ethylene-oxide) mixed with water shows that the results for the coefficient of restitution in polymeric liquids can be collapsed together with the Newtonian fluid behavior if one defines the Stokes number based on the local strain rate.

Wednesday 6:10 Grand Terrace PO88

Analysis of a two coupled Maxwell modes model for concentric cylinder flow

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Laminar flow profiles for the Two Coupled Maxwell Modes Model have been computed for concentric cylinder flow with inner/outer cylinder rotation and axial through-flow. In the limit of linear viscoelasticity the flow problem has been solved analytically. For a non-vanishing coupling parameter between the two Maxwell modes, the model equations have been solved numerically with a shooting algorithm. We present the flow profiles for concentric cylinder flow with axial through-flow, we calculate the volumetric flow rate, and we determine the position of maximum axial velocity in the gap. Furthermore, we present wall viscometric material properties on the inner/outer cylinder and we discuss the effect of cylinder rotation on the volumetric flow rate.

Wednesday 6:10 Grand Terrace PO89

An opposed-nozzle fixture for measuring the extensional properties of low viscosity liquids using a conventional controlled strain rheometer

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We present a new opposed jet device for measuring the apparent extensional viscosity of low-viscosity fluids at large extension rates. This design builds upon the original opposing-jet device of Cathey & Fuller that was commercialized as the RFX instrument by Rheometrics. In contrast to the RFX stand-alone system, the new opposed-nozzle fixture can be mounted onto a controlled strain rheometer such as the ARES or ARES-G2. It consists of two opposed jets mounted on rigid arms and terminated with interchangeable disposable syringe needle tips. The first arm is directly connected to the force rebalance transducer (FRT) sensor of the rheometer while the second one is attached to a three-axis translation stage for accurate alignment of the two opposing nozzles. The two jets are either immersed in a beaker filled with the test fluid, or can be operated directly in air. The sample is either drawn into the jets (suction mode) or forced out through the nozzles (expulsion mode) by the action of a twin syringe pump. The resulting stagnation flow generates, respectively, an approximately uniform uniaxial or biaxial extension field. The torque acting on the arm connected to the FRT is recorded for each imposed volumetric flow rate, which allows us to compute an apparent extensional viscosity of the test fluid as a function of the extension rate. By using small gauge nozzles (0.51 mm in diameter) it is possible to achieve extension rates as large as 10,000 s^{-1}. In this work, we study two different pairs of solutions. Each pair consists of a Newtonian glycerol/water mixture and a viscoelastic dilute polymer solution with matched zero-shear-rate viscosities. Various size nozzles are investigated in order to explore the operating envelope of the FRT. Particular attention is paid to the effect of inertia on the measured apparent extensional viscosity for both the expulsion and suction operating modes. In addition, our results are validated by comparison with data from the original RFX using the same test fluids.

Wednesday 6:10 Grand Terrace PO90

New advances in multiwave and arbitrary waveshape testing

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The ability to input complex deformations during rheological testing has many advantages. Experiments that require such deformations include Multiwave and Arbitrary Waveshape testing. The multiwave test method superimposes multiple frequencies up to the 256th harmonic and allows for faster data acquisition compared to a standard frequency sweep experiment. The Arbitrary Waveshape test allows you to define the strain history used to deform the sample by supplying one or more equations for strain as a function of time. Up to four different equations, each with a specified time period can be used. Background and detailed examples will be shown.

Wednesday 6:10 Grand Terrace PO91

Statistical and rheological properties of quasistatically driven dense granular materials

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We present a framework for analyzing the rheology of driven dense granular materials. The framework is based on a recent proposal of a stress-based ensemble for grains by Bulbul Chakraborty & Silke Henkes (2007). In this ensemble, fluctuations in a granular system near jamming are controlled by a temperature-like parameter, the angoricity, which is conjugate to the stress of the system; and the stress distribution of the system follows the Boltzmann distribution. The first part of our work uses the quasistatic shear simulation data by Steve Teitel (unpublished) to confirm the statistics predicted by the stress ensemble. We find the angoricity and the density of states of jammed configurations as functions of the packing fraction. In the second part, we develop a model for slowly driven granular materials based on the stress ensemble and the idea of a landscape in stress space. The idea of an activated process driven by the angoricity has been shown by Behringer et al (2008) to describe the logarithmic strengthening of granular materials. Just as in the Soft Glassy Rheology (SGR) picture, our model represents the evolution of a small patch of granular material (a mesoscopic region) in a stress-based trap landscape. The angoricity plays the role of the fluctuation temperature in SGR. We determine (a) the constitutive equation, (b) the yield stress, and (c) the distribution of stress dissipated during granular shearing experiments, and compare these predictions to experiments of Hartley & Behringer (2003).

Wednesday 6:10 Grand Terrace PO92

Another look at cone-plate rheometry and new tools for viscometry and rheological analyses with Brookfield equipment

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1. Cone-Plate Flow Stability/Instability: Prompted by a customer inquiry, flow instability with Wells-Brookfield Cone-Plate Rheometers/Viscometers was investigated. Low-viscosity liquids, especially water, were analyzed at 25 ^{o}C with the CPE-40, CPE-41 and CPE-42 cone spindles, having angles of 0.800, 3.00 and 1.565^{o}, respectively, using a Brookfield LVDV-II+ Pro CP Viscometer. Flow instability, due to secondary flow, correlated well with the dimensionless, calculated R_t parameter values (after the work of Sdougos, et al). This correlation was far superior to using Reynolds number, *Re*, alone. The CPE-40 cone spindle provided measurements within tolerance, over its speed range tested, 40 to 200 rpm, corresponding to shear rates of 300 to 1500 s^{-1}.

2. Shampoos - that is, aqueous polymer solutions - were successfully tested using new conditional loops in Rheocalc(tm) software, allowing automated adjustment of speeds to ensure on-scale torques in multi-speed testing with automated temperature changes and control.

3. New equipment (a) permit easier changing of spindles with the EZ-Lock(tm) mount system, (b) testing of smaller quantities of materials requring Small Vanes, and (c) Yield Stress measurements with YR-1's with "BB" modification to minimize mechanical backlash or "slack", especially when testing materials with higher yield stresses.

Wednesday 6:10 Grand Terrace PO93

Evaluation of structured materials in the linear viscoelastic region and by large amplitude oscillatory strain (LAOS)

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Representative structured materials, including industrial sealants and food products, have been evaluated by unidirectional tests and oscillatory tests in the Linear Viscoelastic Region to corroborate differences in product performance. More in-depth testing has also been performed in the non-Linear Viscoelastic Region by Large Angle Oscillatory Strain (LAOS) methods to observe trends in the higher order harmonics. Testing was performed on an ARES-G2 rheometer, which is well suited for LAOS testing, as it is a Separate Motor and Transducer rheometer, where inertia effects are minimized. The LAOS technique can be a useful additional tool in characterizing structured materials.

Wednesday 6:10 Grand Terrace PO94

Master viscometer for viscosity standard of non-Newtonian fluid in Japan

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National Metrology Institute of Japan (NMIJ) has developed the new master viscometer for viscosity standard of non-Newtonian fluid. The viscometer will be a primary standard of viscosity measurement of non-Newtonian fluid. In the near future, we will open a measurement service of viscosity of non-Newtonian fluids. There are plans to provide non-Newtonian reference liquids for rotational viscometer. In this report, we present the new measurement system of master viscometer and the concept of traceability chain for viscosity measurements. The viscometer uses coaxial-cylinders and an electronic balance. The motion of coaxial-cylinders is not rotational but translational. The outer cylinder is translated along an axis of coaxial-cylinders. The central axis of the cylinders is set vertically. The inner cylinder is suspended from the electronic balance. Sample liquid fills into the gap between the cylinders. When the outer cylinder is translated vertically, the inner cylinder is subjected to a shear stress from the liquid. The viscous force is detected by the electronic balance. Measurement ability of displacement of the outer cylinder is ensured by the traceability chain of length and time. The electronic balance is calibrated by standard test weights which are calibrated by the division of mass and force standards in NMIJ.

Wednesday 6:10 Grand Terrace PO95

Dissipative particle dynamics simulation of particulate suspensions

Prakorn Kittipoomwong[1], Ahmad Jabbarzadeh[2], and Howard See[1]
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The rheological behavior of particulate suspensions has been investigated by a dissipative particle dynamics (DPD) simulation. In addition to the conservative, dissipative and random forces normally considered in a DPD model, the hydrodynamic lubrication force has been explicitly included to prevent particle overlap as proposed by Martys [1]. The simple DPD fluid velocity profile in Poiseuille flow and simple shear flow agree with Newtonain fluid results. The validity of the model in suspension modeling has been assessed in a variety of situations including drag coefficient of spherical rigid inclusion in DPD fluid and Jeffery orbit of nonspherical particle.

Reference: [1] N. S. Martys, Study of a dissipative particle dynamics based approach for modeling suspensions, J. Rheol. 49(2), 401-424 (2005)

Wednesday 6:10 Grand Terrace PO96

Effectiveness of solvent trap for measuring volatile samples

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Preventing solvent evaporation is critical for accurate rheological testing of volatile samples. Commercial rheometers offer pressure vessels and solvent trap approaches for characterization of such materials. The former approach is very effective for controlling evaporation, but is typically difficult to use and severely limits instrument low-end torque sensitivity and geometry flexibility. For these reasons, the latter technique of using a solvent trap system which incorporates a vapor barrier to inhibit evaporation during testing is preferred. Different solvent trap configurations were evaluated and compared to gain a better understanding of the factors which influence the effectiveness of solvent trap systems. A summary of the challenges involved and the considerations for using solvent trap systems is presented.

Wednesday 6:10 Grand Terrace PO97

'Psycho-tribological' measurements on cloth materials with a rheometer and a novel measuring geometry

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Determining the 'bulk' haptical surface properties of cloth materials is normally a relative subjective issue since it relies on the impression the human test persons have of the material. Therefore it would be very desirable to have a more objective instrumental technique to measure these properties.

In this paper new techniques for measuring the haptical properties of cloth, leather and artificial leather materials used for car seats are described. For these measurements a standard rheometer equipped with an especially developed novel measuring geometry was used. Different samples from different materials were submitted to normal force hysteresis and rotational friction measurements (tribological measurements). The results of these measurements were compared with the subjective impressions test persons gave about these materials during seating tests. A very good correlation between the friction measurements and the subjective impressions was found. The measurement results give tangible information for the development of cloth materials for car applications.

We will present details on the technical realisation as well as experimental results.

Wednesday 6:10 Grand Terrace PO98

Simultaneous observation of shear-induced structure using small angle light scattering and parallel superposition

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Small angle light scattering systems have recently been commercialized to permit the facile observation of shear-induced structures under conditions of controlled temperature and flow. While light scattering permits the observation of shear-induced structures, the imposition of an oscillatory stress or strain over the steady shear profile permits the measurement of the viscoelastic parameters of these shear-induced structures. Performed simultaneously, these techniques inform and confirm the observations of one another.

Wednesday 6:10 Grand Terrace PO99

Cahn-Hilliard simulation of moving contact lines in viscoelastic fluids

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In our previous work, we have shown that the Cahn-Hilliard diffusion model is consistent with slip models in predicting the macroscopic behavior of moving contact lines in Newtonian systems. Different from slip models, the Cahn-Hilliard model features a strong shear region at the contact line, with a size of an effective slip length and a shear rate inversely proportional to this length. In this work, we will show that when one of the two fluid components is viscoelastic, although the Weissenburg number in the bulk flow is small, a large polymer stress may build up in the contact line region. This polymer stress only exists on the viscoelastic side of the interface and has to be balanced by the capillary force. As a result, for a viscoelastic fluid displacing a Newtonian fluid, the interface exhibits a higher local curvature at the contact line than the Newtonian-Newtonian counterpart. However, due to the small size of the shear region, the overall effect on the interface shape is limited. This qualitatively agrees with the experimental observation in Boger fluids.

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Plenary Lectures

8:30 AM Lecture Hall

Monday, October 19

Microstructure and rheology relationships for concentrated colloidal dispersions: Shear thickening fluids and their applications
Norman J. Wagner
Department of Chemical Engineering, University of Delaware

Tuesday, October 20
Bingham Lecture

Interrogating the physics of amorphous solids: Rheological and mechanical measurements
Gregory B. McKenna
Department of Chemical Engineering, Texas Tech University

Wednesday, October 21

Spatio-temporal chaos and negative shear rate fluctuations in sheared soft matter systems
Ajay K. Sood
Department of Physics, Indian Institute of Science

Social Program

Sunday, October 18

Industry / Faculty / Student Mixer
4:00 PM – 6:00 PM Madison Ballroom A
Sponsored by a generous contribution from the Industrial Outreach Program of the American Institute of Physics

Welcoming Reception
7:00 PM – 9:00 PM Grand Terrace – West
Sponsored by a generous contribution from Malvern Instruments

Monday, October 19

Society Luncheon
12:00 Noon – 1:45 PM Grand Terrace
Sponsored by The Society of Rheology

Society Reception
7:00 PM – 9:00 PM Grand Terrace
Sponsored by the Journal of Rheology

Tuesday, October 20

Society Business Meeting
6:10 PM Hall of Ideas, Section G or J

Awards Reception
7:00 PM Grand Terrace – East
Sponsored by a generous contribution from Xpansion Instruments

Awards Banquet
8:00 PM Madison Ballroom A – B

Wednesday, October 21

Poster Session Reception
6:10 PM – 8:10 PM Grand Terrace
Sponsored by a generous contribution from Anton-Paar USA

The Society gratefully acknowledges the generous contributions of American Institute of Physics, Anton-Paar USA, Malvern Instruments, Thermo Scientific, and Xpansion Instruments