THE SOCIETY OF RHEOLOGY

79TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Hilton Salt Lake City Center
Salt Lake City, Utah
October 7 - 11, 2007

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Meeting Schedule

Monday, October 8, 2007

8:30	F. Waleffe (PL1)			
9:20	Coffee			
9:45	SC1	FM1	MR1	PS1
10:10	SC2	FM2	MR2	PS2
10:35	SC3	FM3	MR3	PS3
11:00	SC4	FM4	MR4	PS4
11:25	SC5	FM5	MR5	PS5
11:50	Lunch			
1:30	SC6	FM6	MR6	PS6
1:55	SC7	FM7	MR7	PS7
2:20	SC8	FM8	MR8	PS8
2:45	SC9	FM9	MR9	PS9
3:10	Coffee			
3:35	SC10	FM10	MR10	PS10
4:00	SC11	FM11	MR11	PS11
4:25	SC12	FM12	MR12	PS12
4:50	SC13	FM13	MR13	PS13
5:15	End			

Tuesday, October 9, 2007

8:30	J. F. Brady (PL2)			
9:20	Coffee			
9:45		FM14	MR14	PS14
10:10	SC15	FM15	MR15	PS15
10:35	SC16	FM16	MR16	PS16
11:00	SC17	FM17	MR17	PS17
11:25	SC18	FM18	MR18	PS18
11:50	Lunch			
1:30	SC19	FM19	MR19	PS19
1:55	SC20	FM20	MR20	PS20
2:20	SC21	FM21	MR21	PS21
2:45	SC22	FM22	MR22	
3:10	Coffee			
3:35	SC23	FM23	MR23	BS1
4:00	SC24	BE1	MR24	BS2
4:25	SC25	BE2	SM1	BS3
4:50	SC26	BE3	SM2	BS4
5:15	End			
5:30	Business Meeting			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, October 10, 2007

8:30	J. A. Lewis (PL3)			
9:20	Coffee			
9:45	SC27	BE4	SM3	BS5
10:10	SC28	BE5	SM4	BS6
10:35	SC29	BE6	SM5	BS7
11:00	SC30	BE7	SM6	BS8
11:25	SC31	BE8	SM7	BS9
11:50	Lunch			
1:30	SC32	BE9	SM8	BS10
1:55	SC33	BE10	SM9	BS11
2:20	SC34	BE11	SM10	BS12
2:45	SC35	BE12	SM11	BS13
3:10	Coffee			
3:35	SC36	BE13	SM12	BS14
4:00	SC37	BE14	SM13	BS15
4:25	SC38	BE15	SM14	BS16
4:50	SC39	BE16	SM15	BS17
5:15	SC40		SM16	
5:40	End			
6:00	Poster Session & Reception			

Thursday, October 11, 2007

8:05	SC41	BE17	SM17	SG1
8:30	SC42	BE18	SM18	SG2
8:55	EP1	BE19	SM19	SG3
9:20	EP2		SM20	SG4
9:45	Coffee			
10:10	EP3	BE21	SM21	SG5
10:35	EP4	BE22	SM22	SG6
11:00	EP5	BE23	SM23	SG7
11:25	EP6	BE24	SM24	SG8
11:50	EP7	BE25	SM25	SG9
12:15	End			

Session Codes

BE = Blends, Emulsions and Multiphase Fluids
BS = Biological and Self-assembled Systems
EP = Rheology in Energy Production
FM = Non-Newtonian Fluid Mechanics
MR = Microrheology, Microfluidics and Confined Systems
PL = Plenary Lectures
PS = Polymer Solutions
SC = Suspensions, Colloids and Granular Media
SG = Solids and Glasses
SM = Entangled Solutions and Melts

Contents

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Grand Ballroom C PL1

Exact coherent states: controlling turbulence and transition

Fabian Waleffe

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Is turbulence the random collisions of eddies leading to an enhanced diffusion suitably modeled by an eddy-viscosity? Is it a cascade of energy from large scales to small scales? Experimental and numerical observations show that turbulence is full of coherent structures. What are those and how do they fit with our notions of turbulence? Recent work to understand the nature of these coherent structures has led to the discovery of 3D traveling wave solutions of the Navier-Stokes equations as well as time-periodic and relative periodic solutions. All those solutions are unstable, yet at low Reynolds numbers a single such solution can capture the key statistics of turbulent flows and the qualitative and quantitative similarity with near-wall coherent structures observed in turbulent shear flows is very good. The solutions typically arise in pairs, upper and lower branches, through saddle-node bifurcations. There is evidence that the upper branches are organizing centers for turbulent flows while lower branches are the backbone of the phase space boundary separating turbulent and laminar flows. The further study of these solutions and their stable and unstable manifolds is bound to elucidate further mysteries of turbulent shear flows, and provide new approaches for turbulence control.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Monday 9:45 Alpine East SC1

Molecular hydrodynamics in dilute suspensions

Swapnil Kohale and Rajesh Khare

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We use molecular dynamics simulations to investigate the hydrodynamics in dilute suspensions of nanoparticles. A detailed, molecular model is used to represent both the nanoparticle and the solvent. Hydrodynamics is governed by the intermolecular interactions in such a model system. We track the motion of nanoparticles in the solvent and near a solid surface. Simulation results are used to determine the conditions that lead to deviations from the Stokes law at the nanoscale. Our results are explained in terms of the molecular scale structure of the fluid. Effect of the solid surface on the hydrodynamic interactions as well as the interactions between neighboring particles in a suspension are studied in detail; these simulation results are compared with continuum mechanics predictions.

Monday 10:10 Alpine East SC2

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

Samartha G. Anekal, Juan P. Hernandez-Ortiz, Patrick T. Underhill, and Michael D. Graham

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

Monday 10:35 Alpine East SC3

The analysis of self-diffusion and migration of spheres in nonlinear shear flow using a traction-corrected boundary element method

Ingber Marc[1], Shihai Feng[2], Alan Graham[2], and Lisa A. Mondy[3]

[1]Mechanical Engineering, University og New Mexico, Albuquerque, NM, United States; [2]Los Alamos National Lab, Los Alamos, NM, United States; [3]Multiphase and Nanoscale Transport Processes 1514, Sandia National Labs, Albuquerque, NM 87185-0836, United States

The TC-BEM is extremely accurate in predicting particle trajectories and can be used to calculate both particle self-diffusivity and the newly-defined migration diffusivity for dilute suspensions. It has been demonstrated that the combination of a nonlinear shear flow and particle roughness leads to particle migration in dilute suspensions. The self-diffusivity is independent of the nonlinearity parameter. The migration diffusivity is a strong function of the nonlinearity parameter and arises from the net displacement of the center of gravity of the particle pair. The magnitude of the net center of gravity displacement scales linearly with the nonlinearity parameter. These results indicate that the rheological diffusivity should scale linearly with the nonlinear parameter which coupled with a slip boundary condition can correctly predict the observed particle migration rate scaling as a2.7 - a2.9. This new theory was facilitated by our scale coupling methodology and accurately predicted migration over range of particle diameters ranging from 0.1mm to 3.175mm.

Monday 11:00 Alpine East SC4

Elongational viscosity of particle-filled polymeric fluids by direct simulations

Wook Ryol Hwang[1] and Martien A. Hulsen[2]

[1]School of Mechanical and Aerospace Engineering, Gyeongsang National University, Jinju 660-701, Republic of Korea; [2]Materials Technology, Eindhoven University of Technology, Eindhoven 5600MB, The Netherlands

We present direct numerical simulation results for non-Brownian hard particle suspensions in a viscoelastic fluid (PTT) in planar elongational flow in 2D. We use the extensional bi-periodic frame concept [W.R. Hwang and M.A. Hulsen, JNNFM, vol. 132, p.167-178] such that a single unit cell with a small number of particles could represent suspensions of the infinite number of particles. The extensional frame is a material frame that stretches and contracts affinely with the given elongational flow and it defines the computational domain of the work. A standard velocity-pressure formulation of the finite-element method has been combined with the DLM-like fictitious domain method for the implicit treatment of the hydrodynamic interaction between particle and fluid. For stable and accurate simulation of viscoelastic flow, we use the DEVSS/DG/ALE scheme with re-initialization of polymer stress field. The extensional bi-periodic computational domain concept is introduced with the constraint equation with the Lagrangian multiplers and implemented by the mortar element method. Using the PTT model, we present the transient viscosity of particle suspensions formulated with viscoelastic strain hardening or softening fluids. We reproduced decrease of strain hardening for a polymeric fluid when filled with particles and interpret its origin using the particle distribution and the local stress development during the elongation.

This work has been supported by the Basic Research Program of the Korea Science and Engineering Foundation (Grant No. R01-2006-000-10267-0).

Monday 11:25 Alpine East SC5

Dynamics of a sphere suspended in a viscoelastic liquid subjected to simple shear flow

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The motion of a rigid sphere in a suspending liquid is ruled by the so-called freely rotating condition, whereby the total force and torque acting on the particle must be zero. In the case of shearing flows, it was experimentally observed [e.g., Astruc et al., Rheol. Acta 42, 421-431 2003] that the viscoelasticity of a suspending fluid slows down the rotational motion of a sphere with respect to the case of a Newtonian suspending liquid. The slowing down is more and more pronounced with increasing the Deborah number. This phenomenon, of course, affects the rheological behaviour of the suspension as a whole. In this work, we analyze the start up of a sphere immersed in a viscoelastic suspending liquid by means of a 3D finite element simulation. The freely rotating boundary condition is implemented with constraints (Lagrange multipliers) in order to impose the rigid body motion. The simulation results describe the transient evolution of the sphere motion, and capture the slowing down effect at the steady state. It is shown that such a phenomenon depends on the specific constitutive equation adopted for the viscoelastic liquid. The bulk rheology of a dilute suspension is also calculated, and the influence of the viscoelasticity of the suspending fluid on the suspension properties is investigated.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Jonathan Rothstein and Patrick Anderson

Monday 9:45 Alpine West FM1

Modeling the inhomogeneous response in steady and transient flows of wormlike micellar solutions

Lin Zhou[1], Paula A. Vasquez[1], L.Pamela Cook[1], and Gareth H. McKinley[2]
[1]Department of Mathematical Sciences, Univeristy of Delaware, Newark, DE 19716, United States; [2]Department of Mechanical Engineering, MIT, Cambridge, MA 02139, United States

Under certain conditions, surfactant molecules self-assemble into long structures known as wormlike micelles. In solution these long structures entangle, thus exhibiting viscoelastic effects like polymers, but, in contrast to polymers, wormlike micelles also break and reform. Wormlike micelles have important uses in the petroleum industry and the health-care products industry among others. In this talk, several viscoelastic constitutive models (VCM, PEC, PEC+M) are investigated numerically and analytically in the cylindrical Taylor Couette geometry. The VCM model is a new two-species network model that represents a discrete version of Cates' breaking and reforming dynamics. The PEC and PEC+M models are, respectively, a one mode and a two mode approximation of the full VCM model without the effects of stress-concentration coupling. The flows described by these nonlinear models are inhomogeneous and exhibit shear banding across the gap, and a plateau in the 'flow curve of shear stress versus steady state shear rate. In this talk, both transient and steady state solutions are considered for two different modes of deformation: start up of steady shearing flow and imposition of a sudden shearing displacement, or 'step strain'. The constitutive predictions of each model are compared with the results of experiments using a wormlike micellar solution. The effects of diffusive terms in the stress equations are also investigated.

Monday 10:10 Alpine West FM2

Flow of viscoelastic wormlike micelle solutions through a periodic array of cylinders

Geoffrey R. Moss and Jonathan P. Rothstein
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Solutions of self-assembled wormlike micelles are used with ever increasing frequency in a multitude of consumer products ranging from cosmetic to industrial applications. Accordingly, a thorough understanding of their behavior in response to a variety of flow situations is required. Owing to the wide range of applications, flows of interest are often complex in nature; exhibiting both extensional and shear regions that can make modeling and prediction both challenging and valuable. Adding to the complexity, the micelles are continually broken and reformed, resulting in a number of interesting phenomenon, such as shear banding and extensional flow instabilities. We present the results of our investigation into the flow fields generated by a controllable and idealized semi porous media: a periodic array of cylinders (PAC). Our test channel geometry consists of six equally spaced cylinders, arranged perpendicular to the flow. Several concentrations of cetyltrimethylammonium bromide in sodium salicylate (CTAB/NaSal) were used as our test fluid at a single cylinder diameter-to-channel ratio. By systematically varying the Deborah number, the flow kinematics, stability and pressure drop were measured. A combination of particle image velocimetry (PIV) in conjunction with flush mount pressure transducers were used to fully characterize the flow, and measure the pressure drop generated by these instabilities, while flow induced birefringence measurements were used to determine the conditions necessary to induce elastic instabilities.

Monday 10:35 Alpine West FM3

Stretching, coiling and folding of viscoelastic micellar jets

Matthieu Varagnat, Trushant Majmudar, and Gareth H. McKinley
Department of Mechanical Engineering, MIT, Cambridge, MA 02139, United States

The study of fluid jets impacting on a flat surface has industrial applications in many areas, including processing of foods and consumer goods, bottle filling, and polymer melt processing. Previous studies have focused primarily on purely viscous, Newtonian fluids, which exhibit a number of different dynamical regimes including dripping, steady jetting, and steady coiling. Here we add another dimension to the problem by focusing on mobile (low viscosity) viscoelastic fluids, with the study of two wormlike-micellar fluids, a cetylpyridinum-salicylic acid salt (CPyCl/NaSal) solution, and an industrially relevant shampoo base. We investigate the effects of viscosity and elasticity on the dynamics of the jets as they impact an impermeable rigid plate. Experimental methods include shear and extensional rheology measurements to characterize the fluids, high-speed digital video imaging, and the use of crossed polarizers to visualize the evolution in the elastic stress difference within the thinning threads. Because of these additional stresses, in sufficiently elastic micellar flows the jet widens at its base as it decelerates, a behaviour reminiscent of delayed die-swell. In addition to the regimes observed in purely viscous systems, the non-Newtonian jets can also exhibit the well-known 'beads on a string' morphology. We also find a novel regime in which the elastic jet buckles and periodically folds on itself instead of coiling. Phase diagrams and scaling laws for the coiling and folding frequency are proposed through a systematic exploration of the experimental parameter space (height of fall, imposed flow rate, elasticity of the solution).

Monday 11:00 Alpine West FM4

The trouble with CaBER: the effect of stretch parameters on extensional rheology measurements

Erik Miller and Jonathan P. Rothstein

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The behavior of viscoelastic materials is qualitatively different in shear and extensional flows. This discrepancy is important in many applications such as food processing, adhesives, and other flows with mixed regions of both shear and extension. While characterization in shear is now easily and commonly performed in shear rheometers, the extensional rheometer has only recently been developed into a commercially available tool; the capillary breakup extensional rheometer (CaBER) is used to measure the extensional viscosity of less concentrated viscoelastic solutions. The elegance of capillary breakup extensional experiments lies in the simplicity of the procedure. A step-strain is applied, after which the experiment essentially drives itself as capillary thinning of the liquid bridge is balanced by surface tension to impose a uniaxial extensional flow on the fluid filament. The diameter of this filament, from which all properties are calculated, is measured until capillary pinch-off brings the experiment to an end. We present a series of experiments in which the step-strain parameters of final length and Deborah number of the stretch were varied and their effects on measured extensional rheology recorded. To focus on the parameter effects, well-characterized surfactant wormlike micelle and polymer solutions were used to include a range of characteristic relaxation times and morphologies. Our results indicate that although guidelines for the technique in general have been established, it is clear that rheological results using the CaBER technique must be properly considered in the context of the stretch parameters and the pre-conditioning effects they have on viscoelastic fluids.

Monday 11:25 Alpine West FM5

Yielding in uniaxial extension of entangled polymer melts, solutions and blends

Yangyang Wang and Shi-Qing Wang

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Uniaxial extension experiments have been carried out on a series of entangled uncrosslinked SBR melts, solutions and blends, with SER Universal Testing Platform. [1] The SER device allows us to probe the whole spectrum of Hencky strain rates, and to identify three different regimes of deformation: terminal flow regime, crossover regime and elastic regime. When a sample is stretched in the elastic regime, steady flow is never possible as the building up elastic retraction force overcomes the cohesive force holding up the entanglement network. In other words, the sample actually yields in the form of necking during extension at a constant Hencky strain rate. The scaling characteristics associated with the yielding are strikingly identical to those observed in startup shear of the same melts (P. Boukany - preliminary results). When the extension is interrupted well before the yield point, instead of quiescent relaxation, the sample also necks over on time scales that are typically shorter than the terminal relaxation time but can be significantly longer than the Rouse relaxation time. We also employed elastic recoil experiments to explore the nature of the yield point. Apparently, the deformation is completely recoverable before reaching the yield point when the Hencky rate is higher than the reciprocal Rouse time. Flow occurs either beyond the yield point or when the strain rate is lower. In the latter cases, there is an irrecoverable component due to breakup of the entanglement network. [1] Part of this work has been submitted to Phys. Rev. Lett. and J. Rheol. for publication.

Symposium MR
Microrheology, Microfluidics and Confined Systems

Organizers: Eric Furst and Jai Pathak

Monday 9:45 Canyon B MR1

From bulk microrheology to tribology

Christian Clasen[1], Pirouz Kavehpour[2], and Gareth H. McKinley[3]

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Tribology and elastohydrodynamic lubrication have traditionally been considered to be a subject apart from classical bulk rheology and the rapidly developing area of microrheological investigation. The principal reason for this separation is that although fluid properties in each field are key to the observed flow and friction phenomena, the experimental approach and the resulting terminology differ substantially and prohibit a direct translation of the results. In particular the lack of well-defined viscometric kinematics for tribological experiments and the difficulties in achieving sufficiently-precise fixture alignment in regular rheometry on the microscale have inhibited the merging of the results from these fields. We show in this paper how recent developments in the area of sliding plate microrheometers with controlled gaps on the order of micro- to nanometers, and triborheometers with defined plate-and-plate geometry parameters and normal stress control can bridge this gap between classical tribology and rheology.

Monday 10:10 Canyon B MR2

Microfluidic rheometry on a chip

Christopher J. Pipe[1], Gareth H. McKinley[1], Mingqiang Yi[2], Seong-Gi Baek[2], and Ross Clark[3]

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Microfluidic devices offer several potential advantages for rheological characterization of complex liquids, including the microlitre sample size required, the ability to impose high deformation rates without entering strongly inertial flow regimes, the absence of a free surface which can lead to evaporation and the possibility to develop a simple, disposable single-pass device. We propose and analyze designs for microfluidic devices that enable the determination of a shear-rate-dependent viscosity as well as providing information on the apparent extensional response.

The devices use monolithic MEMS pressure sensors to measure local pressure variations at several streamwise locations along microfabricated channels. Firstly we show how pressure measurements along a straight microfluidic channel can be used to measure steady shear viscosities at shear rates of up to 10^5 s^{-1} for low viscosity solutions as well as being able to accurately capture the rate-dependent shear viscosity of strongly shear-thinning aqueous polymer solutions, even resolving the approach to the infinite shear rate viscosity. To extract information on the extensional properties of complex liquids, the flow through a microfluidic contraction is studied. The evolution in the pressure profiles up- and down-stream of a symmetric planar hyperbolic contraction-expansion is monitored and streak images coupled with particle image velocimetry are used to quantify the evolution in the flow field. Numerical calculations and experimental observations show that fluid elements on a given plane are subjected to an almost constant extension rate through the contraction/expansion enabling the calculation of an apparent extensional viscosity. Thus the microfluidic device allows the rate-dependent shear viscosity as well as an apparent extensional viscosity to be determined simultaneously. The results are compared with apparent extensional viscosities measured using the capillary break-up and opposed jets methods.

Monday 10:35 Canyon B MR3

Multi-sample micro-capillary rheometry

Kalman B. Migler, Doyoung Moon, and Anthony J. Bur

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We present a multi-sample micro-capillary rheometer (M2R) which is capable of measurements over a broad range of temperatures, viscosities and shear rates. The instrument is simple as the flow is generated by external gas pressure and the shear rate is measured optically. We test the M2R against three NIST SRMs (PS, PDMS and a PIB solution) and report a high level of accuracy and precision. This instrument will be particularly useful as a combinatorial method and in cases of limited material quantity. More generally, the techniques employed here pave the way for the development of polymer melt microfluidics.

Monday 11:00 Canyon B MR4

Nonlinear rheometry of microgel dispersions in confined geometries

Philipp Erni[1], Christian Clasen[2], and Gareth H. McKinley[1]

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The rheology of many materials relevant to consumer products and biomedical applications often depends strongly on the characteristic length scale of the device or flow of interest. For these highly structured fluids, the flows occurring during the actual application of the product are often confined to geometries with dimensions of a few micrometers. Examples include the spreading of skin lotions, or the organoleptic perception of food and pharmaceutical products. In this study, we measure the nonlinear rheology of microgel particle dispersions in narrow gaps from 1-100 micrometers. We use an interferometry-based sliding plate microrheometer to impose large shearing deformations on microliter fluid samples confined between parallel optical flats. The macrorheological response is compared with the flow in the micro-confined geometry. Whereas the bulk rheology is typical of the broad class of soft solid materials with a pronounced yield stress followed by strong shear-thinning, the flow in the confined geometry is dominated by wall slip and the apparent viscosity depends on the degree of confinement, the mass concentration and the volumetric swelling ratio of the microgel particles. The evolution in the slip velocity and extrapolation length of the confined microgel can be systematically determined in this sliding plate rheometer as a function of degree of confinement and shear stress. Thixotropy in the confined samples can also be determined by repeated shearing using periodic large amplitude oscillations.

Monday 11:25 Canyon B MR5

Flow of polymer solutions in planar 90 degree micro-bends

Shelly Gulati[1], Cari S. Dutcher[1], Dorian Liepmann[2], and Susan J. Muller[1]

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The characterization of flows containing macromolecules is critical for the optimal design of microfluidic systems for biochemical analyses. The effects of lambda-DNA on transport in microscale flows are significant because the flow behavior may be influenced by molecular interactions, both viscous and elastic forces dominate inertial forces at this length scale, and the macromolecular length scale L approaches the device length scale D. It has been shown that DNA can undergo dramatic stretching in microfluidic flows with conformational changes occurring in both elongational and shear flows. Our previous studies of flow of semi-dilute DNA solutions in micro-contractions (L/D ~ 0.17 and ~ 0.13) indicate strongly elastic behavior through the observation of vortex enhancement with increasing Re and Weissenberg (Wi) numbers. In the present work, the viscoelastic flow of semi-dilute DNA solutions in planar 90 degree micro-bends (L/D ~ 0.09), another canonical microfluidic structure, is investigated; macromolecular flows in this geometry on a macro or microscale have been essentially unexplored. Micro-particle image velocimetry and flow visualization are used to characterize the flows of water (0c*) and semi-dilute (4c*) DNA solutions. The onset of flow instability occurs at Wi ~ 1. A recirculation region is present in the interior corner of the bend and is enhanced with increasing Re (7 x 10-7 < Re < 8 x 10-4) and Wi (1 < Wi < 190). Flows of concentrated poly(ethylene) oxide (PEO) solutions were also explored in this geometry across a similar parameter range to determine the influence of polymer extensibility and flexibility on the onset and growth of elastic instability. PEO solutions were chosen to match the longest relaxation time of the DNA solutions from small amplitude oscillatory shear measurements and the characteristic relaxation time from capillary breakup extensional rheometry (CaBER).

Symposium PS
Polymer Solutions

Organizers: Ralph Colby and Ravi P. Jagadeeshan

Monday 9:45 Canyon A PS1

Comparison of the viscosity and elasticity yield of water soluble polymers

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The applicability of water-soluble polymers in technical, medical and pharmaceutical areas as well as in the food industry depends on the magnitude of their viscous and elastic properties in solution. Depending on the molar masses, water-soluble polymers are utilized in a broad range of applications. In addition, the viscoelastic flow behavior is also controlled by the chemical structure of the polymers, the concentration, the thermodynamic quality of the solvent and the temperature. The states of solution for practical applications range from dilute and semi-dilute particle solutions to semi-dilute network solutions. In these cases, the conformation of the polymer coils may vary from compact spheres, coils in the theta state, expanded coils to rigid rods depending on the interactions between the macromolecule segments and the chosen solvent. In case of aggregate formation due to strong intermolecular interactions (e.g., hydrogen bonds) or polymer backbones which are not statistically substituted, rheological investigations are the only way to get comprehensive information about the viscoelastic properties of a corresponding solution. In this contribution we would like to present the different rheological approaches (stationary and non-stationary shear flow, small amplitude oscillatory shear, elongational flow and rheo-optical measurements) for the determination of the viscoelastic material functions of several simple- and complex-structured water soluble polymers / polyelectrolytes.

Monday 10:10 Canyon A PS2

Inter- and intramolecular interactions of associative polymers in solution

Ralph L. David and Julia A. Kornfield
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Model polymers with matched backbone length are used to examine the effects of chain length, degree of functionalization, and type of interaction (self-associating or donor-acceptor) on shear and extensional viscosity of associative polymer solutions. A series of polymers with pair-wise, hydrogen bonding stickers were made by functionalization of 500 kg/mol 1,2-PB with carboxylic acid groups (0 to 2%). We examined the shear viscosity of 0 to 30% wt solutions in chlorododecane (giving c*=0.4% wt for the unmodified polymer) and found that the self-associating stickers had very little effect on the zero shear viscosity until concentration exceeded 3-4c*. Instead of increasing the viscosity, stickers reduced the viscosity even at concentrations up to 2-3c*. Intramolecular association and the consequent reduction of coil size, thus, have a dominant effect even at c*, overlooked in prior literature. To favor interpolymer association, we used donor-acceptor pairs: the acid functionalized chains (A-chains) served as donors and polymers bearing tertiary amines (N-chains, 1 to 12% functionalization) were used as acceptor chains. We examined solutions as a function of degrees of functionalization (fA and fN), the molar ratio of acid to amine groups, and overall concentration. Depending on fA and fN, many donor-acceptor pairings resulted in phase separation into gel and sol phases. Those pairs that provided homogeneous solutions were examined further. Dynamic light scattering showed that large aggregates formed in dilute solution. The zero shear viscosity increased sharply with concentration even below c*, crossing the viscosity-concentration curve of the unfunctionalized polymer solutions below c*. Capillary Breakup Extensional Rheometery (CaBER) was used to assess the extensional viscosity of the solutions. The increase in extensional viscosity appeared to parallel that of the shear viscosity. Ongoing work examines the effect of increasing chain length: results on chains of 1e6 g/mol will be presented.

Monday 10:35 Canyon A PS3

Viscoelasticity, gels and glasses in block copolymer micellar solutions

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Block copolymer exhibit a remarkable capacity to self-assemble into various organized structures. The final morphology is influenced by many parameters such as the molecular architecture, the block composition and, for the case of copolymer solutions, the affinity between the solvent and the different blocks. When the solvent is selective, the copolymers aggregate into micelles. The blocks that are incompatible with the solvent constitute the core of the micelles, while the soluble blocks form a soft and deformable corona. Micelles are hybrid objects that share common features with colloids and polymers very much like star polymers or multibranched polymers. Although a rich phenomenology has been reported, the implications of this interplay between colloidal and polymer behaviors and their generality remain open issues.

We investigate acrylic AB and ABA block copolymers synthesized by controlled radical polymerization, which form spherical core-shell micelles in apolar solvents. Dilute solutions have a purely viscous behaviour. The increase of the viscosity with concentration and temperature can be quantitatively described using a colloidal approach. Interestingly at high concentrations, the micellar solutions can be either viscoelastic liquids, gels or glasses. We can switch the behavior from one to another by increasing the concentration, or by changing the temperature of applying a mechanical stress. For instance, viscoelastic solutions shear-thicken and become gels upon shearing. The gels are rejuvenated and return back to viscoelastic solutions upon heating. Systematic investigations combining rheological measurements and rheo-SAXS synchrotron structural investigations allow us to relate this wealth of behavior to the structure of the micelles and ultimately to the block copolymer characteristics.

Monday 11:00 Canyon A PS4

Correlating the extensional viscosity of automotive basecoats with their appearance

Deepanjan Bhattacharya[1], Kab Sik Seo[2], and Chip Williams[1]
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One of the primary goals in developing high solids solvent-borne automotive basecoat formulations is to achieve a distinct rheology profile providing good atomization or sprayability along with sag resistance as well as flow and leveling. Since most paint application processes for automotive coatings involve shear rates greater than 40,000 s-1 it is critical to have a good appreciation of the viscoelastic profiles of the paints at such high shear rates. Due to the non-Newtonian nature of most coating systems, their viscosities vary over a wide range of shear rates. We have recently reported the impact of cellulose esters on the shear profiles of automotive basecoats at very high shear rates. The data indicated that there was a distinct correlation between the high shear rheological properties of automotive basecoats and some of the post-application characteristics such as flake alignment and flow and leveling. In this report we have attempted to outline the impact of the extensional viscosity of solventborne automotive basecoats on final film properties. Automotive OEM basecoat formulations containing different grades of Cellulose Acetate Butyrate (CAB) were analyzed using an opposed jet extensional viscometer. All of the samples were adjusted to the same Ford Cup viscosity. The extensional viscosities of the basecoat formulations were inversely related to the molecular weight of cellulose ester. Attempts were made to correlate the extensional viscosity of the coating with the post-application properties like the 'flop index'. Data generated from elongational and shear viscosity measurements was used to calculate Trouton's ratio. Incorporation of cellulose esters in the basecoat formulation resulted in the coating exhibiting a more Newtonian flow behavior.

Monday 11:25 Canyon A PS5

Evaluating tackiness of polymer containing lubricants by open-siphon method: experiments, theory and observations

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Preparing and testing various lubricants with enhanced tackiness is in high demand for lubricant applications. However, no quantitative method has been currently proposed or used for tackiness evaluations. Present paper employs for this purpose the well-known open-siphon method [1] where elastic liquids are vertically withdrawn out of a jar by a vacuum connected capillary. The suction pulls a tacky liquid upwards out of the jar forming a free jet. More tacky fluids draw a longer jet in air than less tacky ones, whereas non-tacky fluids are not drawn upwards at all. In current experiments, the flow situation changed upon time, with the level of liquid in the jar slowly decreasing. Quantitative experimental time dependences of the length (tackiness), shape of jets and flow rate were obtained for several values of vacuum and for several lubricant liquids. The experimental liquids included very dilute solutions of polyisobutylenes (PIB) of various molecular weights (MW) and concentrations, and a low concentration blend of a high MW PIB with a low MW non-tacky ethylene propylene copolymers. For all the tested liquids, these experimental data were well described and interpreted by a quasi-stationary extension of the stationary theory developed and tested in Ref. [2]. Many unusual patterns of two-phase flow in sucking capillary were also observed. Obtained results show that the open-siphon can serve as a reliable quantitative method for evaluating tackiness of polymer containing lubricants. 1. G. Astarita and L. Nikodemo, Chem. Eng. J., 1, 57-61 (1970) 2. A.I. Leonov and A.N. Prokunin, Nonlinear Phenomena in Flows of Viscoelastic Polymeric Liquids, Chapman & Hall, New York (1994), pp. 106-108, 338-342.

Monday Afternoon

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Monday 1:30 Alpine East SC6

Far-field multiparticle interactions in weakly viscoelastic flows

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Multipole moment expansions can be used to investigate far-field, multiparticle interactions in viscoelastic fluids in the limit of low Deborah number. Here this approach is applied both to particles sedimenting in a stagnant fluid and to neutrally buoyant particle interacting in shear flows. It is shown that the particles' effect on the neighboring fluid can be interpreted in terms of clouds of point-force dipoles, and the velocity disturbances produced by these dipoles provide a partial explanation for particle chaining in viscoelastic flows. The results of the multipole expansions are presented in the form of dynamic, numerical simulations of small groups of particles and full suspensions.

Monday 1:55 Alpine East SC7

Rigid rods in nonhomogeneous shear flow

Micah J. Green[1], Robert C. Armstrong[1], and Robert A. Brown[2]

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A generalized numerical framework is developed for the simulation of rodlike liquid crystals in nonhomogeneous shear flow. Although the time-periodic behavior of rigid rods is well-characterized for homogeneous shear flow, rod dynamics in nonhomogeneous shear flow are poorly understood, particularly anchoring and out-of-plane instabilities. Continuum elastic theories of structure evolution lack the ability to describe domain boundaries and interfacial motion while the simplified Doi molecular theory predicts an aphysical texture buildup in pressure-driven nonhomogeneous shear flow. Our method avoids these simplifications through a finite-element discretization of the full nonhomogeneous Doi diffusion equation for the rod distribution function with no closure approximations. The dynamic simulation uses a parallel, discretized form of the full nonhomogeneous Onsager intermolecular potential which accurately captures excluded-volume interactions of the rods and walls in order to resolve thin interfaces between domains. The method is used to characterize defects, interfaces, and out-of-plane instabilities in planar Couette flow and Poiseuille flow as a function of system size and Deborah number. The method is also used to assess the impact of various anchoring conditions at walls.

Monday 2:20 Alpine East SC8

Modeling fiber interactions in non-dilute fiber suspensions

Julien Ferec[1], Gilles Ausias[2], Marie-Claude Heuzey[1], and Pierre J. Carreau[1]

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A model is proposed to predict the rheological behavior for non dilute suspensions of rigid cylinders in a Newtonian fluid. The constitutive equation is the sum of three contributions: the matrix and hydrodynamic stresses, similar to that of the Dinh and Armstrong theory [1], while the last stress contribution comes from the fiber-fiber interactions. The latter is modeled by a linear hydrodynamic friction coefficient proportional to the relative velocity at the contact point and weighted by the probability that such a contact occurs. Moreover, an expression for the time evolution of the fiber orientation is derived, in which new conformation tensors, called interaction tensors, are implemented. Experimental stress growth data obtained for suspensions of short glass fibers in a Newtonian polybutene are compared with the model predictions. The stress growth behavior in forward and reverse flows is well predicted. The steady viscosity is also correctly described by the theory, which predicts a quadratic dependence on the fiber volume fraction.

[1] Dinh S. M. and R. C. Armstrong, "A Rheological Equation of State for Semiconcentrated Fiber Suspensions," J. Rheol. 28, 207-227 (1984).

Monday 2:45 Alpine East SC9

Hindered rising functions for concentrated polydisperse suspensions

Bing Dai[1], Alan Graham[1], Shihai Feng[1], Stephen Altobelli[2], and Kim Rasmussen[1]

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Based on Boundary Element Method calculation of polydisperse colloidal suspensions we develop a technique to effectively determine the appropriate hindered settling (or rising) functions. Our method allows accurate consideration of the hydrodynamic interactions as well as system specific colloidal interactions. We compare our results to hindering rising functions determined by hybrid Brownian dynamics/Lattice Boltzmann simulations. This comparison reveals surprising differences for dilute suspensions where the semi-empirical Richardson-Zaki relationship is known to fail. Finally, we compare to experimental results by applying our determined hindering functions in simulation of the appropriate conservation equations.

Monday 3:35 Alpine East SC10

Flow of small cohesive particles in a channel

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Flow of small particles micron in size is important in several industrial applications such as digital imaging, polymer processing, powder coating,ceramics and in dispersing fertilizers. Compared to dry granular particles like sand, cohesive particles soil, polymeric particles are different in coefficient of restitution properties (elasticity, damping and plasticity). Inter-particle forces, bulk properties (compressibility and cohesion) and stresses (frictional, cohesive and viscous stresses) have been used to analyze powder flow. In inter-particle forces, the presence of humidity can result in capillary forces (surface tension) being important along with both electrostatic(particle charge) and van der Waal forces (hardness) in affecting flow. Hardness and modulus of a particle or particles are important material variables in van der Waal forces. In addition to material variables, particle to particle separation distance and particle radius are significant variables in electrostatic and van der Waal forces. Flow of small particles in a channel flow is analyzed by considering driving force from applied shear energy against constraints of extrinsic constraints (consolidation, boundary) and intrinsic constraints(cohesion, compressibility and inter-particle forces). Of the several shear cells used for measuring stresses, Freeman tester, Jenike shear cell and Seville tester, Freeman tester is used to analyze shear stresses and normal stresses in polyester and polyacrylate particles with the purpose of determining friction and size dependence as scaling law.

Monday 4:00 Alpine East SC11

Dynamics and self-organization of flowing granular chains

Amy Shen

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Many micro- and macro-scopic systems consist of collections of chain-like molecules. Examples of such systems include polymeric fluids, DNA strands, and soybean stalks. To date, most experimental studies of the dynamical influences of chain structure have been involved single chains. Here, we report results concerning the dynamical behavior of collections of beaded chains rotated in a two dimensional cylinder. During our experiments, we observe a variety of complex spatio-temporal patterns. The nature of these patterns depends on the chain length, the size of the system, and the rotation rate of the cylinder. Our primary focus is on measuring the porosity of the granular chains under flow, the conformation of chains, and the averaged end-to-end distance of chains with varying experimental conditions.

Monday 4:25 Alpine East SC12

Microstructural investigations of yielding behaviour in field-responsive fluids

Charles C. Ekwebelam and Howard See

School of Chemical and Biomolecular Engineering, University of Sydney, Sydney, NSW 2006, Australia

Field responsive fluids are known to possess yield stresses, and experimental investigations to date have shown that the yield stress and yielding behaviour is dependent on the particle size distribution of the disperse phase. However, the mechanism associated with this dependence is still unclear. We have employed particle level simulations to explore this particle size dependence for a magneto-rheological fluid, and the results under steady shearing have shown that bidisperse systems possess higher yield stresses than monodisperse systems for a given volume fraction and particle size ratio. This is in agreement with previous studies (Kittipoomwong et al, J. Rheol, 49, 1521 (2006)). These results are explored in more detail with the aim of understanding the mechanism behind this particle size dependence, as well as developing a methodology for characterizing the structures of these materials during the yielding process.

Monday 4:50 Alpine East SC13

Effects of oxidation on magnetorheology

Sunil Sunkara[1], Thatcher W. Root[1], Daniel J. Klingenberg[1], and John C. Ulicny[2]

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Magnetorheological (MR) fluids, typically composed of iron particles in hydrocarbon or silicone oils, can be utilized in a variety of damping and torque transfer devices. The performance of devices can degrade over time, which may be attributed to the tendency of the suspended iron

particles to oxidize. In this presentation, we will describe the processes governing oxidation of MR fluids and their impact on the MR effect. The relationship between extent of oxidation and the rheological properties of MR fluids will be determined experimentally. These results will be compared to various models of MR fluid behavior in order to understand the underlying mechanisms causing the changes in rheological behavior. Methods for controlling oxidation and its impact on fluid behavior will be described as well.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Jonathan Rothstein and Patrick Anderson

Monday 1:30 Alpine West FM6

Using LAOS and rheological fingerprinting to physically interpret the nonlinear behavior of a biopolymer gel

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Large amplitude oscillatory shear (LAOS) is used increasingly as a tool to measure nonlinear rheology. For many systems we find the practice of reporting only "viscoelastic moduli" as calculated by commercial rheometers (typically the first harmonic Fourier coefficients G1', G1") to be insufficient and/or misleading in describing the nonlinear phenomena. Although the higher Fourier harmonics of the material response capture the mathematical structure, they lack a clear physical interpretation. We introduce a framework for physically interpreting deviations from linearity which we call "rheological fingerprinting." Rheological fingerprinting considers the 2D Pipkin space of frequency and strain-amplitude. A portion of our analysis is based on the geometrical interpretation of Cho et al. (2005) which separates a nonlinear stress response into elastic and viscous stress signals using symmetry arguments. We introduce the use of Chebyshev polynomials to orthogonally decompose these stresses into nonlinear parameters with physical interpretation. We apply these ideas to model systems, showing that strain-stiffening is indicated by a positive 3rd order elastic Chebyshev coefficient, e_3, and shear-thinning is indicated by a negative 3rd order viscous Chebyshev coefficient, v_3. We illustrate the technique using a soft physical gel by studying its Lissajous curves of stress vs strain under oscillatory shear. In the linear domain the Lissajous figures can be described by the two critical gel parameters; additional parameters are required in the nonlinear regime. Rheological fingerprinting highlights two features of the material. Firstly a gradual softening with increasing strain-amplitude indicated by the clockwise rotation of curves. Secondly, a distortion from the elliptical shapes indicative of local strain-stiffening. This approach will be invaluable for characterizing a wide range of materials such as biopolymer gels, regenerative polymer networks, entangled melts and micellar solutions.

Monday 1:55 Alpine West FM7

Normal stress difference of PIB/PB based Boger fluid under large amplitude oscillatory shear flow

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The dynamic response of viscoelastic fluids under large amplitude oscillatory shear (LAOS) has been a subject of long history. In the LAOS flow, the analysis has been mostly focused on shear stress, possibly due to the lack of accurate measurement of normal stress. However, as the instrumentation advances, it becomes possible to get more reliable data. In this work, PIB/PB based Boger fluid was used to investigate the behavior of normal stress difference under LAOS flow. The elastic(G') and viscous(G") modulus were nearly constant upon the increase of strain amplitude. When Fourier transform was performed, the third harmonic was negligible. But at larger strain amplitude, the first normal stress difference was measurable and was sinusoidal at a frequency twice that of the excitation. It showed a nonzero average value that was equal to the elastic modulus multiplied by the square of the strain amplitude. It was also found that the shape of the first normal stress difference strongly depended on the shear strain and frequency. At higher frequency, they showed asymmetric patterns in contrast to the shear stress.

Monday 2:20 Alpine West FM8

Nonlinear elastic instabilities in shear flows with straight streamlines

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While the mechanisms of elastic instabilities in curvilinear shear flows are well-understood, the question whether elastic flow transitions could occur in shear flows with straight streamlines (e.g. Couette, Poiseuille flows) has remained unresolved. Planar shear flows are known to be linearly stable, i.e. stability analysis against small perturbations using a variety of constitutive models predicts the disturbance to decay and hence the basic Couette/Poiseuille flow to be stable for arbitrarily large Weissenberg numbers. Recently, theoretical and computational studies have suggested that such flows may be prone to nonlinear instabilities. Here we derive a general instability criterion, which shows that these flows exhibit a nonlinear instability, with a critical threshold of the perturbation amplitude that decreases as the Weissenberg number is increased. The threshold is essentially independent of the wavenumber k of the perturbation. Semi-analytic expansion techniques and numerical simulations confirm these predictions. The k-independence of the threshold amplitude implies that many scales kick in as soon as the instability occurs and hence, the flow is prone to becoming chaotic over relatively short time scales.

Monday 2:45 Alpine West FM9

Purely elastic instabilities in a cross-slot flow

Robert J. Poole[1], Manuel A. Alves[2], Alexandre Afonso[2], Fernando T. Pinho[3], and Paulo J. Oliveira[4]
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In a recent paper Arratia et al. [Phys. Rev. Lett. Vol. 96(14) (2006)] demonstrated experimentally that the low Reynolds number flow of a viscoelastic polymer solution in a microfluidic cross-slot geometry can produce two types of instabilities. In the first instability above a critical Deborah number the flow becomes asymmetric, but remains steady. Upon increasing the Deborah number still further a second instability sets in and the flow becomes strongly time dependent.

In the current paper we demonstrate numerically, using a finite-volume method, that both these instabilities can be predicted using the upper-convected Maxwell model under creeping flow conditions, in so doing demonstrating that both instabilities are purely elastic in nature. We also show the stabilizing effect of inertia in reducing the flow asymmetry, and we highlight these effects in a *De-Re* map, identifying the regions of steady symmetric, steady asymmetric and unsteady (asymmetric) flow regimes. The effects of rounding the corners and the use of more realistic viscoelastic constitutive equations will also be discussed.

Monday 3:35 Alpine West FM10

A mechanism for oscillatory instability in viscoelastic cross-slot flow

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Interior stagnation point flows of viscoelastic liquids arise in a wide variety of applications including extensional viscometry, polymer processing and microfluidics. Experimentally, these flows have long been known to exhibit instabilities, but the mechanisms underlying them have not previously been elucidated. We computationally demonstrate the existence of a supercritical oscillatory instability of low-Reynolds number viscoelastic flow in a two-dimensional cross-slot geometry. The fluctuations are closely associated with the "birefringent strand" of highly stretched polymer chains associated with the outflow from the stagnation point at high Weissenberg number. Additionally, we describe the mechanism of instability, which arises from the coupling of flow with extensional stresses and their steep gradients in the stagnation point region.

Monday 4:00 Alpine West FM11

Low inertia mixing of viscous fluids by a chemically triggered shear flow instability

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We study experimentally the mixing of two viscous fluid streams by a low Reynolds number shear flow instability triggered by a fast chemical reaction. The viscous fluids are evenly injected side by side in a T-shaped straight channel. An acid-base reaction taking place at the interface between a Newtonian fluid and a Carbopol-940 solution leads to a strong viscosity stratification, which locally destabilizes the flow. As one advances down stream, complex secondary flow patterns develop resulting in efficient mixing. We also present preliminary analysis of the flow and instability, via a simplified model based on averaging through the channel height.

Monday 4:25 Alpine West FM12

The effects of poly(ethylene oxide) on the stability boundaries of flow regimes in co- and counter-rotating Taylor-Couette flow

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The presence of just a few parts per million of high molecular weight linear polymers is known to have a significant impact on turbulent features in flow, namely polymer-induced turbulent drag reduction. To contribute to the quantitative understanding of this dramatic phenomenon, the authors have studied the influence of dilute polyethylene oxide (PEO) solutions on isolated secondary flow features by mapping the stability boundaries of multiple flow regimes in a Taylor-Couette (TC) geometry. This work expands on previous work involving PEO solutions by mapping the boundaries for both co- and counter- rotational flows, with a focus on modification of higher order transitions (up to $\mathrm{Re}_{\mathrm{inner}} \sim O(10^3)$). The elasticity, defined as the ratio of the polymer relaxation time to the inertial time scale, for the PEO solutions in a viscosified aqueous solvent, ranges from $O(10^{-4}$ to $10^{-1})$. The polymeric solutions are characterized by a number of independent techniques, including dynamic and steady shear flows, extensional flows (CaBER), sessile drop experiments and dynamic light scattering. Changes in stability in TC experiments were found during adiabatic increases of the inner cylinder Reynolds number using spectral analysis and flow visualization in 2D planes of radial, axial, projected azimuthal and time dimensions. The resultant flow state transitions are compared to previous stability maps for Newtonian fluids obtained in our TC geometry of radius ratio 0.912 and aspect ratio 60.7. As a result, the effect of elasticity on the critical

conditions and the stability range are illuminated for transitions to axisymmetric, wavy, spiraling and turbulent modes. The effect of elasticity is both non-monotonic and mode dependent. Also, axisymmetric modes appear to be suppressed by the presence of PEO.

Monday 4:50 Alpine West FM13

Self-sustaining process in plane Couette flow of viscoelastic fluids

Alexander Morozov
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Recently, Fabian Waleffe proposed a mechanism by which Newtonian turbulence in parallel shear flows is sustained [1]. In his mechanism, a small number of coherent structures (streamwise vortices, streaks and 3D vortices) are able to sustain themselves via a series of non-linear interactions and instabilities. This theory, dubbed the self-sustaining process, has been very successful in describing the main features of weakly turbulent states close to the transition threshold.

Here we present a generalisation of this theory to viscoelastic flows. We perform a semi-analytic calculation similar to [1] for a FENE-P fluid and find the region of stability of the self-sustaining process for large Reynolds numbers and weak viscoelasticity which is relevant to the drag-reduction problem. We identify the part of the self-sustaining cycle which is affected most by the presence of polymers. The results are compared to the recent numerical simulations by M. Graham et al [2-3]. We also discuss the possibility that these solutions are connected to the solutions at low Reynolds numbers, which could be relevant for purely elastic turbulence.

[1] F. Waleffe, Phys. Fluids, v.9, 883 (1997). [2] P. A. Stone et al., Phys. Rev. Lett., v.89, 208301 (2002). [3] W. Li et al., JFM, v.565, 353 (2006).

Symposium MR
Microrheology, Microfluidics and Confined Systems

Organizers: Eric Furst and Jai Pathak

Monday 1:30 Canyon B MR6

Multilayer microfluidic flows of suspensions and flow focusing

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Only a limited amount of work to date covers the fundamentals of particle behavior during flow in microchannels, especially those with complex geometries. This experimental study quantified the spreading of parallel streams with viscosity contrast in multilayer microfluidic flows. Three streams converged into one where a test fluid was sheathed between two layers of a Newtonian reference fluid. The different test fluids were Newtonian fluids with a range of viscosities (1.1 to 48.2 cP) and suspensions of 10 micron diameter PMMA particles (volume fractions from 0.16 to 0.30). The reference and test fluids were dyed with different concentrations of a fluorescent dye, and the interface position was monitored by fluorescence microscopy. The steady state width of the center stream is strongly dependent on the viscosity ratio between the adjacent fluids and exhibits a near power-law relationship. While the low concentration suspensions spread in the same manner as the Newtonian fluids, the high concentration suspension diverges from Newtonian behavior. The suspension behavior can be attributed to shear-induced particle migration occurring in the entrance channel. Additional results from flow focusing of a microfluidic multilayer flow will be presented.

Monday 1:55 Canyon B MR7

Examining and influencing order in the flow of worm-like micelles through porous media

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Surfactants are widely used as viscosity modifiers or thickening agents in the food, personal care, and pharmaceutical industries. In the energy industry, they are used as hydraulic fracturing fluids to increase oil and gas recovery, where their usage is complicated by their propensity to align and / or band under shear or confinement.

To enable the study of the behavior of these micelles in porous media, a series of silicon-and-glass microfluidic cells capable of withstanding pressure drops up to 400 psi were constructed and quantified with particle-imaging velocimetry (PIV).

In-situ concentration studies were performed by tagging the micelles with hydrophobic dyes. Accumulation of surfactant in the porous media micromodels was examined as a function of flowrate and surfactant species, and two different accumulation processes are described.

Recent work in this field has examined the shear-banding and phase separation in conventional rheological geometry. However, this work has the advantage of being able to measure surfactant accumulation in real-time in a geometry that more closely mimics the environment in which it is typically used. Furthermore, the role of hydrophobically-modified polymers to control ordering is examined.

Monday 2:20 Canyon B MR8

Micro-cantilever based rheology of polymer solutions

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The vibrational characteristics of a cantilever are highly dependent on the properties of the surrounding medium. This principle can be used in the measurement of fluid properties as was demonstrated by Boscovic et al in 2002. They developed a technique for characterizing simple fluids in which the vibration of a microcantilever due to the Brownian motion of the surrounding fluid is measured with the optics of an atomic force microscope (AFM). The fluid properties are then determined using the frequency response of the microcantilever. This method is limited to fluids with low viscosity because in highly viscous fluids, the vibrations due to Brownian motion of the fluid are not detectable. In this project, the technique was modified for complex fluids with higher viscosities. For this purpose, the fixed end of the cantilever is vibrated using a piezoelectric material, and the response of the cantilever immersed in the fluid is observed by the AFM optics. In order to study the performance of this technique two series of solutions were studied. First, solutions of glycerol in water at varying concentrations providing a wide range of viscosity without elasticity were studied. Then lightly entangled solutions of polystyrene in diethyl phthalate were studied. With this experimental study we are able to observe the different effects of a viscoelasticitic medium as compared to a Newtonian medium on the vibrational characteristics of micro-cantilevers. Using the results we hope to be able to measure the rheological properties of fluids on the micrometer scales with tiny amounts of liquid.

Boscovic S, JWN Chon, P Mulvaney, JE Sader, J. Rheol. 46(4), 891-899 (2002).

Monday 2:45 Canyon B MR9

Electrophoretic stretching of DNA using microscale T-scale junctions

Jing Tang and Patrick S. Doyle
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Controlled trapping and stretching of DNA molecules is critical for single molecule genomic and polymer physics studies. We present a microfabricated T-junction which can trap and stretch single free DNA molecules using electrophoretic forces (Tang and Doyle, Appl. Phys. Lett. 2007). The device does not require special end-functionalization of the DNA. The purely elongational nature of the electric field allows us to use thin fluidic channels. We show that two physical mechanisms of stretching can occur depending on the length of the DNA relative to the channel width in the junction region. In one case the governing dimensionless group is a Deborah number and in the other a Peclet number. Stable trapping and stretching of DNA molecules up to lengths of 485 kilobasepairs is demonstrated. Applications in single molecule mapping will also be demonstrated.

Monday 3:35 Canyon B MR10

DNA relaxation dynamics when confined in a nano/microfluidic channel

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With the development of nanotechnology, new applications have been created for separating and manipulating biomolecules using micro- or nano-fluidic devices. It is therefore essential to understand the underlying physics and transport properties of highly confined macromolecules. Such knowledge will not only be important for the development of polymer physics, but also could help the design and optimization in future applications. Here we experimentally study the relaxation dynamics of large DNA in thin gaps. The longest relaxation time is determined in one of two ways- either by monitoring the rotational motion of molecules at equilibrium or by following the relaxation of stretched DNA back to equilibrium. In addition, we measure the long-time diffusivity of the DNA at equilibrium. We compare our results to scalings predicted by blob theories. Of note is the fact that in blob theory the product of the diffusivity and relaxation time is proportional to the equilibrium size of the DNA - thus we can test both dynamical and static predictions of blob theory. For the case of a stretched DNA relaxing in a slit channel, we find new regimes that are absent when compared to relaxation of an unconfined polymer.

Monday 4:00 Canyon B MR11

A general method to study equilibrium partitioning of macromolecules into confining geometries

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The distribution of macromolecules between a confined microscopic solution and a macroscopic bulk solution plays an important role in understanding separation processes such as Size Exclusion Chromatography (SEC). In this study, we have developed an efficient computational algorithm for obtaining the equilibrium partition coefficient (pore-to-bulk concentration ratio) and the concentration profile inside the confining geometry. The algorithm involves two steps. First, certain characteristic structure properties of the studied macromolecule are obtained by sampling its configuration space, and second those data are used for the computation of partition coefficient and concentration profile for any confinement size. Our algorithm is versatile to the model and type of the macromolecule studied, and is capable of handling three types of confining geometries (slit, rectangular channel and rectangular box). Results for linear random walk chain, linear self avoiding walk chain, and nonlinear random walk chain of various architectures (star, pom-pom, comb, and centipede etc.) will be presented. From these results, a characteristic molecular dimension can be deduced, which is relevant to SEC separation. The use of this dimension rather than Rg (radius of gyration) or Rh (hydrodynamic radius) gives a better universality in the plot of the partition coefficient as a function of the chain dimension relative to the pore size.

Monday 4:25 Canyon B MR12

DPD simulation of depletion layer and polymer migration in micro- and nanochannels for dilute polymer solutions

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Fluid dynamics problems involving micro- and nanoscale channels are of both fundamental and practical importance in variety of applications such as microfluidic devices, Lab-on-Chip devices and real biological systems. In many applications the channel size is of the same order as the size of suspended particles or macromolecules. In such systems depletion layers are observed next to solid-fluid interfaces, even in equilibrium. The imposition of flow results in further cross-stream migration of the particles. In this work we employ dissipative particle dynamics (DPD) to study depletion and migration in dilute polymer solutions in channels several times larger than the radius of gyration (R_g) of bead-spring chains. We compare depletion layers for different chain models and levels of chain representation, solvent quality, and relative wall-solvent-polymer interactions. By suitable scaling the simulated depletion layers compare well with the asymptotic lattice theory solution[1] of depletion near a repulsive wall. The results for chain migration across Poiseuille flow show that the center of mass distribution develops two symmetric off-center peaks which increase with the Peclet number. These off-center peaks identify the preferred chain positions across the channel. These are governed by the balance of wall-chain repulsive interactions and an off-center driving force of the type known as the Segre-Silberberg effect[2].

[1] E. Eisenriegler and R. Maassen, *J. Chem. Phys.* 116(1), 449 (2001). [2] G. Segre and A. Silberberg, *Nature* 189, 209 (1961).

Monday 4:50 Canyon B MR13

Stochastic Rotation Dynamics (SRD) simulation of electrokinetic polymer motion in a microchannel with spatially varying wall charge

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The motion of polymers in electro-osmotic flow in a microchannel with sinusoidally varying wall charge is studied, using the Stochastic Rotation Dynamics (SRD) method. The microchannel consists of two parallel planes with a sinusoidal charge distribution on each wall and this charge distribution induces a complex flow field in the channel when an electric field is imposed in a direction parallel to the planes. In order to couple hydrodynamically the motion of the polymer and the solvent flow, we employed Stochastic Rotation Dynamics method, which incorporates Brownian solvent "particles" that transport momentum and hence allow for inclusion of polymer hydrodynamic interactions. The simulation results show molecular-weight-dependent center-of-mass distributions of polymers in the channel depends on whether the polymer is neutral or charged. The possibility for using such geometries for DNA size separation is considered.

Symposium PS
Polymer Solutions

Organizers: Ralph Colby and Ravi P. Jagadeeshan

Monday 1:30 Canyon A PS6

Rheological characterization and fiber spinning of cellulose ionic liquids solutions

Sameer S. Rahatekar[1], Jan P. Plog[2], Asif Rasheed[3], Rahul Jain[3], Satish Kumar[3], and Jeffrey W. Gilman[1]

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Ionic liquids are a new generation of "green" solvents, which are claimed to be less toxic than the solvents traditionally used for processing and fiber-spinning of cellulose and silk. In the last years there has been a significant effort to use ionic liquids in the production of fibers and films of regenerated cellulose and silk (Phillips, et al, J. Mater. Chem., 2005, 15, 4206-4208; Zhang Macromolecules, 38 (20), 8272 -8277, 2005). However, no detailed rheological characterization of cellulose in ionic liquids has been conducted so far. This contribution is focused on the shear- and extensional rheological characterization of cellulose in ionic liquids as a function of concentration (dilute and semi dilute regime) and molecular weight as well as the type of ionic liquid itself. The shear- and extensional flow characteristics, determined via capillary break-up extensional rheometry, may serve as a useful guideline for cellulose fiber spinnability of the respective cellulose in ionic liquid solution.

Monday 1:55 Canyon A PS7

Is the Blob model applicable to dilute polyelectrolyte solutions undergoing shear flow?

J. Ravi Prakash and Sudip K. Pattanayek

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The blob model, proposed by de Gennes et al., achieves a significant reduction in the number of parameters that are required to describe the static behaviour of dilute solutions of weak polyelectrolytes. The 'bare' model requires five parameters: the number of monomers N_k, the length of a monomer b_k, the number, s, of uncharged monomers that lie along the length of the chain between monomer units carrying an elementary charge, the Bjerrum length l_B, and the Debye screening length l_D. On the other hand, only two parameters (that can be estimated from the 'bare' parameters), appear in the blob model: the number of blobs X, and the mean size of a blob relative to the screening length, Y. Several scaling theories and extensive Monte Carlo simulations have shown that a single polyelectrolyte chain's structure at equilibrium can be neatly classified into various regimes depending on the values of X and Y. While currently there are a few scaling theories based on the blob model that describe the behaviour of dilute polyelectrolyte solutions subject to flow, the validity of the blob model in far from equilibrium situations has so far not been examined by simulations. We show, in the context of Brownian dynamics simulations, that (i) the scaling picture at equilibrium can be accurately reproduced by a suitable choice of parameters in a bead-spring chain model, and (ii) with the inclusion of the characteristic shear rate β as the additional scaling variable in shear flow, the blob model achieves a remarkable data collapse, even for rheological properties. As a result, regardless of the degree of coarse-graining, i.e. the number of beads N in the bead spring chain model (provided $N \geq X$), identical results are obtained as long as X, Y and β are maintained constant.

Monday 2:20 Canyon A PS8

Solvent effects on polyelectrolyte charge, conformation and viscosity in solution

Ralph H. Colby and Shichen Dou

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We study partially quaternized poly(2-vinyl pyridine) in a wide range of solvents, with chloride or iodide counterions. The solvents have different affinity for the neutral poly(2-vinyl pyridine) and also have different dielectric constants (ethylene glycol $\varepsilon = 37$ good solvent; water $\varepsilon = 78$ poor solvent; formamide $\varepsilon = 110$ poor solvent; glycerine carbonate $\varepsilon = 110$ good solvent and N-methyl formamide $\varepsilon = 182$ good solvent). Dielectric spectroscopy (conductivity) determines the effective charge on the polymer, which increases systematically with solvent dielectric constant, but is significantly smaller than the Manning prediction for strongly charged polyelectrolytes in high dielectric constant solvents. Small-angle X-ray scattering and specific viscosity are used to provide two independent measures of the correlation length. The results motivate us to include ion solvation effects and both ion-dipole and dipole-dipole attraction effects in the 'solvent quality' of the Dobrynin scaling model. For instance, the stronger dipole of condensed iodide converts ethylene glycol to a poor solvent, while ethylene glycol is a good solvent for the polymer with chloride counterions. Also, in solvents that impart significant counterion condensation, the polyion solutions at high concentrations actually have lower viscosity than the neutral poly(2-vinyl pyridine), suggesting that dipolar attraction plays a vital role.

Monday 2:45 Canyon A PS9

Dynamics of single DNA molecules in oscillatory shear flow

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Single molecule experiments using fluorescence microscopy and Brownian Dynamics (BD) simulations have provided valuable insights into macromolecular conformational dynamics in planar steady shear flows. Specifically, it has been demonstrated that DNA molecules tumble in shear flows with a characteristic tumbling frequency (fc), and their average conformational properties have been well characterized and documented for various values of Weissenberg (We) number. In this work, we have investigated the average conformational properties of a model semi-flexible macromolecule namely DNA in an oscillatory shear flow via BD simulations. Based on these simulations, we have found that at sufficiently high We when the Deborah number (De), defined as the product of polymer relaxation time and the angular forcing frequency, is less than a critical Dec, which corresponds to fc/2, the macromolecule exhibits similar dynamics in each half cycle as observed in shear flow. However, when the De is greater than Dec, odd harmonics are observed in the macromolecular orientation-frequency response where the forcing frequency determines the fundamental frequency mode. The mechanism responsible for the occurrence of odd harmonics will be presented, and we will also report the existence of intriguing scaling laws based on the numerically derived average conformational properties for the overall size and shape of the molecule as a function of De and We.

Monday 3:35 Canyon A PS10

Studies of polymer collisions: electrophoresing DNA colliding with a single post or an array of posts

Aruna Mohan, Ju Min Kim, and Patrick S. Doyle

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Polymer collisions arise in several scenarios ranging from flowing polymer solutions, polymer brushes interacting with free chains and DNA separations in polymers or sieving arrays. Here we study the model problem of a single DNA electrophoresing past an obstacle or an array of obstacles using Brownian dynamics (BD) simulation, stochastic modeling, and single molecule experiments. For the single post problem, we develop simple micromechanical models for the types of collisions that occur and compare these to experiments and extensive BD simulations.

Next we consider a DNA molecule in an array of posts and extend the continuous-time random walk model of chain dynamics (Minc et al., Phys. Rev. Lett. 2005) in the obstacle array with account for incomplete chain extension. In addition, we evaluate the accuracy of the model by performing Brownian dynamics simulations of DNA chains of different lengths in a self-assembled array of magnetic beads at various electric field strengths.

Monday 4:00 Canyon A PS11

Rheological characterization with DPD

Theis F. Clarke and Robert C. Armstrong

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The rheology of dilute solutions of polystyrene in simple shear and planar elongation flows is studied via computer simulation using the Dissipative Particle Dynamics (DPD) method. Polymer molecules are modeled as bead spring chains with FENE springs. The implementations of DPD due to Shardlow [*SIAM J. Sci. Comput.*, **24**, No. 4, 1267, (2003)] and Lowe [*Europhys. Lett.* **47** (2), 145, (1999)] are compared for these non-equilibrium flows. A secondary thermostatting method is introduced to remove the excess heat that evolves when flow is applied. Simple shear flow is modeled with Lees-Edwards boundary conditions, and planar elongational flow is implemented by using the boundary conditions developed by Kraynik and Reinelt [*Int. J. Multiphase Flow* **18**, No. 6, 1045, (1992)], which were originally applied to non-equilibrium molecular dynamics studies. The effects of varying the molecular weight and polymer concentration on chain conformation and steady state material functions (shear and elongational viscosity, normal stress coefficients) are studied as well. We demonstrate shear-thinning of the viscosity and first normal stress coefficient, and a clear coil-stretch transition in planar elongation.

Monday 4:25 Canyon A PS12

Dynamics of the coil-stretch transition in long, flexible polymers subjected to mixed linear flow fields

Brendan D. Hoffman[1] and Eric Shaqfeh[2]

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The properties of a dilute solution of flexible polymers are highly coupled to the conformations of its constituent molecules. Consequently, the study of single molecule dynamics is of critical importance to the understanding of bulk rheology. Recently, Schroeder et al. (2003, 2005) have demonstrated the existence of a coil-stretch (CS) hysteresis in long, flexible polymers subjected to planar extension, both experimentally and via Brownian dynamics simulations (BDS). As postulated by De Gennes (1974) and formulated by Beck & Shaqfeh (2007), this transition from a coiled to a stretched conformation within the hysteretic region of extension rate is 1st order and can be understood as diffusion over an effective 1D conformational energy barrier. In contrast, no hysteresis exists in shear flow, where molecules freely sample both conformations. We now present a new kinetic theory which describes the CS transition in extension-dominated planar mixed flows. These represent a class of flows in which vorticity is added to planar extension, approaching shear. We find that in congruence with the work of Hur et al. (2001) and Babcock et al. (2003), the addition of vorticity enhances molecular conformational fluctuations which are critical to understanding the transition. As a result, the CS hysteresis vanishes for all otherwise hysteretic extension rates at a fixed Hencky strain. We demonstrate that the growth of length fluctuations is due to the polymer rapidly sampling a shear gradient via Brownian displacements orthogonal to the stretch axis. Our kinetic theory, verified by BDS, allows us to determine the rate at which a coiled molecule unravels (or a stretched molecule coils) for all extension-dominated planar mixed flows. We show that the rate of the CS transition increases with increasing vorticity and, if the molecule is sufficiently long, can be analyzed using a convective dispersion analysis. This analysis is extended to non-planar mixed flows which demonstrate new, unique characteristics in the CS transition.

Monday 4:50 Canyon A PS13

Capillary breakup and shear rheology of dumbbell polymers

Christian Bailly[1], Merina Rajan[2], Uday S. Agarwal[2], Chen-Yang Liu[1], and Piet Lemstra[2]

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Small amounts of high molecular weight polymer additives can have a profound influence on the rheology of viscous fluids. These effects mainly result from a coil-stretch transition in extensional flow, leading to enhanced elongational viscosity. Experiments and molecular simulations have shown that the uncoiling of linear polymers at very high strain rates can be retarded by an intermediate hairpin fold formation, thereby weakening the viscoelastic effect. In this work, we study the influence of a dumbbell architecture for the polymer additives. The solvent drag should pull apart the high friction ends effectively, thus reducing the formation of folded structures. Likewise, when the flow is stopped, the large drag at the chain ends may slow down chain relaxation from the extended state. High molecular weight dumbbell polymers have been prepared by a combination of techniques which include living radical polymerization as well as polymer - polymer coupling. The elongational response of a dilute solution of dumbbell and corresponding linear polymers in oligomeric styrene has been investigated by means of a capillary break-up rheometer. The dumbbell polymer with its unique architecture demonstrates faster stretching and higher elastic contribution to transient extensional viscosity. In particular, the dumbbell shows a significant region of elasto-capillary behavior with exponential diameter decay and constant strain rate while the corresponding linear polymer with the same total molecular weight shows pure visco-capillary breakup. Also the transient elastic contribution to the stress is higher for the dumbbell. The transient response in shear of weakly entangled solutions has also been investigated. The dumbbell polymers follow slower retraction dynamics than the corresponding linear molecules.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Grand Ballroom C PL2

Single particle motion in colloids: from microrheology to osmotic propulsion

John F. Brady

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The motion of a single individual particle in a complex material is fundamental to understanding the dynamical properties of the material. Monitoring such motion has given rise to a suite of experimental techniques collectively known as 'microrheology,' with the ability to probe the viscoelastic properties of soft heterogeneous materials (e.g. polymer solutions, colloidal dispersions, biomaterials, etc.) at the micrometer (and smaller) scale. In microrheology, elastic and viscous moduli are obtained from measurements of the fluctuating thermal motion of embedded colloidal probes. In such experiments, the probe motion is passive and reflects the near-equilibrium (linear response) properties of the surrounding medium. By actively pulling the probe through the material one can gain information about the nonlinear response, analogous to large-amplitude measurements in macrorheology. But what exactly is measured in a microrheological experiment? And how does the micro-rheological response compare with conventional macrorheology? To answer these questions, we consider a simple model - a colloidal probe pulled through a suspension of neutrally buoyant bath colloids - for which both micro- and macro-results can be obtained exactly. The moving probe distorts the dispersion's microstructure resulting in a reactive entropic or osmotic force that resists the probe's motion, which can be calculated analytically and via Brownian Dynamics simulations and used to infer the dispersion's 'effective microviscosity.' It is also shown that this out-of-equilibrium osmotic force can be generated by the probe itself to produce autonomous motion - osmotic propulsion.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Tuesday 10:10 Alpine East SC15

Non-Boltzmann distribution of polymers and suspensions in dissipative systems: cross-stream migration vs. differential relaxation

Todd M. Squires

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Polymers and Brownian rods have been predicted and observed to migrate *across* streamlines in flowing systems, impacting rheological measurements, material processing, and microfluidic systems. In particular, gradients in cross-stream diffusivity evidently give rise to cross-stream migration, in direct contrast with expectations from equilibrium statistical mechanics. Here, we provide a simple, physicially intuitive understanding of the subtle physics that underlies this counter-intuitive effect, and identify the three minimal ingredients: i) a cross-stream diffusivity that depends upon internal degrees of freedom of the suspended species; ii) internal d.o.f. that are driven non-conservatively and inhomogeneously, and iii) a mechanism for relaxation to steady state. Significantly, we argue that some inhomogeneous steady-state distributions that have been observed do not result from directed cross-stream migration; rather, from anisotropies in rates of relaxation. In fact, we show that no such migration occurs in systems without relaxation. We propose and predict analogous behavior in a variety of new systems, including colloidal models, externally-orientable Brownian rods, and externally-triggerable two-state molecules. Finally, we demonstrate that thermal gradients give rise to weak concentration gradients that might otherwise be interpreted in terms of thermophoresis.

Tuesday 10:35 Alpine East SC16

Shear-induced migration of suspensions in 1D, 2D, and 3D open flows

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At relatively moderate to high volume fraction of solids, hydrodynamic interactions result in normal forces that induce migration of particles toward regions of low shear. This self-organization occurs despite dispersion via diffusion in simple shear flows. Alternatively, it is well known that mixing in many systems can be enhanced by inducing chaotic advection by breaking symmetries of the flow. Chaotic mixing has been demonstrated at various length scales, most recently in microchannels for lab-on-a-chip applications. What is unclear is how does shear migration interplay with chaotic advection. This interplay results in complicated concentration gradients that are dictated both by the underlying flow topology and the fluid rheology. Using high speed confocal laser scanning microscopy, particles are tracked in microfabricated channels having various flow topologies to determine their 3D positions and generate 2D concentration and velocity profiles, giving us details of the resulting particle migration.

Tuesday 11:00 Alpine East SC17

Concentration, velocity and pressure distributions for a concentrated suspension flowing through an abrupt, annular contraction-expansion

Tracey Moraczewski and Nina C. Shapley
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The aim of this research is to enhance the fundamental understanding of the flow of a concentrated suspension through an abrupt contraction-expansion. Contraction-expansion flows can be encountered in such applications as materials processing or flow in the circulatory system. The abrupt, axisymmetric contraction-expansion is a classic flow geometry that has been utilized in many flow studies of Newtonian fluids and single-phase, non-Newtonian materials. However, contraction-expansion flows of concentrated suspensions have received less attention in the literature. Of particular interest is the relationship of the particle concentration distribution, which can be spatially nonuniform, to the length of recirculating regions in the expansion and to the total pressure drop.

In this study, suspensions of neutrally buoyant, noncolloidal spheres in viscous, Newtonian liquids undergo steady, pressure-driven flow in an abrupt, axisymmetric 1:4 contraction-expansion. Nuclear magnetic resonance imaging (NMRI) is used to measure the steady-state particle concentration and velocity profiles. Wall-mounted pressure transducers record the pressure drop across the contraction-expansion tube section. The effect of shear-induced particle migration on the concentration, velocity, and pressure fields in the system is investigated, and the role of particle and flow properties (e.g. particle volume fraction, particle size, flow Reynolds number, and inlet conditions) is examined. Comparison of experimental results with continuum model functions can provide further insight into suspension flow behavior in a complex geometry.

Tuesday 11:25 Alpine East SC18

The particle pressure in sheared suspensions and an osmotic interpretation of particle migration phenomena

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Using Stokesian Dynamics simulation and the hydrodynamic functions which describe the isotropic particle stress, the particle pressure in sheared suspensions of Brownian hard spheres is studied for a range of Peclet numbers, Pe (dimensionless ratio of shear to thermal motion). The particle pressure is shown to asymptotically approach the osmotic pressure of a quiescent dispersion in the limit of vanishing Pe, in agreement with the theoretical prediction of Brady [J. Chem. Phys. 98, 3335 (1993)] that the quiescent particle pressure is equivalent to the osmotic pressure. This leads to the conclusion that the particle pressure in flow drives relative motion between the particle and liquid phase, or shear-induced migration, in much the same way that thermal osmotic pressure is related to gradient diffusion in a quiescent dispersion. An experimental means of evaluating the particle pressure under shear flow conditions by an analogue of the U-tube osmometer, in which the liquid response to the particle pressure is measured, has been developed and will be shown to provide a direct measurement of the particle pressure under a range of shear rates and particle volume fractions; analytical arguments will be presented to show that the particle pressure cannot be measured by standard rheometric methods. The nonequilibrium thermodynamic approach to particle flux driven by an osmotic pressure gradient will be extended to apply at any shear rate, providing a unified description of particle migration from equilibrium to strong shear.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Jonathan Rothstein and Patrick Anderson

Tuesday 9:45 Alpine West FM14

Near-transition dynamics of viscoelastic turbulence and drag reduction in plane Poiseuille flow

Li Xi, Wei Li, and Michael D. Graham
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Nonlinear traveling wave solutions have been found for the Navier-Stokes equations in all canonical parallel flow geometries. These solutions capture the main dynamical features of turbulent flows, especially for near-wall coherent flow structures. Our previous study of the effects of polymer additives on one class of these so-called exact coherent states (ECS) suggests that turbulent drag reduction can be better understood through these traveling waves. Many key aspects of experimental observations can be related with the existence and evolution of ECS solutions in viscoelastic flows. Guided by these results, we conduct direct numerical simulations (DNS) in a minimal flow unit that captures the smallest self-sustaining structure in turbulence. The simulations are performed in a parameter regime close to the laminar-turbulent transition, where our earlier results predict that the laminar-turbulent transition, the onset of drag reduction and the maximum drag reduction (MDR) regime are close to each other in Reynolds number. The connection between these DNS results and traveling waves will be described, and the dynamical structures outside of the existence boundary of ECS will also be investigated, the latter of which could be a good starting point of understanding the nature of MDR.

Tuesday 10:10 Alpine West FM15

Settling of an isolated spherical particle in a yield stress fluid

Andreas M. Putz[1], Teodor I. Burghelea[1], Ian A. Frigaard[2], and Mark D. Martinez[3]
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We visualize the flow induced by an isolated non-Brownian spherical particle settling in an shear thinning yield stress fluid using particle image velocimetry. With Re <1, we show a breaking of the fore-aft symmetry and relate this to the rheological properties of the fluid. We find that shape of the yield surface approximates that of an ovate spheroid with its major axis approximately 5 times greater than the radius of the particle. The disagreement of our experimental findings with previous and current numerical simulations is discussed.

Tuesday 10:35 Alpine West FM16

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

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

Tuesday 11:00 Alpine West FM17

Friction drag behavior of dilute polymeric solutions in prototypical complex kinematics flows: a multiscale simulation approach

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In the past two decades tremendous progress has been achieved towards developing first principles models and simulation techniques that can accurately and robustly predict the dynamics of polymeric flows. Yet a problem of fundamental and great pragmatic interest, namely, the relationship between friction drag and flow rate in inertialess flows of highly elastic polymer solutions in complex kinematics flows has defied solution to years of ardent research. This is primarily because the research, to date, has mostly relied on the continuum level simulation approach using closed form constitutive models, such as the FENE-P and FENE-LS models, which can at best provide qualitative predictions of the macromolecular dynamics in simple kinematics flows [Shaqfeh, JNNFM, 2005; and Larson, J. Rheol. 2005]. In this presentation, we focus on the first principles-based solution to this long-standing problem in non-Newtonian fluid mechanics. For this, a parallel, multiscale simulation technique has been developed, which combines continuum-level finite element solvers for the conservation of mass and momentum with fast integrators of stochastic differential equations that describe the evolution of polymer configuration described by bead-spring micromechanical models. The technique has been implemented in simulation of a prototypical complex kinematics flow, namely, the 4:1:4 axisymmetric contraction and expansion flow to determine the degree of complexity required in the micromechanical models describing the polymer dynamics to achieve the experimentally observed [Rothstein and Mckinley, JNNFM, 1999,2001] flow dynamics and friction drag behavior. In turn, a hierarchical approach for the simulation of dilute polymeric solutions in prototypical complex kinematics flows will be presented.

Tuesday 11:25 Alpine West FM18

New formulation for stress calculation: application to flow in a T-junction with viscoelastic fluids

Helder M. Matos[1], Manuel A. Alves[2], and Paulo J. Oliveira[1]
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In the present study we propose a new formulation for the calculation of stresses at control-volume faces, within the context of cell-centred finite-volume methods, and present results of calculations for the viscoelástic fluid flow through a T-junction. Our previous formulation for stress interpolation yielded results that would depend on the time step value employed, even in steady state problems. We have removed this slight inconsistency by devising an improved method that is shown to be more robust, giving results independent of the time step and for a wider range of Deborah numbers. The test case of flow in a planar 2D T-junction has been intensively analysed with Newtonian and GNF fluids due to its connection to hemodynamics and occurrence of vascular diseases in zones with flow recirculation. Since blood is known to possess

viscoelastic properties, this geometry needs to be studied now with some of the constitutive models in common use. We apply the FENE-MCR and FENE-CR models and obtain results for varying Deborah number and retardation ratio, at values of Reynolds number and extraction ratio typical of hemodynamical applications.

Symposium MR
Microrheology, Microfluidics and Confined Systems

Organizers: Eric Furst and Jai Pathak

Tuesday 9:45 Canyon B MR14

Direct and inverse modeling for stochastic data in microbead rheology

Christel Hohenegger[1], Lingxing Yao[2], John Fricks[3], Timothy Elston[4], M. Gregory Forest[5], David B. Hill[6], and Richard Superfine[7]
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In microrheology where bead tracking is the fundamental probe of viscoelastic properties, our group has developed direct and inverse tools to support experiments by R. Superfine and D. Hill. The focus of this presentation is on stochastic methods for noisy time series data, starting with the Mason-Weitz protocol for single bead path data, then going to the Crocker-Levine-Lubensky protocol for 2-point statistics, and finally allowing deterministic forcing (e.g., a laser trap). The motivating application is for characterization and simulations of transport mechanisms in lung airway surface liquids within the Virtual Lung Project at UNC Chapel Hill. We are interested in pathogenic diffusion for the purposes of this lecture, for which the Mason-Weitz and Crocker-Levine-Lubensky protocols are ideally suited, independent of their relation to macroscopic stress-strain relations. Thus we model stochastic time series of single or multiple beads with a generalized Langevin equation, and view the memory kernel as a diffusive transport modulus, which is specific to the host material, bead geometry, bead-solvent chemistry, and any imposed deterministic forcing. Our methods come from the maximum likelihood methodology and Kalman filter which were developed for parameter inversion from noisy time series. We build fast and statistically accurate direct simulation tools as well as inversion methods which yield normal distributions for parameters in the memory kernel. Illustrations of the tools will be provided, both on numerical benchmarks and on experimental data.

Tuesday 10:10 Canyon B MR15

The effect of tracer-medium interactions on microrheology measurements

Ileana C. Carpen
Chemical Engineering, Tennessee Tech University, Cookeville, TN 38505, United States

Microrheology is a tool that is seeing increasing interest in fields involving complex and biological materials. The various methods that are collected under the microrheology umbrella have shown themselves to be useful in studying heterogeneous systems at the microscopic level, providing both average and local property information. However, as with macroscopic measurements, microrheology measurements are also dependent upon the validity of certain assumptions. For example, particle-tracking microrheology, in which the motion of a colloidal 'tracer' particle is used to infer system properties, assumes that the tracer particle does not interact with the material being studied other than as a hard object. Thus, for example, the tracer cannot chemically react with the medium, nor should it be attracted to (or conversely, repelled by) the substance it is submerged in. The effect of such 'extra' interactions upon microrheology measurements is therefore a matter for concern.

This talk presents the results from various sets of Brownian Dynamics simulations used to study the effects of tracer-medium interaction potentials for (1) a tracer in a colloidal dispersion and (2) a tracer in a dilute polymer solution. The results of the simulations show the sensitivity of microrheology measurements to the (ignored) tracer-medium interactions.

Tuesday 10:35 Canyon B MR16

Oscillatory laser tweezer microrheology of a colloidal suspension

Indira Gopal and Eric M. Furst
Chemical Engineering, University of Delaware, Newark, DE 19716, United States

We investigated the microrheology of a colloidal suspension using actively-driven oscillating probe particles. The experimental system is an aqueous suspension of fluorinated ethylene propylene (FEP) particles, which are refractive index matched to the solvent. Monodisperse probe particles, either 2 um diameter silica or 3 diameter um diameter polystyrene, are trapped and oscillated using laser tweezers at amplitudes of 25-400 nm and frequencies between 5-1000 Hz. The oscillation amplitude and phase of the probe are measured, and these values are used to calculate the frequency dependent microviscosity of the suspension. Frequency thinning of the microviscosity is observed at all concentrations, and is most significant for volume fractions above 0.3. There is no dependence of the microviscosity on the probe amplitude over the range of

amplitudes investigated. The results are in quantitative agreement with both previous measurements of the suspension microviscosity by pulling probe particles at constant velocity [1] and recently developed theory of active, oscillatory microrheology [2].

[1] Meyer, A., et al., Journal of Rheology. 50(1), 77-92, (2006). [2] Khair, A. S., and J. F. Brady, Journal of Rheology. 49(6), 1449-1481, (2005).

Tuesday 11:00 Canyon B MR17

Real Space Imaging of flow and yielding in soft particle pastes

Fabrice Monti[1], Jyoti Seth[2], Michel Cloitre[1], and Roger Bonnecaze[2]
[1]Ecole Supérieure de Physique et de Chimie Industrielles, Paris, France; [2]University of Texas at Austin, Austin, TX, United States

Soft particle pastes form a broad class of materials made of soft and deformable particles that pack together in an amorphous state at high volume fraction. Well-known examples include emulsions, micellar solutions, polyelectrolyte microgels, and vesicles. These materials behave like weak elastic solids at low stresses but they can yield and flow much like viscous fluids when a stress exceeding the yield stress is applied. This remarkable property is generally associated with many other fascinating phenomena such as shear thinning, aging and memory, wall slip and/or fracture. Although the understanding of soft particle pastes has stimulated much experimental and theoretical work, the microscopic mechanisms at work in these materials remain to be elucidated.

In order to gain a new insight into the local dynamic of soft particle pastes, we have developed a high-resolution micro-rheology apparatus that allows the direct and quantitative imaging of pastes during flow and yielding. This technique combines fluorescence video-microscopy with particle tracking techniques, making it possible to reconstruct the trajectories of tracer particles or labelled particles embedded. The excellent spatial resolution (0.2 μm in the plane of observation and 1 μm in the out-of-focus direction) and the wide range of velocities that are accessible (10^{-3} μm/s<V<10^{2} μm/s) allow us to investigate the dynamics of pastes both in bulk and near confining surfaces. After describing the technique, we use it to quantitatively investigate the microstructural changes that take place in a polyelectrolyte microgel paste[1] during and after flow cessation. The results will be compared to recent 3D molecular dynamics simulations of soft particle suspensions.

Meeker, S. P., R. T. Bonnecaze, and M. Cloitre, "Slip and flow in pastes of soft particles: Direct observation and rheology," J. Rheol. **48**, 1295-1320 (2004).

Tuesday 11:25 Canyon B MR18

High throughput rheology using driven and diffusive microbeads

Richard Chasen Spero[1], Onejae Sul[1], Jeremy Cribb[1], Susan Lord[2], Leandra Vicci[3], and Richard Superfine[1]
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While high throughput systems for microscopy have received great attention for their potential to speed biomedical research, there remains an unmet need for systems for a high throughput rheology system. We report on the design and implementation of a magnetic high throughput system (MHTS), designed specifically with rheometry of biomaterials in mind. Our instrument uses passive- and driven-microbead rheometric techniques in a 16-well design, scalable to 96 wells. It is based on commercial standards for high throughput screening.

Microbead techniques, in which probes are on the order of 0.1 - 10 Um, are an attractive choice for high throughput system rheology for a number of reasons. First, they work with small sample volumes (<10 uL). Second, the range of probe sizes allows characterization of materials from material mesh sizes at the smallest dimensions up to bulk rheology for the largest probes. Finally, while diffusive bead rheology probes linear phenomena, we have shown that driven bead rheology can access linear and non-Newtonian phenomena such as shear thinning, consistent with bulk rheological characterization.

We report on experiments that take advantage of high-throughput rheometry, including mechanical measurements of simple newtonian fluids, viscoelastic polymer solutions, and highly elastic crosslinked polymer networks.

Symposium PS
Polymer Solutions

Organizers: Ralph Colby and Ravi P. Jagadeeshan

Tuesday 9:45 Canyon A PS14

Brownian dynamics simulations of dilute polymer chains with bending and torsional potentials

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The bead-spring model which is extensively used for describing the linear viscoelastic properties of high molecular weight polymers is justified through a coarse-graining approximation valid at long time and distance scales. At these scales, individual bonds corresponding to a single spring are assumed to relax quickly enough to sample their equilibrium configuration distribution. In fast flows or at high frequency, the number of bonds that can be successfully represented by a spring remains unclear. To understand this and the mechanism of energy dissipation at high

frequencies, we carry out a Brownian dynamics study of a linear polymer chain with beads representing individual carbon atoms, stiff Fraenkel spring forces to maintain the distance between carbon atoms as 1.53 A^0, random Brownian force to represent the molecular motion of the continuum solvent, bending forces to maintain tetrahedral bonding, and realistic torsional forces to induce the chain to take on the preferred torsional configurations. With this model, we find that while the end-to-end vector autocorrelation function is in excellent agreement with the theoretical Rouse model predictions, the autocorrelation function of the bond orientation vectors which reflects the relaxation of the stress tensor, exhibits a decay rate that differs from Rouse predictions except near the longest relaxation time. We find that both the bending and torsional potentials suppress the contributions of fast relaxation times in the Rouse spectrum, bringing the relaxation of short chains (<50 bonds) closer to single exponential, in agreement with observations of birefringence relaxation made years ago by Shrag and coworkers (J. Polym. Sci. (1982), 20:1409). The results are in agreement with a recent model that invokes the notion of a "dynamical Kuhn length" that, because of torsional barriers to chain motion, can be longer than the ordinary static Kuhn length, leading to a loss of high frequency modes of relaxation (Larson RG, Macromol. (2004) 37:5110).

Tuesday 10:10 Canyon A PS15

Two-dimensional turbulence in dilute polymer solutions - computational prediction through a microscopic-continuum interaction approach

Sorin M. Mitran

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A microscopic-continuum computation of 3D polymer chains evolving in a thin layer of Newtonian fluid is presented. It is well known that small quantities of dissolved polymers can lower turbulent fluctuations in pipe flow. A similar phenomenon has been observed experimentally in soap-film flows. In the simulation presented here, the constitutive law for the continuum polymer model is dynamically updated by averaging quantities from simultaneous microscopic simulations of dumbbell and FENE spring models. The microscopic simulations are carried out in a small fraction of the computational cells of the continuum model. Comparisons of the observed microscopic statistics to the theoretical power tail law for polymer extensional state are presented. The hypothesis of polymers being passively transported is critically investigated. Continuum turbulent statistics are presented as a function of polymer concentration and elasticity.

Tuesday 10:35 Canyon A PS16

Kinetic models for flows of biaxial liquid crystal polymers

Sarthok Sircar[1] and Qi Wang[2]

[1]Math, FSU, Tallahassee, FL 32306, United States; [2]Mathematics, Florida State University, Tallahassee, FL 32306, United States

We develop a kinetic theory for flows of liquid crystal polymer solutions with biaxial molecular anisotropy. The Smoluchowski equation, the elastic as well as the viscous stress are derived. The molecular biaxial and the phase biaxiality will be addressed. Phase behavior in simple flows will be discussed in the talk. A Wigner function based spectral method is implemented to solve the Smoluchowsi equation.

Tuesday 11:00 Canyon A PS17

Study of elongational properties of short glass fiber reinforced thermoplastics

Monica F. Naccache[1], Aline A. Abdu[1], Paulo R. Souza Mendes[1], Christophe Mobuchon[2], Marie-Claude Heuzey[2], and Pierre J. Carreau[2]

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Composite thermoplastic materials are used increasingly in several industries. In particular, glass fiber reinforcements are chosen to improve the mechanical properties of thermoplastics. However, few data on the rheological properties of these materials are available in the literature, especially in elongational flow. In this work, a study of shear and elongational properties of a commercial short glass fiber reinforced polypropylene is presented. The shear and elongational viscosities were obtained using the pressure drop measured in a capillary rheometer, with axisymmetric converging dies. Two different die geometries were used: semi-hyperbolically convergent dies and conical convergent dies. In the last case, the apparent elongational viscosity was obtained using the Cogswell and Binding analysis. Comparisons with data previously obtained on an on-line rheometer were performed. The on-line rheometer consists of a slit die with an hyperbolic entrance and can measure steady shear viscosity, first normal stress difference, and apparent extensional viscosity of polymer melts and composites for high strain rates, up to 200 s^{-1} in extension (*). Numerical simulations were also performed to investigate the flow field in the extrusion die process, and to evaluate the pressure drop and elongational viscosity. The conservation equations of mass and momentum were solved via the finite element method, using the commercial program POLYFLOW (Ansys). The Phan-Thien-Tanner (PTT) constitutive equation was used to model the viscoelastic behavior of polypropylene, and the results were compared to experimental data obtained from the capillary and slit die rheometers.

(*) Mobuchon et al., Polymer Composites, 26(3), 247-264

Tuesday 11:25 Canyon A PS18

Modeling polymer-particle nanocomposite flows

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We will present a kinetic theory for flows of polymer-particle nanocomposites. The nanoparticles are either nematic thin rods or nematic thin platelets of semiflexibility. We account the entropic contribution to the free energy from the semiflexible nanoparticles and partiel polymer interaction. Using a quasistatic approximation, we derive the second tensor based closure models. The model prediction in simple flows will be discussed.

Tuesday Afternoon

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Tuesday 1:30 Alpine East SC19

NMR measurement of irreversibility and particle migration in dilute sheared Brownian suspensions

Joseph D. Seymour[1], Jennifer R. Brown[1], Sarah L. Codd[2], Einar O. Fridjonsson[1], and Giles R. Cokelet[1]
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The direct measurement of the dynamics of the discrete particle and fluid phase of dilute ($\phi < 0.10$) suspensions of 4 μm Brownian particles under shear flow in a capillary by nuclear magnetic resonance (NMR) indicate particle migration and irreversible dynamics. The observed dynamics are typically associated with concentrated non colloidal suspensions, and the presence of this behaviour in dilute Brownian systems indicates the applicability of theoretical concepts previously applied to concentrated non colloidal systems. Particle migration in Brownian suspensions under pressure driven flow has been shown previously using an optical technique for concentrated suspensions, and non colloidal flow models were applied to quantitatively account for the migrations [1]. The optical experiments showed indications of particle migration at dilute volume fraction ($\phi \sim 0.05$) but not at levels beyond the uncertainty of the measurement. The NMR data clearly demonstrates particle migration in the dilute regime. The ability of NMR methods to reverse the impact of coherent motion on the measured nuclear spin magnetization is exploited to measure irreversible dynamics of the Brownian particles as a function of experimental observation time. The presence of irreversibility as a function of total strain indicates many body hydrodynamics impact the particle motions [2]. The concepts of chaotic dynamics, previously applied to irreversibility in concentrated non colloidal suspensions [2], also appear to apply to dilute sheared Brownian suspensions.

[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. [2] D.J. Pine, J.P. Gollub, J.F. Brady and A.M. Leshansky, Chaos and threshold for irreversibility in sheared suspensions, Nature, **438** (2005), 997-1000.

Tuesday 1:55 Alpine East SC20

Isochronal stress-strain response and 'aging' of concentrated latex suspensions

Gregory B. McKenna[1], Tetsuharu Narita[2], and Francois Lequeux[2]
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Highly concentrated colloidal suspensions are often considered to exhibit behavior similar to that of glass-forming systems. While there is considerable rheological information in the literature concerning the flow behavior of such systems, there is little that has examined the mechanical response in a fashion that makes explicit comparisons with the relaxation behavior of molecular or polymeric glasses. On the other hand there is a significant literature that looks at 'shear melting' and subsequent aging of such glass-like or 'pasty' liquids. Here we report results for two polymer latex particle systems in which stress relaxation experiments and aging after shear melting experiments were performed in a concentration regime near to the glass-concentration of 58%. The materials were both commercial latexes, one was a Hexion PL266 which has a particle size by light scattering of 300 nm. The other system was a Latexia 300 having a particle size of 200 nm. We worked with concentrations from 50% to 66%. Single step stress relaxation results presented as isochrones of stress vs. strain show typical behavior of polymers when the concentrations are low. That is there is a linear regime of behavior (generally less than a deformation of 1%) followed by a nonlinear response and subsequent yield. At higher concentrations, while the linear behavior is retained, the 'yield-like' response is much more abrupt. Interestingly, we find an effect of loading sequence on these isochrones and this will be discussed. Aging behavior was examined subsequent to either single steps in shear or multiple sinusoidal solicitations, and the results were similar. Importantly, in all instances where 'aging' occurred we found that there was no time-aging time superposition, which is contrary to the postulate that the shear melting has the effect of changing the effective temperature. These results will be discussed.

Tuesday 2:20 Alpine East SC21

A Hertzian model for the deformation and cracking of saturated colloidal packings

William B. Russel, Ning Wu, and Weining Man

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Drying colloidal dispersions to create particulate solids or continuous polymer films is common to a range of technologies designed to create a layer of specified thickness and controlled porosity. Processing of such films encounters conflicting constraints for successful film formation and performance demanded by the applications. As the fluid evaporates the concentration of particles increases, eventually producing a gel or close packed glassy or ordered phase. Further evaporation generates a negative capillary pressure that puts the dispersion in tension and is capable of deforming even a close packed colloidal solid. Modeling the deformation requires a relationship between stress and deformation or rate of deformation that captures both the nature of the packing and the stresses within the particles. For spheres in contact that respond to contact forces either elastically, we formulate constitutive equations in which the stress varies as the 3/2 power of the strain or rate of strain. Coupling this constitutive equation with conservation equations allows us to address prototypical problems relevant to film formation and cracking. First, the driving force - air-water, particle-water, or particle-air surface tension - that controls the formation of a void-free film for polymer latices with a glass transition temperature in the vicinity of the process temperature is controlled by two dimensionless groups that distinguish wet sintering, capillary consolidation, and dry sintering regimes. Second is the question of cracking for elastic particles at temperatures below the glass transition temperature. To open a crack the elastic energy recovered must exceed the surface energy expended. We calculate the stress relaxation, both normal and parallel to the substrate, by linearizing the constitutive equations about the homogenously deformed base state and employ a thin film or lubrication approximation. The outcome is a lower bound on the capillary pressure necessary for the first crack.

Tuesday 2:45 Alpine East SC22

Micromechanical approach to the rheology of suspensions: microstructure and effective behavior

Xavier Chateau and Kien Luu Trung

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Even if the behavior of suspensions have been the subject of numerous studies, a general method allowing to estimate the overall properties of the material as a function of the informations available on the microstructure does not seems to exist yet. Among the difficulties one has to solve in order to built such a method, one is related to the fact that only partial information on the distribution of the constituents is available. In the first part of the presentation, we briefly report the main feature of Continuum micromechanics, a theory developed to provide estimates and bounds from these informations and we show how it is possible to compute new estimates for the viscosity of a Newtonian suspension as a function of the solid fraction and of the size distribution of non-Brownian and noncolloidal particles. Comparisons with classical estimates (Einstein, Krieger-Dougherty, ...) and with experimental results are presented. Then, we address the behavior of a bidisperse suspension made up of two populations of particles: a colloidal one and a coarse one. Even if no interaction forces exist between the colloidal and the coarse particles, depletion of the small particles in the vicinity of large particles boundary can occur, inducing an increase of the solid concentration in the colloidal suspension. A morphological model was built to account this effect: the coarse particles are surrounded by a thin layer made up of the colloidal particle free suspendind fluid, this composite sphere being embedded in the equivalent homogeneous medium. The colloidal suspension occupies spherical domains embedded in the same equivalent homogeneous medium. Estimates for the overall properties of the bimodal suspension are computed. It is shown that these estimates account for more of the phenomena observed by means of experimental approaches to the behavior of such a suspension. To conclude, theoretical results are compared to experimental data founded in the literature.

Tuesday 3:35 Alpine East SC23

Influence of short-range interactions on wall-slip in microgel pastes

Jyoti Seth[1], Roger Bonnecaze[1], and Michel Cloitre[2]

[1]University of Texas at Austin, Austin, TX, United States; [2]Ecole Supérieure de Physique et de Chimie Industrielles, Paris, France

Microgel pastes along with materials like compressed emulsions, slurries and many biological fluids are complex fluids that behave like elastic solids at rest but flow like viscous fluids when sheared with a stress greater than the yield value. The nature of the yielding transition depends on whether the shearing surface is rough or smooth. In the former, the paste yields at the bulk yield stress σ_y and exhibits a uniform bulk flow at higher stresses. But when sheared with a smooth wall, instead of yielding at σ_y the paste continues to move and eventually stops at a much lower stress σ_s. It has been reported by Meeker *et al.* (J. Rheol.48, 1295-1320, 2004) that with smooth surfaces and for an applied stress between σ_y and σ_s there is no bulk flow and the paste moves only due to slip. They proposed an elastohydrodynamic lubrication model that accounts for the variations of the slip velocity with $\sigma \gg \sigma_s$. However, the slip mechanism at lower stresses and the physical origin of σ_s remain two important unsolved issues.

In this talk we analyze how the nature of the shearing surface influences wall slip. We present experiments performed with different shearing surfaces and varying paste properties. Two distinct slip behaviors are identified: depending on whether the interaction between the microgel particles and the wall is attractive or repulsive, wall slip can be either suppressed or promoted. We also propose a slip model, which is still based on elastohydrodynamic lubrication but with possible adhesion or repulsion due to short-range interactions between the microgel and the shearing surface. The onset of slip is then determined from a balance between the interaction forces and the elastohydrodynamic lift generated by lubrication. The predicted relationships agree well with the experimental results, providing guides to control wall slip in practical situations.

Tuesday 4:00 Alpine East SC24

Rheological measurements of colloidal glasses and shear-induced crystals coupled with Light Scattering Echo

Nick Koumakis and George Petekidis
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We present linear and non-linear rheology in suspensions of hard-sphere colloids with particular reference to the rheological behaviour of shear induced crystals. Using practically monodisperse hard spheres, we are able to examine glassy suspensions and give comparison to the rheology of their shear-crystallized counterparts. It is evident, that shear-induced crystallization causes a significant drop in the elastic modulus G' due to the structural rearrangements of crystal formation. The properties of rheological aging on glass and crystal are also probed. It seems that both glassy and crystal hard sphere solutions exhibit an increase of both G' and G" with the passage of time. Furthermore, the microscopic particle rearrangements during the shear-induced crystalization are followed by the technique of Light Scattering Echo.

Tuesday 4:25 Alpine East SC25

Effects of particle hardness on shear thickening colloidal suspension rheology and STF-composite performance

Norman J. Wagner, Dennis Kalman, and Joseph Houghton
Chemical Engineering, University of Delaware, Newark, DE 19716, United States

Literature reports of a second shear thinning regime after shear thickening in dense colloidal dispersions are examined from the viewpoint of the material properties of the particle phase. We hypothesize that the particle modulus can limit the extent of shear thickening, and that the second shear thinning regime is a manifestation of particle softness. Model poly(methyl methacrylate) (PMMA) colloidal dispersions are synthesized and purified. Stable suspensions are shown to exhibit strong shear thinning and thickening, followed by a second shear thinning regime. Using roughened plates, we determine that the second shear thinning regime is not an artifact of slip, or adhesive failure with the rheometer tooling. These shear thickening fluids (STF)s are fabricated into composites with ballistic materials. Testing of these composites in quasistatic puncture and ballistic testing indicates shows a correlation between the suspension rheology and STF-composite performance. These results demonstrate the important role of particle hardness in dense colloidal suspension rheology.

Tuesday 4:50 Alpine East SC26

Flow mechanics of filled polymer melts

Benjamin J. Anderson and Charles F. Zukoski
Department of Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

In this paper we explore the effects of filler particles on the flow mechanics of polymer melts while varying the polymer molecular weight and particle volume fraction. These studies were conducted as part of an effort to understand polymer mediated particle-particle interactions, filler effects on polymer chain dynamics, and potential particle-polymer phase separation. The phase behavior of filled polymers will be governed by enthalpic and entropic contributions. A variety of phases are expected as particle volume fraction, polymer molecular weight, and segment-surface interactions are varied: homogeneous fluid, phase separation, or nonequilibrium gel. The development of systematic studies aimed at understanding filler effects on melt mechanics is difficult. Relaxation times are long for high molecular weight polymers. This makes attaining equilibrium questionable. To circumvent this issue, we have investigated nanosilica dispersions in low molecular weight polyethylene glycol (PEG) and PEG derivatives of increasing molecular weight. In previous work, nanosilica was shown to be stable in PEG melts witnessed by the particle second virial coefficient being slightly greater than unity and to interact as hard spheres of slightly larger excluded volume through measurement of the particle structure factor. These results imply immobilized polymer on the particle surface which provides steric stabilization due to a favorable attraction between the particle surface and polymer segments. In recent studies, we find the relative viscosity to increase upon addition of filler particles as Einstein predicts but the slope of the increase is greater for higher MW polymers. As we raise the filler volume fraction, we see an arresting of chain dynamics witnessed by a plateau in the elastic modulus that depends on filler volume fraction and polymer molecular weight suggesting a phase transition. At the same time, multiple relaxation behavior is seen in the viscous modulus when approaching the transition volume fraction.

Symposium FM
Non-Newtonian Fluid Mechanics

Organizers: Jonathan Rothstein and Patrick Anderson

Tuesday 1:30 Alpine West FM19

On a method for non-Newtonian compressible flow calculations

Ana S. Duarte and Paulo J. Oliveira
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Compressibility effects may be important in flows subjected to large pressure differences, of the order of hundreds of bars, when a large portion of fluid is driven into a time-dependent motion. These kinds of conditions occur in many industrial processes involving non-Newtonian liquids such as extrusion and injection moulding. Here we are particularly concerned with the flows generated by the Multi-Pass Rheometer (MPR) devised at Cambridge by Mackley and co-workers. In this rheometer, a given specimen of a non-Newtonian fluid is set in motion by the movement of two pistons, whose displacements may follow a sinusoidal variation or a sudden start/stop pre-specified profile, and flows through a die having any desired shape (usually an axi-symmetric or planar contraction/expansion). This die links the two reservoirs that serve to guide the movement of the pistons. It is important to have means of predicting the flows generated by this type of devise. In a series of recent papers, Webster and co-workers have developed and applied a compressible method in the context of finite-element calculations. Here we wish to follow the same line of investigation but within the context of the finite-volume approach and with new features in mind: first, the method should be adequate to cater for moving meshes, a necessary feature to simulate the flow induced by the moving pistons in the MPR; second, the emphasis of the applications will be on time-dependent flows, where the effects of compressibility are expected to be magnified. In this presentation we will give the basis of our methodology and show preliminary results of its application.

Tuesday 1:55 Alpine West FM20

Spurious modes in the computation of incompressible viscoelastic flows: diagnosis and correction

Sorin M. Mitran and Lingxing Yao
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Numerical methods for the computation of unsteady incompressible viscoelastic fluids described by a differential constitutive law may introduce spurious stresses due to the typical splitting procedures employed. The incompressibility constraint prohibits longitudinal elastic modes in the fluid, and imparts an overall elliptic constraint on the system of partial differential equations describing the flow. To avoid the computational expense of simultaneously solving for fluid velocities and stresses, splitting procedures are used. A common approach is to enforce the elliptic constraint at the end of a computational time step through a projection method. The polymeric stress equation is typically advanced in time before the constraint is applied. The nonlinear terms present in the upper convected derivative can introduce spurious longitudinal modes which then are used in the momentum update. This talk presents a diagnosis of this problem in currently accepted algorithms (projection method, artificial compressibility method) and introduces an algorithm that eliminates the spurious longitudinal modes.

Tuesday 2:20 Alpine West FM21

Dimensionless non-Newtonain fluid mechanics

Paulo R. de Souza Mendes
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We present an alternative reasoning for the choice of characteristic quantities to be employed in the non-dimensionalization of the governing equations of non-Newtonian fluid flow problems. The usual non-dimensionalization procedure generates well known dimensionless groups such as the Reynolds number, Deborah or Weissenberg number, Carreau number, Bingham number, and capillary number. The groups that represent dimensionless rheological properties (e.g. Deborah number, Carreau number, Bingham number) involve flow quantities such as characteristic velocities or deformation rates. Consequently, for a fixed flowing material, the values of these groups change with the flow rate. In the alternative procedure, the resulting dimensionless rheological groups are actually dimensionless rheological properties, and thus remain fixed for a given flowing material. The proposed non-dimensionalization procedure is physically more sound, and renders simpler both the application of dimensionless results to engineering situations and the comparisons between numerical and experimental results in scientific investigations.

Tuesday 2:45 Alpine West FM22

Polydomain simulation of liquid crystalline polymer orientation in channel flows

Jun Fang and Wesley R. Burghardt
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The ultimate properties of liquid crystalline polymers are strongly affected by the molecular orientation state induced by flow fields during processing. LCP orientation development under flow is quite complex, due to the propensity towards 'director tumbling' dynamics in rodlike nematics, and the complex 'polydomain' distributions of orientation that are typically observed. A wide range of models exist that can in principle describe the coupling between processing flows and the resulting fluid structure. Many of these begin with a detailed description of the molecular orientation state, possibly including a molecular-level description of distortional elastic effects. While well suited for simulations of fundamental rheological and structural phenomema in simple flows, application of these models to processing flows is still far out of reach. Conversely, the model of Larson & Doi, which treats distortional elasticity in polydomain LCPs in a phenomenological way, is sufficiently simple to allow for its application to process simulations. This is further facilitated by a nearly exact analogy between the Larson-Doi model and the Folger-Tucker model for predicting orientation in fiber dispersions, which is incorporated in commercial process simulation software. We use this available modeling infrastructure to test the ability of the Larson-Doi model to predict orientation distributions in kinematically complex but isothermal channel flows of liquid crystalline polymers, comparing simulation results orientation distribution data previously obtained using in situ x-ray scattering methods.

Tuesday 3:35 Alpine West FM23

The interplay of thermal-induced and flow-enhanced crystallization in the analysis of steady state and transient high-speed fiber spinning

Anthony J. McHugh and William Kohler

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Results of 2-D steady-state and 1-D transient analyses of fiber melt spinning based on our two-phase model for flow-enhanced crystallization (FEC)will be shown. The model employs the extended pom-pom (XPP) constitutive equation for the amorphous phase and the rigid rod equation for the semi-crystalline phase. Calculations are carried out for the high-speed spinning of nylons, polyethylene terephthalate (PET), and pure poly(L-lactic acid) (PLLA), as well as racemic mixtures of the latter (rPLA). The 2-D analysis shows that radial variations in temperature and degree of crystalline transformation and microstructure for the PLLA, rPLA, and higher speed PET examples exhibit significant patterns in the skin and core regions of the fiber that reflect the interplay between FEC and thermal-induced crystallization (TIC). Insight is gained into the relationship of TIC and FEC in determining radial birefringence profiles. Likewise, similar considerations for the particular Nylon and lower speed PET examples indicate their less pronounced radial effects are the result of the same interplay. A linearized 1-D sensitivity and stability analysis investigates the relative roles of flow-enhanced crystallization (FEC) and thermal-induced crystallization (TIC) on the process dynamics. The effects of changes in various process variables (principally air cooling rate and temperature) on the system sensitivity are shown. Results show that higher crystallization, whether from TIC or FEC, generally equates to lower spinline sensitivity. However, factors such as high-speed necking induced by FEC, viscoelastic stresses, and thermal transport properties are also shown to impact trends in the sensitivity.

Symposium BE
Blends, Emulsions and Multiphase Fluids

Organizers: Matt Liberatore and Sachin Velankar

Tuesday 4:00 Alpine West BE1

Component terminal dynamics from tracer blends

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Previously, we presented several methods of obtaining component terminal dynamics in miscible polymer blends using a commercial rheometer. These utilize steady and dynamic measurements of tracer blends, examining the relaxation of a few long chains in lower molecular weight blend matrices of varying composition. We applied these methods to PEO / PMMA blends. The results agreed well with PEO diffusion data obtained from forced Rayleigh scattering. Results showed that the mobility of PMMA, the slow component, is strongly affected by the presence of PEO, whereas the PEO component is less affected by the addition of PMMA. Moreover, the PMMA mobility can be directly correlated with the matrix viscosity, whereas that of PEO decouples from the matrix viscosity at high PMMA content. This is reminiscent of the behavior of a polymer and a solvent in their corresponding solution. In order to investigate this possibility further, we repeated some of the measurements while varying the molecular weights of the matrix components. We present these data and discuss their implications.

Tuesday 4:25 Alpine West BE2

Viscoelastic and dielectric behavior of a miscible polyisoprene/poly(4-t-butyl styrene) blend

Hiroshi Watanabe

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Linear viscoelastic and dielectric behavior was examined for a LCST-type blend of polyisoprene (PI; M = 20K) and poly(4-tert-butyl styrene) (PtBS; M = 70K) with the PI/PtBS composition of 8/2 (wt/wt). At temperatures examined, T = 70C, this PI/PtBS blend was in a statically homogeneous state. The PI chain has the type-A dipoles parallel along the backbone and its large-scale motion activates prominent dielectric relaxation, while the PtBS chain has no type-A dipoles and its large-scale motion is dielectrically inert. In fact, the dielectric signal exclusively attributed to the PI motion was observed for the blend. The time-temperature superposition failed for the dielectric loss of the PI chains, despite the fact that the blend was statically homogeneous. This result suggested that the frictional environment for the large-scale motion was not the same for all PI chains. Namely, the PtBS chains relaxed more slowly than PI (as revealed from comparison of viscoelastic and dielectric data) and their dynamic concentration fluctuation was frozen in the time scale of PI relaxation to give a non-uniform frictional environment for the PI chains. The magnitude of this non-uniformity changed with T thereby leading to the failure of the time-temperature superposition for PI. In contrast, the superposition worked excellently for the viscoelastic modulus of the PtBS chains (obtained by subtracting the PI contribution from the blend modulus). This result suggested that the PI chains relaxing faster than PtBS erased the heterogeneity in the time scale of the PtBS relaxation to provide all PtBS chains with the same frictional environment.

Tuesday 4:50 Alpine West BE3

Concentration fluctuation effects on blend dynamics

Wenjuan Liu[1], Ralph H. Colby[1], and Dmitry Bedrov[2]
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We develop a model to account for the effects of chain connectivity, thermally-driven concentration fluctuations and density fluctuations on segmental dynamics of miscible weakly interacting polymer blends. These fluctuations naturally lead to local variations in T_g and hence, a distribution of segmental relaxation times. Thermally-driven density fluctuations create a distribution of local volumes that a given small mass of material occupies, which can be described by statistical mechanics and then translated into a distribution of segmental relaxation times using the Doolittle equation. At the same time, concentration fluctuations and chain connectivity lead to a distribution of environments around a given segment in a single-phase blend, which can be generated utilizing atomistic, coarse-grained and lattice bond-fluctuation model and translated into a distribution of segmental relaxation times. The most-probable composition (distribution peak) differs considerably from the mean-field estimation of Lodge and McLeish for compositions significantly different from 50/50 because the self-concentration and pure component limits naturally truncate the Gaussian distribution of compositions surrounding a given segment. We then compare the predictions with experimental results for poly(vinyl methyl ether) / polystyrene (PVME / PS) blends, measured by a Novocontrol Broadband Dielectric Spectrometer in the frequency range of 10^{-2}~10^{6} Hz. We show that it is possible to model the segmental peak of PVME's dielectric relaxation spectrum by considering concentration fluctuations at the scale of the Kuhn length (the shortest Rouse mode), which we take to be both composition and temperature independent.

Symposium MR
Microrheology, Microfluidics and Confined Systems

Organizers: Eric Furst and Jai Pathak

Tuesday 1:30 Canyon B MR19

Linear-to-nonlinear microrheology transitions: extensions of the Ferry shear wave method

M. Gregory Forest[1], David B. Hill[2], Brandon Lindley[3], Sorin M. Mitran[3], Richard Superfine[4], Lingxing Yao[3], and Jeremy Cribb[4]
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A classical method for linear rheological characterization is due to Ferry and Sawyer: a shear wave is propagated through a strain-birefringent bulk sample from an oscillating plate. Snapshots of the propagating shear wave yield storage and loss moduli at each frequency from the wavelength and attenuation length. As part of the Virtual Lung Project at UNC, we rheologically characterize human airway surface liquids and other low-volume biological materials, and we seek to understand nonlinear thresholds. So motivated, we have designed a device to probe microliters with control over imposed bulk strains. While providing a broadly applicable characterization of viscoelasticity, our geometry also mimics the boundary conditions and strain rates of cilia-mediated mucus clearance. Snapshots are replaced by microbead tracking which yields height-dependent signals of the propagating wave. We model the one-dimensional propagating shear wave velocity and stresses, extending Ferry's analysis to finite depth and nonlinearity, and building numerical solvers in the strongly nonlinear regime. Direct and inverse characterization tools are combined with bead tracking on benchmark viscoelastic materials to validate the experimental and modeling protocols.

Tuesday 1:55 Canyon B MR20

Linking probe dynamics and transport to intracellular rheology

Siva A. Vanapalli, Yixuan Li, Michel H. Duits, and Frieder Mugele
Physics of Complex Fluids, University of Twente, Enschede, The Netherlands

Mechanical properties of living cells contribute to many important cellular functions such as shape, motility, division and intracellular transport. Such integrative mechanical behavior is thought to be due to the coupling of the dense interconnected maps of proteins (actin, intermediate filaments, and microtubules) to ATP-driven motor activity in the cytoskeleton. However, the underlying mechanism is yet to be completely unraveled. In this work we use particle-tracking microrheology to probe the mechanical properties of the cytoskeleton. A variety of intracellular probes (endogenous granules, endocytosed and ballistically injected particles) were used and their dynamics was visualized using confocal microscopy. Our particle tracking analysis reveals that the probe type influences both the collective and single-particle dynamics. Moreover our single-particle dynamics shows that these probes exhibit sub-diffusive, diffusive and super diffusive behavior, reflecting the complex dynamics of the cytoskeleton. A hierarchical approach to extract the local mechanical properties from such heterogeneous probe dynamics will also be discussed.

Tuesday 2:20 Canyon B MR21

Time-cure superposition for self-assembled oligopeptide hydrogels using microrheology

Travis H. Larsen and Eric M. Furst

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

We characterize the viscoelastic properties of self-assembling oligopeptide hydrogels using multiple particle tracking microrheology. From the particle tracking experiments, the mean-squared displacements of embedded probe particles are calculated. The mean-squared displacement shows increasingly subdiffusive dynamics of probes as the material gels. Time-cure superposition is performed to rescale the mean-squared displacement data onto a single master curve. The horizontal shift factor accounts for divergence of the longest relaxation time of the hydrogel as the gel point is approached, and the vertical shift factor characterizes the decrease in compliance as the gel network forms and becomes more elastic. By analyzing the shift factors based on scaling relationships near the liquid-solid transition, we are able to accurately determine both the gel time and scaling exponents for the incipient gel. The gel point provides a key reference from which to define the kinetics of gelation, while the critical exponents provide insight into the gel connectivity. The gel point is verified using dynamic light scattering to monitor the onset of non-ergodicity, and the critical exponents are compared to theoretically predicted values and those obtained in the literature for similar systems.

Tuesday 2:45 Canyon B MR22

Microrheological investigation of acrylate photopolymerization kinetics

Ryan P. Slopek and Victor Breedveld

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Free-radical photopolymerization plays an important role in a range of industries, including the automotive, electronic, medical, optical, and coating industries. In spite of its wide-spread application, photopolymerization models are surprisingly poor at predicting the evolution of mechanical properties. A key limitation is the lack of experimental data with sufficiently high spatial resolution to validate and parameterize such models.

In this study, photopolymerization of model acrylate resins was investigated by monitoring the changes in mechanical properties of illuminated samples via particle tracking microrheology. The technique enabled us to dissect the kinetics of the process via carefully designed experiments with spatially and temporally modulated illumination profiles.

By using lithographic masks to generate well-defined UV illumination patterns with characteristic dimensions of tens of micrometers, it could be shown unambiguously that the diffusion of oxygen, an inhibitor, plays a critical role in the polymerization reaction. The experiments are in excellent agreement with a simple two-step model of oxygen consumption followed by polymerization.

The use of high-speed electronic shutters in the UV light path enabled us to control the illumination time of the samples with high precision. Microrheological analysis could be used to reconstruct three-dimensional profiles of partially polymerized samples. Traditional photorheometry is not capable of resolving the evolution of sample rheology with such spatial resolution. In addition, experiments with pulsed illumination were used to quantify the role of dark reactions due to residual free radicals after termination of UV illumination.

These advanced microrheology experiments provided unique information that is unattainable with other characterization methods typically used to study photopolymerization (FTIR, DSC) and this knowledge can be used to develop a more quantitative understanding of the process.

Tuesday 3:35 Canyon B MR23

Microfluidic interfacial tensiometry

Jai A. Pathak[1], Steven D. Hudson[2], and Samuel P. Forry[3]

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A microfluidic instrument to measure liquid-liquid interfacial tension during flow has been developed and tested. The measurement principle rests on the deformation and retraction dynamics of drops (in the small deformation limit) under extensional flow. Fluid flow is tracked by drop motion and matches creeping flow predictions. Surfactant dynamics were also modeled to explore the validity of the small deformation limit. Experimental conditions (such as residence time, flow rate, and geometrical factors) were adjusted to probe the dynamic response of mixtures containing surfactant.

Tuesday 4:00 Canyon B MR24

Dynamics of microfluidic droplet breakup of viscoelastic polyelectrolyte solutions

Gordon Christopher and Shelley Anna

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As lab-on-a-chip devices using droplets as self-contained reactors become widely used, it is necessary to consider the role that the droplet contents play on dropletformation. In addition, useful emulsion-based products often contain polymers to modify emulsion rheology. We report a systematic study of the role of long-chain polyelectrolytes on the breakup dynamics of low-viscosity droplets at microfluidic T-junctions.

The present study considers model elastic liquids formulated from dilute solutions of sodium poly(styrene sulfonate) (NaPSS) dissolved in glycerol-water mixtures with no added salt. The solvent mixture is designed to yield a constant shear viscosity over a wide range of shear rates.

Four NaPSS molecular weights are used, ranging from $2x10^5$ to $5x10^6$ g/mol. Small amplitude oscillatory shear rheology has been performed to obtain the spectrum of relaxation times for each liquid. Capillary breakup rheometry has been performed to characterize elongational flow properties. We have compared these results with existing scaling models for polyelectrolyte solution dynamics as a function of molecular weight. Finally, static and dynamic surface tension have been measured to obtain an indicator of the surface activity of the polyelectrolytes.

We visualize the droplet breakup behavior of the polyelectrolyte solutions at microfluidic T-junctions as a function of capillary number. Compared with the breakup of corresponding Newtonian liquids, we observe similar primary droplet sizes, with stable liquid filaments persisting between the primary droplets, as others have recently reported. We compare the resulting primary droplet size with a model we have developed for Newtonian liquids that encompasses a wide range of conditions from unconfined droplets that break due to shear stresses, to large plugs that break due to upstream confining pressures. We examine the kinematics of the stretching thread as a function of capillary number and polyelectrolyte molecular weight.

Symposium SM
Entangled Solutions and Melts

Organizers: Jay Schieber and James Oberhauser

Tuesday 4:25 Canyon B SM1

Using cone-partitioned plate to achieve steady state measurements in both controlled stress and controlled speed shear of entangled polymer solutions

Sham S. Ravindranath and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

We have made an important improvement in rheometric measurements of nonlinear flow behavior of entangled polymers by constructing a cone-partitioned plate shear cell. Previously, startup shear measurements with cone-plate usually need to be "prematurely" terminated to avoid any buildup of sample loss due to edge fracture. As a result, it has not been obvious whether steady state is achieved in such a continuous shear test. The same difficulty associated with edge fracture has cast doubt on our previous controlled-torque measurements that claimed to have observed an entanglement-disentanglement transition (EDT) [Macromolecules 37, 9083 (2004)]. The characteristic of EDT is a remarkable rise over time in the apparent shear rate (Ω/δ) at a fixed applied torque, where Ω and δ are the angular velocity of the moving cone and cone angle respectively. Our new measurements appear to reveal the same features as reported in 2004 of an impressive increase of (Ω/δ) at a fixed torque without the complication due to edge instability. Moreover, the new setup allows us to conclude that our previous controlled-speed measurements reported in 2004 were not steady state results of continuous shear. Finally, our particle tracking velocimetric observations apparently reveal inhomogeneous shear flow even in the controlled-torque mode. In other words, the entangled solutions were found to experience inhomogeneous shear in the stress plateau region irrespective of the applied mode of shear.

Tuesday 4:50 Canyon B SM2

Differences between annealing and geometrical methods used to generate primitive path networks

Sachin Shanbhag[1] and Martin Kroger[2]
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We critically compare the original "annealing" and newer geometrical approaches to obtain primitive path networks of monodisperse, linear polymer melts. A systematic discrepancy of about 15% is observed in the mean primitive path length obtained by these methods. This deviation is attributed to disentanglement that occurs during annealing. To discriminate the relative contribution of the two possible disentanglement mechanisms (slip and constraint release by end-looping) we considered a system of knotted ring polymers in which end-looping is prohibited. We found that about half the discrepancy persists and may be attributed to slip alone. The asymptotic limit in which the discrepancy between the two methods vanishes is identified.

Symposium PS
Polymer Solutions

Organizers: Ralph Colby and Ravi P. Jagadeeshan

Tuesday 1:30 Canyon A PS19

Investigating the dispersion of nanoparticles in a polymer solution

Deepika R. Gollamandala and Ileana C. Carpen
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Composite materials are becoming increasingly important in a number of industries, due to their various advantageous properties, a factor that has led to growing interest in the development of new compounds. The combination of nanoparticles and polymers is amongst the most promising of these new materials, but also introduces unique production issues. One of the most troubling of these is the issue of dispersion. Nanoparticles tend to aggregate, and designing a well-mixed system of nanoparticles and polymers is difficult. Experimentally, the level of dispersion is difficult to determine and therefore difficult to alter, but this problem can be avoided by studying the material in silico. By using computer simulations to study systems of nanoparticles and polymers (of varying chain length), we are able to investigate the factors affecting the dispersion of nanoparticles in the monomer/polymer matrix. In particular, we examine the effects of nanoparticle-polymer interactions and volume fractions upon degree of dispersion and agglomeration.

Tuesday 1:55 Canyon A PS20

Nano-rod suspension flows: a 2D Smoluchowski-Navier-Stokes solver

Ruhai Zhou[1], M. Gregory Forest[2], and Qi Wang[3]
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We present a numerical algorithm for nano-rod suspension flows, and provide benchmark simulations of a plane Couette cell experiment. The system consists of a Smoluchowski equation for the orientational distribution function of the nano-rods together with the Navier-Stokes equation for the solvent with an orientation-dependent stress. The rigid rods interact through nonlocal excluded-volume and distortional elasticity potentials and hydrody- namic interactions. The algorithm resolves full orientational configuration space (a spherical harmonic Galerkin expansion), two dimensional physical space (method of lines discretization), and time (spectral deferred corrections), and employs a velocity-pressure formulation of the Navier-Stokes equation.

Tuesday 2:20 Canyon A PS21

Dimensional percolation & induced electrical conductivity of sheared nano-rod dispersions in a weakly conducting matrix

Xiaoyu Zheng[1], M. Gregory Forest[2], Ruhai Zhou[3], Richard Vaia[4], and Michael Arlen[4]
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It is well known that effective percolation among highly conducting particles in a poorly conducting matrix will dominate electrical conductivity of the composite. We focus here on nano-rod composites, where geometry, volume fraction, and shear rate are "processing controls" for films or molds. Traditional homogenization theory resolves volume-averaged properties, but must be extended to capture the sharp transitions associated with percolation thresholds of the particle phase. If the rod orientational distribution is isotropic, then universal scaling laws from percolation theory offer threshold criteria. We focus in this talk on non-equilibrium, shear-induced orientational distributions of nano-rod dispersions. We first present dimensional percolation phase diagrams, in which the percolating paths are either 3d, 2d, or 1d. Next, anisotropic conductivity is calculated numerically based on the geometry of the rod network and conductivity of each phase.

Symposium BS
Biological and Self-assembled Systems

Organizers: Bob Prud’homme and Pat Doyle

Tuesday 3:35 Canyon A BS1

Water-based interpenetrating networks with tunable properties

Soumitra Choudhary and Surita R. Bhatia
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Tunable biocompatible materials were developed for possible applications in tissue engineering and drug delivery. Our goal is to design materials having mechanical properties similar to human tissues without using harsh processing conditions. Water-based semi-IPNs (Interpenetrating Polymer Networks) were prepared by mixing two biopolymers, alginate and hydrophobically modified ethylhydroxy ethyl cellulose (HM-EHEC), followed by crosslinking the alginate by in-situ release of calcium ions. It is known that HM-EHEC form physical gels by hydrophobic interactions, and the strength of these gels depend on the length of the hydrophobic moiety attached to the polymeric backbone, whereas alginate forms gels through ionic crosslinking. Thus by altering two different parameters, hydrophobic chain length and calcium crosslinker concentration, we were able to fine tune the rheological properties of the semi-IPNs. Rheological studies in the linear viscoelastic region indicate storage moduli comparable to soft tissue for hydrogels having 90 wt% water. To elucidate structure-property relationships for these materials, small angle scattering was performed to gain insight into the nano and micro scale structure.

Tuesday 4:00 Canyon A BS2

Self-assembly of hydrophobically-modified hyaluronic acid into physical gels

Madhuvanthi A. Kandadai[1], Jules J. Magda[1], Grant D. Smith[2], Dmitry Bedrov[2], Jimmy Mays[3], and George Sakellariou[4]

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Hyaluronic acid (HA) is a high molecular weight anionic glycosaminoglycan found in the synovial fluid. It has a large hydrated volume and forms an entangled interfibrillar molecular network with viscoelastic properties that help to cushion and lubricate articular joints such as the knee. The molecular weight of HA in synovial fluid decreases significantly in osteoarthritis (OA). The consequent loss in viscoelasticity results in poor mechanical protection of the joint surfaces and increased nociceptor nerve firing (a measure of pain). In order to restore viscoelasticity, intra-articular injections of high molecular weight HA are currently administered during the early stages of OA. However, the lifetime in the body of these "viscosupplements" is very short (< 5 days). Furthermore, relatively high weight concentrations of HA must be injected in order to obtain physically entangled HA networks with desirable viscoelastic properties. Therefore, to develop a better synovial fluid viscosupplement, we propose to modify HA with polypeptide side chains containing hydrophobic self-assembling residues. The comb-branched HA derivatives obtained should behave as associative thickeners as a result of hydrophobic attractions between peptide branches on neighboring HA chains. Rheological results will be presented for time dependent network formation by the novel comb-branched HA derivatives, and for network re-formation after shear flows at very high shear rates (such as during injection). Values will also be presented for the osmotic pressure of the networks, and their resistance to enzymatic degradation by hyaluronidases.

Tuesday 4:25 Canyon A BS3

Cooperative networks: viscoelastic control in solutions of wormlike micelles and polymers

Matthew W. Liberatore and Nathan Work

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

Mixtures of polymers and surfactants in solution are important in a wide range of applications including detergents, personal care products and oil recovery fluids impacting the chemical, pharmaceutical and petroleum industries. The objective of this project is creating synergy between the polymers and wormlike micelles allowing the properties of the solution, especially the rheology, to be tuned. Maintaining the wormlike micelle state of surfactant aggregation in the presence of an entangled polymer network is a viable challenge. Experimental protocols for studying the polymer-micelle mixtures include flow and oscillatory rheology, rheo-optics, scattering using light and neutrons, and phase mapping. Using theoretical models from surfactant and polymer science, this experimental characterization allows tremendous insight into important length scales (from the nanoscale to macroscopic) and time scales of the co-entangled network. Exploitation of solution conditions to increase the overall length of the wormlike micelles creates either entangled or branched networks, which changes the viscosity of the solution. Preliminary studies have identified solution conditions that change the rheology from weakly shear thinning to strongly shear thinning to shear thickening. Overall, experimental control of pressure, temperature, macromolecule concentration and other variables allows structure-property relations of wormlike micelle-polymer cooperative networks to be measured. Thus, an enhanced understanding of surfactant-polymer interactions allows for the creation of new products for a wide range of industries.

Tuesday 4:50 Canyon A BS4

The effect of branching on the shear and extensional rheology of wormlike micelle solutions

Manojkumar Chellamuthu and Jonathan P. Rothstein

Department of Mechanical & Industrial Engineering, University of Massachusetts, Amherst, MA 01003, United States

Wormlike micelles are used in variety of applications including many household and cosmetic products as well as rheological modifiers. The morphology of the micelles can have a large impact on both the shear and extensional rheology of the fluid. In this talk, we present the results of our extensional rheology measurements for a series of linear and branched sodium oleate (NaOA) and octyl trimethyl ammonium bromide (C_8TAB) worm-like micelle solutions using capillary breakup extensional rheometer (CaBER)and filament stretching extensional rheometer (FiSER). The goal of this study was to understand, how branching affects the extensional rheology of wormlike micelles and to determine whether extensional rheology could be used as a tool for distinguishing between branched and linear micelles. The ratio of NaOA to C_8TAB was fixed at 70/30 and the total surfactant concentrations were varied. Cryo-TEM images have shown that in these systems branching begins to occur for concentrations greater than about 3wt%. Both CaBER and FiSER measurements of the extensional viscosity were found to decrease with increasing concentration and correspondingly the number of branch points. All filament stretching experiments were observed to end with a rupture of the fluid filament before the fluid reaches a steady-state value of the extensional viscosity although steady-state extensional viscosities were obtainable in capillary break up. When coupled with the non-monotonic growth of the shear viscosity which shows a maximum at 4wt% and the monotonic increase of the elastic modulus with increasing concentration, these observations demonstrate how sensitive the extensional rheology is to branching in micelles. We will propose a number of possible mechanisms to explain these observations.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Grand Ballroom C PL3

Novel ink designs for direct writing in three dimensions

Jennifer A. Lewis
Dept. of Materials Science and Engineering, University of Illinois, Urbana, IL, United States

The ability to pattern functional materials in planar and three-dimensional forms is of critical importance for several technological applications, including photonics, sensors, microfluidics, and tissue engineering scaffolds. Direct ink writing enables one to rapidly design and fabricate materials in arbitrary shapes without the need for expensive tooling, dies, or lithographic masks. Recent advances in the design of concentrated inks composed of colloidal, polyelectrolyte, and organometallic building blocks with tailored rheological properties will be highlighted with an emphasis on patterning 3D structures at the microscale.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Wednesday 9:45 Alpine East SC27

Rheological studies of fluorocarbon-based microemulsion gels with triblock copolymers

Xiaoming Pan and Surita R. Bhatia
Chemical Engineering, University of Massachusetts, Amherst, MA 01003, United States

Fluorocarbon has many unusual properties, such as stability, high gas solubility, high fluidity, etc. Most of them are stable and inert chemically and biologically, making them compatible broadly in biomedical and industrial application, like blood substitutes and blood oxygenation. Perfluorooctylbromide(PFOB) can enhance the tumor echogenicity so it has been popularly used as a contrast material for CT, MRI and ultrasound imaging, especially for hepatosplenography and tumor-imaging. PFOB emulsions were also used for oxygen carriers in cell culture like bio-artificial liver support system. Upon the requirements of bioengineering and biomedical research, the control over structure and rheology properties of the PFOB products is fundamentally important. In this work stable elastic perfluorocarbon-based microemulsion gels were formed by mixing PFOB, water, fluorinated surfactant Zonyl FSO-100, and triblock copolymer Pluronic F127. The gels were investigated in terms of phase stability, rheology, and structure. The behaviors in phase stability investigation were in agreement with rheological properties. Thermosensitivity and thermoreversibility were found in these systems. Most of the formed gels can switch from transparent to cloudy back and forth within a certain range of temperature. The rheological properties of gels can be tuned by composition and temperature. SAXS and confocal microcopy observations suggest a hexagonally close-packed structure with microemulsion droplets which are linked together by Pluronic F127 chains.

Wednesday 10:10 Alpine East SC28

Rheological properties of stable responsive block copolymer micelles

Evelyne van Ruymbeke[1], Andreas Pamvouksoglou[1], Dimitris Vlassopoulos[1], George Petekidis[1], Grigoris Mountrichas[2], and Stergios Pispas[2]
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We prepared block copolymer micelles with crosslinked cores and varying core-to-shell ratio. These stable systems represent model soft colloids where the core can deform and shrink under the influence of external stimuli (such as osmotic forces). We focused on the concentration and temperature dependence of the rheological properties of polystyrene-polybutadiene micelles with covalently cross-linked polybutadiene core, suspended in an intermediate solvent (dibutyl -phthalate). A tunable non-monotonic behaviour of the relative zero-shear viscosity as a function of temperature was found. In particular, an initial viscosity increase with temperature was attributed to the swelling of the core and thus, to an increase of inter-particles interactions. For concentrations above the overlapping limit, we observed a solid-to-liquid transition followed by a liquid-to-solid transition by further increasing the temperature. Then, for still higher concentrations, the system vitrified. For such a system, both the mass concentration and the temperature increase yielded a larger effective volume fraction and thus induced a kinetic arrest. On the other hand, master-curves of the relative zero-shear viscosity versus the effective volume fraction could not be obtained, pointing to the quantitative different effect of mass concentration and temperature on the system's response.

Wednesday 10:35 Alpine East SC29

Self induced microstruture in sheared suspensions of anisotropic dicolloids

Amit Kumar and Jonathan L. Higdon

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Large scale simulations are presented for concentrated suspensions of anisotropic dicolloids. The particles under study consist of composite particles formed from two intersecting spheres of arbitrary radii and center-center spacing. Recent experimental efforts have reported synthesis techniques for such anisotropic dicolloids with sizes ranging from 250 nanometers to several microns. Experiments have suggested a range of interesting phase behavior with order-disorder-order transitions as a function of Pe and volume fraction. In the present study, we use high precision Stokesian dynamic simulations and reduced precision near field lubrication models to study the dynamics of sheared suspensions of these anisotropic particles as a function of volume fraction, interparticle forces and Peclet number. We capture the order-disorder-order transitions reported in experiments and investigate more subtle changes in suspension microstructure in sheared systems at large Pe. In particular, we describe the formation of systems with a high degree of positional order and varying degrees of orientational ordering. We show how the degree of particle anisotropy affects the degree and alignment of orientational order relative to the shear, gradient and vorticity axes. The affect of external fields on the orientational ordering and its effect on order-disorder transiitons for positional ordering is discussed. The ability to induce subtle changes in positional and orientational ordering through external tuning provides an interesting mechanism which may be exploited for novel applications of anisotropic dicolloids.

Wednesday 11:00 Alpine East SC30

Experimental determination of the relationship between fiber orientation distribution and stress growth in start-up of flow for non-Newtonian fluids containing short glass fibers

Aaron P. Eberle[1], Donald G. Baird[1], and Peter Wapperom[2]

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In this paper we investigate the nonlinear viscoelastic behavior in simple shear flow of polymeric fluids containing short glass fibers. These composite melts are notorious for exhibiting a relatively large overshoot in both the shear stress and first normal stress growth functions when compared to the rheology of the neat suspending medium. Interestingly this behavior is not reversible. The overshoot does not reappear after the sample has reached steady state and the flow is removed or interrupted. Even after a long rest time between flows. Mechanisms have been proposed that account for such behavior but no thorough analysis to confirm the relationship between fiber orientation and the transient stresses that occur in start-up of flow has been reported. Understanding this relationship is imperative to the development of a constitutive equation that can not only predict the rheology of glass fiber filled non-Newtonian fluids but the corresponding fiber orientation. Our interest lies in determining this relationship between the overshoot in the stress growth functions and the evolution of the fibers' orientation distribution within the sample. For this study we use a short glass fiber (30 wt%, L/D = 16) filled polybutylene terephethalate. Stress growth experiments in start-up of flow are performed on a Rheometrics Mechanical Spectrometer (RMS-800) using cone and plate geometry. Samples initially at rest and in equilibrium are deformed at a constant rate for a specific time (i.e. strain) that correlates to various points on a stress growth vs. time plot and then the flow is stopped. The sample temperature is then lowered below the melt temperature of the suspension to "freeze" the fibers' orientation. The fiber orientation distribution within the sample is then determined using X-ray tomography and/or by using a reflection microscopy technique termed the "Leeds method" at Oak Ridge National Labs. The fiber orientation distribution within samples subject to various flow histories is then compared.

Wednesday 11:25 Alpine East SC31

Effect of aggregate structure and length of carbon nanotubes on the rheological properties of nanotube/epoxy suspension

Sameer S. Rahatekar[1], Krzysztof K. Koziol[2], Alan H. Windle[2], Rahul Jain[3], Satish Kumar[3], Erik K. Hobbie[1], and Jeffrey W. Gilman[1]

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The addition of carbon nanotubes to polymer matrices has yielded significant improvement in thermal and electrical properties. The state of dispersion of carbon nanotubes significantly influences the electrical and rheological properties of polymer/nanotube composites. It is critical to understand the effect of shear flow on the state of dispersion of nanotubes, which in turn determines the electrical properties of the dispersion. Current work describes rheological measurements and associated optical microstructure observations of multiwall carbon nanotubes (MWCNTs) suspended in an epoxy resin matrix. Above a critical concentration of nanotubes, we observe a progressive increase in the zero shear viscosity with increasing nanotube concentration, which we correlate with an increase in nanotube aggregate interaction. With increasing shear rate, shear thinning behavior was observed due to the yielding and ultimate de-aggregation of a nanotube network. We also studied the effect of nanotube length on the scaling behavior of the viscosity and elastic shear modulus of the epoxy nanotube suspension.

Symposium BE
Blends, Emulsions and Multiphase Fluids

Organizers: Matt Liberatore and Sachin Velankar

Wednesday 9:45 Alpine West BE4

Rheological characterization of blends of linear and long-chain branched polypropylene

Pierre J. Carreau and Seyed H. Tabatabaei
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Blends of a long-chain branched polypropylene (LCB-PP) and a linear polypropylene (L-PP) were prepared using a twin screw extruder. Linear viscoelastic properties such as complex viscosity, storage modulus, weighted relaxation spectrum, and compliance were determined as functions of LCB-PP content. Good agreement for the logarithmic mixing rule of the complex viscosity was observed for all samples suggesting miscibility of both PP components and confirming differential scanning calorimetry (DSC) results. The Cox-Merz relation was verified for the unblended components as well as for the blends, using shear data obtained from commercial rheometers and from a novel slit die rheometer, installed on an injection molding machine. Uniaxial elongational data were obtained using a SER unit mounted on an ARES rheometer. A significant strain hardening was observed for the neat LCB-PP as well for all the blends, but the strain hardening decreased with increasing strain rate.

Wednesday 10:10 Alpine West BE5

Mechanical hole burning spectroscopy in an SIS tri-block copolymer

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We have previously developed a Mechanical Hole Burning Spectroscopy (MSHB) technique that promises to be a powerful tool for the investigation of dynamic heterogeneity of polymeric materials. This is because, unlike its dielectric analogue, MSHB can be used to characterize materials having a weak dielectric response, a particular feature of polymeric materials. However, while both mechanical and dielectric hole burning show behaviors that are consistent with dynamic heterogeneity in the materials, it is still unclear what the relationship between the hole properties, e.g., frequency and amplitude, and the actual nature of the heterogeneity and particularly the length scale being probed. Here, we provide first evidence that a known length scale can be probed by the MSHB method by using a tri-block copolymer as a "calibration" sample. The heterogeneity of a styrene-isoprene-styrene copolymer was investigated in the vicinity of the order-disorder transition temperature (ODT). It was found that the amplitudes of the mechanical holes gradually decrease as the phase boundary is approached from the two-phase region to the one-phase region, i.e., as the order-disorder transition is traversed. In the disordered state of the block copolymer, no apparent mechanical holes were detected. In contrast, mechanical holes were burned in the heterogeneous (ordered) state and the hole amplitude increased as the depth into the ordered phase increased. Hence, the MSHB technique provides a qualitative correlation between the amplitude of the burned holes and the corresponding heterogeneity.

Wednesday 10:35 Alpine West BE6

Rheology and morphology of cocontinuous polymer blends during coarsening and pinch-off

Carlos R. Lopez-Barron, Joel R. Bell, and Chris Macosko
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The microstructure evolution and viscoelastic properties of blends made of fluorescently-labeled polystyrene (FLPS) and polymethylmethacrylate (PMMA) or styrene-acrylonitrile copolymer (SAN) during coarsening and pinch-off processes have being investigated. The highly curved interface present in cocontinuous structures indicates that an excess free energy is stored in the boundary between the two immiscible polymer phases. The coarsening of the morphology is driven by minimizing the interfacial free energy of the system to decrease the interfacial area. We used scanning electron microscopy (SEM) to obtain 2D images and laser scanning Confocal microscopy (LCSM) followed by 3D structural analysis to directly measure the time evolution of interfacial area per unit volume and the interface curvatures These results were related to the evolution of viscoelastic properties during coarsening via the elasticity contribution of the interface between the phases. It is shown that systems of initial off-symmetric and symmetrical compositions show different characteristic viscoelastic properties corresponding to droplet-matrix and cocontinuous morphologies. At certain ranges of off-symmetric composition it is possible to obtain cocontinuous structures with a subsequent transition to disperse morphologies (pinch-off) after sufficient annealing. Diblock copolymers can dramatically slow coarsening. The coarsening rate is used to determine interfacial tension which is found to be strongly influenced by copolymer architecture.

Wednesday 11:00 Alpine West BE7

Preparation and rheology of double emulsion morphologies in compatibilized immiscible polymer blends

Jeffrey D. Martin and Sachin Velankar
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Block copolymers, termed compatibilizers, are often added to immiscible polymer blends to improve blending. It is well known that a compatibilizer improves blending through a combination of a decreased interfacial tension and the ability to suppress droplet coalescence. The aim of this research is to exploit the ability of the compatibilizer to suppress coalescence to create unusual morphologies in immiscible polymer blends. Drop-in-drop morphologies (double emulsions) were created using specific mixing protocols on blends of poly(dimethyl siloxane) (PDMS) and polyisobutylene (PIB) compatibilized by a small amount of a PIB-PDMS diblock copolymer. Previous work has shown that for this system coalescence is suppressed by the compatibilizer only if PIB is the continuous phase.

We used a stress-controlled rheometer to study the steady shear viscosity, creep recovery after cessation of shear, and dynamic oscillatory behavior of the double emulsion blends, along with their simple emulsion counterparts containing the same component volume fractions. Previous results on simple emulsions show that the blend viscosity and recovery increase slightly with small amounts (less than 1%) of compatibilizer. Both of these results are seen here, but additional increases in viscosity and recovery are seen in the double emulsion blends, and are attributed to the higher effective volume fraction of the double emulsion drops. Through the use of an emulsion model, we show that the double emulsion blends may behave rheologically like simple blends with an increased effective volume fraction and a drop phase that has the properties of a blend itself.

Furthermore, we found that under high-stress, rapid mixing, the double emulsion sub-drops were able to "leak" from the outer drops and coalesce with the matrix. We were able to use rheology, along with fluorescence microscopy, to probe the effectiveness of double emulsion formation, i.e. if a double emulsion is formed and if major sub-drop leakage occurred.

Wednesday 11:25 Alpine West BE8

Porod SAXS studies of shear-induced droplet deformation in a concentrated immiscible polymer blend

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Droplet deformation, break-up and coalescence of immiscible polymer blends under flow is fundamental to understanding both the effect of processing on ultimate blend properties, as well as the excess rheological properties associated with deformation of the multiphase structure. Rheo-optical methods have frequently been employed to gain insight into these processes. For sufficiently large droplets direct visualization via optical microscopy may be used; for smaller droplets, small-angle light scattering and conservative dichroism have both been employed. In most cases, optical methods are restricted to quite dilute concentrations, owing to concerns of high turbidity and multiple scattering. Here we explore used of time-resolved synchrotron small-angle x-ray scattering as an alternative method to study multiphase materials under shear. Typical blend droplet sizes of ~ 1 micron are large relative to length scales typically probed by SAXS; however, the wide-angle limit of small-angle scattering (i.e. the Porod regime) is directly sensitive to interfacial structure of multiphase materials and, when rendered anisotropic by shear flow, provides direct insights into the deformation and orientation of interface. We report scattering studies in the flow-gradient plane of a polystyrene/poly(methyl methacrylate) blend, which is approximately viscosity matched, to step-strain deformations. Postulating that each droplet is deformed to a geometrically similar shape, data are analyzed in the context of a model of Porod scattering from ellipsoids.

Symposium SM
Entangled Solutions and Melts

Organizers: Jay Schieber and James Oberhauser

Wednesday 9:45 Canyon B SM3

Constraint release relaxation in entangled polyisoprene systems

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Linear viscoelastic behavior was examined for a series of binary blends of linear polyisoprenes (PI). The blends contained high molecular weight (M) component chains (probe) that were dilute and entangled only with the lower-M matrix chains. The probe exhibited the Rouse-like constraint release (CR) relaxation in the matrix chains much shorter than the probe, but this CR-dominance vanished on a moderate increase of the matrix molecular weight because of the competition with other mechanisms such as reptation. These features are qualitatively similar to, but quantitatively different from, those observed for binary blends of linear polystyrenes (PS): For the probe having a given entanglement number (= M(probe)/Me), the CR-dominance was observed in a matrix of larger M(matrix)/Me in the PI/PI blends than in the PS/PS blends. This difference suggests that the entanglement dynamics is not uniquely determined by the entanglement number and the local friction coefficient but is affected by additional molecular factors such as the local CR gate number. Furthermore, comparison of the behavior of monodisperse linear and star PI chains suggested that the CR mechanism is more important for the star chains than for the linear chains.

Wednesday 10:10 Canyon B SM4

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

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In this work, we show how to modify our single-chain slip-link model to incorporate constraint release in a fully self-consistent, fully fluctuating way. We include fluctuations in entanglement number, primitive path length, and monomer density along the chain. Entanglements in the middle of the primitive path are created and destroyed in a manner consistent with the algorithm of Doi and Takimoto to both linear and branched chains without coupling different chains in the ensemble. Rouse dynamics are avoided. Moreover, the resulting algorithm is easily generalized to allow for multichain entanglements, instead of only binary interactions. Comparison with bidisperse linear blend data show much improvement over the typical assumption of Rouse dynamics for the primitive path. The formulation is also applicable to branched chains.

Wednesday 10:35 Canyon B SM5

Thermodynamically guided Nonequilibrium Monte Carlo methodology for generating realistic shear flows of polymer melts

Chunggi Baig[1] and Vlasis G. Mavrantzas[2]

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We present the first successful implementation of a non-dynamic method for the simulation of the steady-state dynamic properties of a polymer system beyond equilibrium. The new method, GENERIC (General Equation for the Nonequilibrium Reversible-Irreversible Coupling) Monte Carlo (MC) [1-3], proposes MC simulations in a generalized ensemble using properly defined fields which excite structure in a polymer melt in the same way as the imposed flow field in a dynamic (e.g., non-equilibrium molecular dynamics, NEMD) method. In its present stage, the fields (conjugate variables to properly chosen state variables, like the conformation tensor) are calculated iteratively until convergence with the results of the brute-force NEMD method [4] for the given system is achieved. At convergence, the values of these fields have been defined in terms of the real, physical field (i.e., shear rate). The present work demonstrates the applicability of GENERIC MC to practical flowing systems of polymeric liquids and justifies the basic principles underlying GENERIC. It also provides us with invaluable information for the 'true' free energy function of the nonequilibrium system. But more importantly, the new method (built around a set of very drastic moves for equilibrating polymer melts at all length scales) has the great potential for investigating the viscoelasticity of entangled polymeric liquids. For example, when properly incorporated within coarse-grained modeling schemes [5-6], it could make it possible to efficiently study the true reptation regime of long-chain polymer melts.

1. Öttinger, H.C. "Beyond equilibrium thermodynamics" (John Wiley&Sons, New Jersey, 2005) 2. Mavrantzas, V.G.; Theodorou, D.N., Macromolecules 1998, 31, 6310; Mavrantzas, V.G.; Öttinger, H.C., Macromolecules 2002, 35, 960. 3. Baig, C.; Mavrantzas, V.G., in preparation. 4. Baig, C. et al., J. Chem. Phys. 2005, 122, 114103. 5. Kröger, M., Comp. Phys. Comm. 2005, 168, 209. 6. Tzoumanekas C.; Theodorou, D.N., Macromolecules 2006, 39, 4592.

Wednesday 11:00 Canyon B SM6

Different theoretical considerations of nonlinear flow behavior of entangled polymers

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We address the subject of theoretical and experimental foundations of polymer rheology by asking whether well entangled polymers are able to flow smoothly (e.g., homogeneously) without first suffering yield that leads to inhomogeneous flow. Recent experimental observations [Phys. Rev. Lett. 96, 016001 (2006); ibid. 96, 196001 (2006)] based on a combination of conventional rheometry and particle-tracking velocimetry indicated lack of homogeneous flow profiles in startup and large-amplitude oscillatory shear in common apparatuses such as cone-plate and parallel-plate shear cells. After a large uniform step strain, an entangled solution or melt was observed [Phys. Rev. Lett. 97, 187801 (2006)] to undergo macroscopic movement, making it invalid to evaluate such material functions as relaxation modulus or damping function. These observations not only make rheometric measurements challenging but also create problems for determining constitutive relationships in the traditional way. On the other hand, these results urge us to answer the first-order questions of why a well entangled polymer would undergo yielding. Treating these systems as an entanglement network, we refocus our attention on the onset condition for yield in both startup continuous shear/extension and interrupted shear/extension (i.e., step shear/extension). The scaling behavior associated with the yield point, e.g., the point of stress overshoot in either shear or extension, can be understood in terms of force imbalance between the chain retraction force and the inter-chain interactions that caused a given strand between entanglement points to stretch in the first place. It is the residual chain retraction force that produces non-quiescent relaxation after step shear and necking after step extension.

Wednesday 11:25 Canyon B SM7

Simultaneous acquisition of rheological data and microscopic images on molten polymers

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Rheological measurements give information on the macroscopic properties of a material. Usually, for a more comprehensive understanding of a material, additional measuring techniques are required. One important parameter is the microstructure of the material, which can be supplied by complementing techniques like GPC, thermal analysis, (FT)IR, scattering techniques (light, XR, neutron,), microscopy (optical, electronic), etc. Unfortunately these physical methods are performed independently of shearing the material and therefore do not give a direct link between the rheological behaviour and the microstructure organisation.

In this presentation we will discuss the integration of an optical microscope unit (RheoScope module) in a universal rheometer (HAAKE MARS) and the measurement results obtained on molten polymers at temperatures up to 300 °C. With the rheometer and the microscope integrated in one instrument a direct correlation between the rheological measurement and the microscopic images is possible.

The microscope unit is equipped with an electrical upper and lower heating and cooling system for a temperature range of -5 °C to 300 °C, a digital video camera, an integrated polarization filter, and exchangeable lenses (from 5x to 50x). All the functions of the camera and of the microscope are completely controlled by the rheometer software, the rheological data and microscopic images are stored simultaneously. Therefore each rheological data-point is linked to the correspondent microscopic image of the sample.

We will present measurement results of the melting process of POM pellets in a polyethylene matrix as well as the melting of a polyamide - glass fibre mixture with different glass fibre concentrations. Other examples include the mixing of masterbatch pellets with polyethylene at a constant temperature. The combination of the rheological data with the corresponding images of the sample under deformation give new and interesting insights in the material properties.

Symposium BS
Biological and Self-assembled Systems

Organizers: Bob Prud’homme and Pat Doyle

Wednesday 9:45 Canyon A BS5

Microstructural dynamics of salt-responsive block copolypeptide hydrogels

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The microstructural response of self-assembled block copolypeptide (BCP) hydrogels to controlled changes in solvent composition was characterized via particle tracking microrheology and confocal microscopy. Experiments in our homebuilt microdialysis cell provided quantitative insight in the evolution of microscopic heterogeneity and changes in local mechanical properties of gel samples due to the addition and subsequent removal of salt.

One of the key findings of this work is that diffusive exchange of ionic species leads to a distinctively different microscopic structure than convective mixing, which is typically used during sample preparation for macroscopic rheological characterization. Since diffusion is the dominant mass transport mechanism in many biological applications, microrheological measurements in the dialysis cell provide unique insight in the performance of these materials under physiologically relevant conditions. The experiments can be used to optimize hydrogel performance for applications such as tissue engineering and drug delivery.

The microstructural dynamics of the BCP hydrogels was characterized as a function of BCP concentration, ionic strength, tracer particle size and molecular architecture. In this presentation, special attention will be paid to the reversibility of salt-induced microrheological changes.

Wednesday 10:10 Canyon A BS6

Phase behavior and microstructure for colloidal systems with attractive/repulsive interparticle potentials

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Large scale dynamic simulations with hydrodynamic interactions are presented to study the phase behavior and microstructure of concentrated colloidal suspensions with varying strengths of short range attractive potentials. We document the transitions from fluid like states to crystals to gels and investigate the effects of adding varying strengths of long range repulsive potentials on the phase behavior and microstructure. Dynamic simulations confirm equilibrium predictions on the disappearance of crystalline phases with increasing repulsive forces and show significant changes in the microstructure for gel phases. The strength of the repulsive force affects both the strength and connectedness of the gel (as manifest in number of bonds per particle) as well as characteristic length scales and morphology of the gel microstructure. Comparison is made with experimental results from confocal microscopy and scattering experiments. Simulation results include direct visualizations of suspension microstructure, structure factors and statistical measures of gel morphology.

Wednesday 10:35 Canyon A BS7

Correlation of chitosan’s rheological properties to its ability to electrospin

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Chitosan has been investigated extensively for use in biomedical applications ranging from drug delivery to scaffolds for tissue engineering. Therefore, forming nanofibers of this linear polysaccharide is desirable. Electrostatic spinning (electrospinning) is a convenient method to produce nonwoven mats of nanofibers. The ability of the solutions to successfully electospin is closely correlated with the rheological properties of the solutions. Chitosan is challenging to electrospin due to its relatively high viscosity at modest concentrations. Moreover, its viscosity is strongly concentration dependent at short times ($\eta \sim c^{6.0}$, corresponding to an associating polymer), while its behavior is more typical ($\eta \sim c^{4.3}$) after storage for *ca*. 30 days. Solutions of chitosan blended with poly(ethylene oxide) (PEO) have been electrospun successfully with freshly prepared solutions. Chitosan/PEO blend solutions show drastic decreases in zero shear rate viscosity over time, which can be attributed to phase separation. The challenges associated with electrospinning charged biopolymers (chitosan is cationic) will be discussed in terms of their rheological properties. Successes and failures will be highlighted and compared results for readily electrospun neutral polymers.

Wednesday 11:00 Canyon A BS8

Associative polymer facilitated electrospinning of nanofibers: role of viscoelasticity

Sachin Talwar[1], Juan Hinestroza[2], Benham Pourdeyhimi[3], and Saad Khan[1]
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Nanofibers produced via electrospinning present a promising route for development of novel materials with well-defined functionalities. Their unique properties stem in part from their intrinsic dimensional characteristics, i.e., typical diameters between 10-500 nm, result in a very high surface to volume ratio, and render them useful for a number of applications such as membrane technology, filtration devices, smart textiles and tissue scaffolds. A recurring issue in this field is the spinning of polymers at lower concentrations in order to achieve smaller fiber diameters. In this study, we examine the role of rheology in modulating nanofiber properties. In particular, we add comb-like associative polymers with pendant hydrophobes to different polyethylene oxide solutions, otherwise not electrospinnable. We find the characteristic of fibers produced through electrospinning to be a strong function of polymer concentration. One can go from producing polymer droplets to beaded-nanofibers to defect-free nanofibers of increasing fiber diameter with increase in concentration. The critical concentration at which the polymer is spun into uniform fibers is limited by the entanglement density of the polymer solution, as given by critical entanglement concentration (Ce). Rheological measurements show that addition of associative polymers to PEO solutions leads to significant changes in viscosity and viscoelasticity and renders its rheology similar to that of a spinnable polymer solution. These rheological changes translate to bead-free and uniform final nanofiber morphology as well as reduced fiber diameter. This concept of using rheology modifiers is further extended to other associative polymers as well as other polymer systems which are not easily electrospinnable. We further elucidate the role of viscoelasticity in fiber formation by altering the characteristic relaxation time of associative polymer systems using surfactants.

Wednesday 11:25 Canyon A BS9

Coupling of cell orientation to alignment of collagen substrates

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Collagen is one of the most important and abundant proteins in the human body and is present in skin, cartilage, and bone. The structure of collagen on a molecular level is that of a thin rod constructed of 3 polypeptide strands twisted together into a triple helix. When collagen is held in highly concentrated acidic solutions the solution exhibits the behavior of a nematic liquid crystal with a high degree of orientation. The focus of this work is to create a biocompatible substrate with the ability to control cell orientation and proliferation through the structure of collagen. These novel substrates are created by precisely depositing a solution of highly concentrated collagen with a robotic arm on a variety of materials. The organization of the collagen can be quantified using AFM and optical techniques to express the degree and uniformity of the orientation. The deposition technique allows the addition of growth factors and fillers with mechanical or structural properties to the collagen while still presenting an oriented surface. The response of fibroblast cells to an oriented collagen matrix has been shown to result in a high degree of orientation with a stretching of the cells in the direction of orientation. The goal is developing a better understanding of the ability of cells to recognize the oriented collagen and determine how this can be used for greater control over the cellular behavior.

Wednesday Afternoon

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Wednesday 1:30 Alpine East SC32

Electrical conductivity enhancement in carbon nanotube-polymer composites

Emilio J. Tozzi[1], Christian Schilling[2], Wolfgang Bauhofer[2], and Daniel J. Klingenberg[1]
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Carbon nanotubes are a promising electrically conductive filler material for polymers. Composite conductivities of technological interest can be achieved at much lower filler concentrations than those obtained with traditional fillers such as carbon black. Models based on randomly oriented, large aspect ratio inclusions fail to predict reported ultra-low conductivity percolation thresholds. Dynamic effects such as the interplay between shearing history and nanotube interactions are believed to play an important role in the development of configurations with enhanced conductivity. We employ particle-level simulations to investigate the time evolution of the microstructure and the electrical conductivity of nanotube suspensions in shear flow. The simulations allow control of numerous properties, including the matrix viscosity, nanotube aspect ratio, shape, flexibility and interaction forces; the effects of these properties on the electrical conductivity of the composite will be described. The advantages and disadvantages of various methods of calculating the electrical conductivity will also be discussed. Simulation results will be compared with experimental results, as well as predictions from analytical models.

Wednesday 1:55 Alpine East SC33

Rheological behavior of polycaprolactone containing rod-like hydroxyapatite nano particles

Shih-Po Sun[1], Montgomery T. Shaw[2], and Mei Wei[2]
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We present the shear rheology of polycaprolactone (PCL) containing rod-like hydroxyapatite (HA) particles. This biodegradable composition is being considered as an ingredient in a bone graft material. Both PCL melt and its solutions were included in the study. The principal factors were HA particle concentration and the nature of the surfactants used to stabilize the suspension. PCL exhibited Newtonian behavior in the 0.01 to 10 1/s shear rate range, and the mixtures of PCL with HA were also surprisingly Newtonian. However, on addition of 1% ammonium neutralized poly (acrylic acid) (Darvan), the response exhibited two Newtonian regions. In addition an unusual response was observed with PCL that had not been presheared; the behavior was different in the dual-direction mode as uni-direction. These results were compared with similar systems and current theories for near-Brownian and Brownian particle suspensions.

Wednesday 2:20 Alpine East SC34

Using hydrodynamics to sort single wall carbon nanotubes by length

Jaehun Chun, Jeffrey A. Fagan, Barry J. Bauer, and Erik K. Hobbie
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We describe and compare three different methods that exploit hydrodynamics to sort colloidal single-wall carbon nanotubes (SWNTs) by length; size-exclusion chromatogtaphy (SEC), field-flow fractionation (FFF), and centrifugal length sorting (CLS). In SEC, initially polydisperse SWNT suspensions are forced through a column of a porous medium, which separates the nanotubes based on their residence time in the pores. In FFF, the perpendicular superposition of a uniform flow and a channel flow generates fractions based on length-dependent differences in their average position in the channel caused by different diffusivities. In CLS, a logarithmic dependence of the particle flux on SWNT length is exploited to achieve nanotube length separation up a column of dense liquid. We contrast the effectiveness and scalability of each technique for producing SWNT length separations.

Wednesday 2:45 Alpine East SC35

Characterizing dispersion of graphite nanocomposites via melt rheology

Hyunwoo Kim and Chris Macosko
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We have modeled the viscoelastic properties of polymer melt filled with nano-platelets using scaling concepts of an elastic colloidal gel above its percolation threshold (Shih et al. Phys Rev A 42, 4772 (1990), Vermant et al. J Rheol 51 429 (2007)). From a model for a percolated network

of platelets, the aspect ratio of the reinforcement can be related to volume fraction at percolation threshold. Linear viscoelastic properties of poly(ethylene-2,6-naphthalate) dispersed with graphite and exfoliated graphite (functionalized graphite sheets, FGS, Schniepp et al. J Phys Chem B 110(17) 8535 (2006)) were investigated. The decrease in critical strain and increase in shear modulus with increasing concentration was more pronounced with the FGS dispersion. The fractal dimension of FGS was evaluated using a fractal aggregate model and compared to the value determined by small angle x-ray scattering. Aspect ratios of both dispersions were also estimated based on a geometric percolation model. Dispersion parameters from rheological measurements agree favorably with those determined using TEM, tensile modulus and permeability measurements.

Wednesday 3:35 Alpine East SC36

Rheology of clay-GCC coating colors

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An experimental investigation was carried out on the rheology of coating suspensions. The impact of key factors, *viz*. shearing condition, solids content, particle-particle interactions, pigment properties (clay and GCC fractions) and binder (latex or starch) was examined. The specific effects of pigment and binder were observed to be different. While the pigment type affected significantly the coating rheology due to modifications in the suspension microstructure, the partial replacement of latex with starch only reduced the yield stress and viscosity of coating colors consisting of ground calcium carbonate by 45% and 25%, respectively. The partial replacement of the binder did not affect the clay-based coating colors. A modified Maron-Pierce correlation was used to characterize the apparent yield stress and obtain the maximum packing fraction of the suspensions at low shear conditions. Finally, a new 3-parameter model was developed. This model was capable of fitting the entire range of shear rates considered in this work, which includes the apparent yield stress region of the structured materials.

Wednesday 4:00 Alpine East SC37

Laponite-PEO dispersions as glassy systems: rheology, dynamics and structure

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We observe aging behavior of neat laponite systems over the course of 1000 or more days. Under basic conditions, low laponite concentrations (1 wt%) slowly evolve from a viscoelastic liquid to a glass made of clusters acting as constituent elements interacting via long range repulsion. Higher concentrations of laponite (3 wt%) quickly form a glass of individual particles. Intermediate concentrations of laponite form a glass that is a combination of the two mechanisms, clusters and individual particles. The aging rheological response and upturn of the loss modulus at low frequencies are well predicted by models of soft glassy systems (Fielding, et al. 2000, Sollich 1998). If low amounts of high molecular weight (Mn = 163 kg/mol) poly(ethylene oxide) (PEO) are added, the aging behavior follows the dynamical response of the clay. Above a critical ratio, f, of the total polymer surface area to total laponite surface area, the PEO dynamics dominate at high frequencies. SANS and USANS investigations show an upturn at low *q* giving structural insight of the polymer-clay dispersions consistent with the rheological results. It appears that the only parameter needed to tune the rheology of these complex laponite-PEO systems is f.

Wednesday 4:25 Alpine East SC38

Structural analysis and scaling behavior of organoclay dispersions

Christophe Mobuchon, Pierre J. Carreau, and Marie-Claude Heuzey
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In recent investigations we have reported the effect of flow history on the structural recovery of polymer/nanoclay model suspensions. In contrast to published results for colloidal suspensions, we have observed that upon cessation of steady shear flow different equilibrium structures were reached, which strongly depended on the pre-shear rate. The existence of these different equilibrium structures has been attributed to the large excluded volume of the organoclay particles, which restricts the rotational and translational Brownian motion and therefore prevents the relaxation of the flow-induced anisotropy.

In order to investigate the anisotropic nature of these different equilibrium structures, and to describe the structure build-up at rest and under flow, two dimensional small amplitude oscillatory shear flow experiments (2D SAOS) have been performed by synchronizing small amplitude oscillatory motions, parallel and orthogonal to the steady shear flow direction. In this way, the viscoelastic moduli could be obtained in all the directions of the shear plane leading to a measure of the anisotropy of the colloidal structure.

The storage modulus of the organoclay dispersion was shown to decrease from the orthogonal to the flow direction outlining the anisotropic nature of the equilibrium structures in the shear plane. Rather surprisingly, these equilibrium structures appeared to not differ in their anisotropic nature in the shear plane. These observations are consistent with the linear dichroism measurements, namely the degree of alignment, performed both in the velocity gradient and vorticity planes.

Finally, influence of volume fraction, organoclay aspect ratio and temperature on the build-up and breakdown of these equilibrium structures will be discussed using scaling and superposition concepts.

Wednesday 4:50 Alpine East SC39

Dispersion and rheology of single sheet graphene materials

Bulent Ozbas, Douglas Adamson, Jan Vermant, Richard A. Register, Ilhan A. Aksay, and Robert K. Prud'homme
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We present the rheological properties of graphite oxide sheets (GOS) and functionalized graphene sheets (FGS) in various solvents. Exfoliation of GOS and FGS are obtained via sonication of strongly oxidized graphite and rapid thermal heating of graphite oxide, respectively. AFM experiments reveal that the majority of the exfoliated particles are single sheets with a high surface area (~1500 m2/g) and aspect ratio (100-10000). The effects of commercially available fuel detergents and surfactants on the dispersion and resultant rheological properties of GOS and FGS suspensions are studied in oil and water. The intrinsic viscosity measurements of the suspensions are related to the aspect ratio of the sheets using theories available for oblate spheroids and these results are compared to AFM data. The orientation of the seets with shear is studied by dichroism measurements. The effects of sonication time on suspension rheology and particle dimensions will be discussed.

Wednesday 5:15 Alpine East SC40

Flow-induced orientation in exfoliated polystyrene/clay nanocomposites

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Technological applications of polymer/clay nanocomposites will require understanding of the factors that influence the orientation distribution of the dispersed nano-scale clay fillers. We report here on an investigation of flow-induced orientation in model polystyrene-clay nanocomposite samples. The samples were produced via in situ controlled free radical polymerization of styrene in the presence of a clay that had been organically modified by a surfactant with pendant vinyl benzene groups. This functionality allows the organic modifier to be covalently incorporated in the growing polymer chains, and has been shown to produce highly exfoliated samples; indeed, the resulting nanocomposite sample shows no wide-angle x-ray scattering peak associated with clay layers. Rather, small-angle x-ray scattering from the anisotropic clay sheets themselves is monitored to track flow-induced changes in the degree of particle orientation. We employed an annular cone & plate x-ray shear cell which allows probing of orientation within the '1-2' (flow-gradient) plane. In the absence of flow, the scattering pattern is nearly isotropic, but it is rendered anisotropic by application of steady shear at sufficiently high rates. These samples appears to exhibit an unusually short relaxation time over which flow-induced orientation is lost upon flow cessation.

Symposium BE
Blends, Emulsions and Multiphase Fluids

Organizers: Matt Liberatore and Sachin Velankar

Wednesday 1:30 Alpine West BE9

Polymer-polymer interfacial slip measurements in multilayered films

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Most new polymer products contain two or more polymers, which are typically immiscible. At the interface between the polymers, significant polymer-polymer slip can occur due to poor adhesion. The slip is of practical importance because of its effect on morphology and adhesion of these multi-phase materials, such as disordered two-phase blends and multilayer films. In this research, we investigate the amount of polymer-polymer slip over a range of shear stresses from rheological measurements on co-extruded multilayer films Polypropylene (PP) and polystyrene (PS) with matched viscosity and elasticity around 195°C were chosen for our study. The multilayer samples were prepared in a co-extrusion setup (Zhao and Macosko J. Rheol. 2002). The number of PP/PS layers of the sample ranged from 20 to 640 layers. To determine the effect of alternately layered structure on the interfacial slip, three types of rheometers were used: an in-line slit-die rheometer, a rotational parallel-plates rheometer, and a sliding-plates rheometer (SPR). By using three different rheometers, it was possible to study the viscosity of a multilayered sample over a wide range of nominal shear stress. It was observed that the apparent viscosity of a PP/PS multilayer sample decreases as the number of layers increases (i.e., interfacial area between PP and PS increases) above a certain critical shear stress. This demonstrates the interfacial slip between two polymers. The slip velocity (i.e., the amount of macroscopic velocity discontinuity at the interface) with respect to shear stress was calculated from each rheological method and compared.

Wednesday 1:55 Alpine West BE10

Role of desorption kinetics in surfactant-mediated microscale tipstreaming

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Microfluidic flow focusing devices have been used to synthesize micrometer-scale emulsion droplets by exploiting the presence of added surfactant in one or both liquid phases. We have previously identified the thread formation mode of drop breakup, which occurs in a particular range of surfactant concentrations and flow rates. Here, a thin thread is drawn between two primary droplets. As the thread elongates, it disintegrates into a stream of tiny droplets, whose sizes depend on the final thread diameter and the physical properties of the liquids. In the present work, we investigate the role of surfactant desorption kinetics on the evolution of the thread length and on the region of phase space in which thread formation occurs.

We consider a homologous series of three nonionic C_nE_8 (n = 10, 12 and 14) surfactants dissolved in the dispersed phase liquid. These molecules have similar adsorption kinetics and diffusivities but very different desorption rates. We observe that the ultimate length of the thread before it disintegrates into a stream of tiny droplets depends strongly on the desorption kinetics. Using high-speed video microscopy, we observe that the thinnest threads are formed in the presence of the surfactant with the longest alkane tail ($C_{14}E_8$). To quantify the effects of these surfactants on the thread formation process, we measure the thread length as a function of dimensionless time and determine the appropriate dimensionalization for the problem. We also construct phase diagrams to indicate the ranges of surfactant concentration in which thread formation occurs as a function of dimensionless parameters. Our results suggest that the thread formation process can be optimized to form ever smaller droplets through the fine tuning of the timescales for the convection, diffusion, adsorption, and desorption of the surfactants.

Wednesday 2:20 Alpine West BE11

Numerical modeling of electrorheological emulsions

Arturo Fernandez
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The results of fully three-dimensional direct numerical simulations of the effects of electric fields on emulsions of drops will be presented. The examination of the rheological properties of these systems is performed by imposing a simple-shear flow between two plates where the drops are immersed. An electric potential difference is applied perpendicular to the plates. The resulting electric field leads to two effects: a polarization of the drops and a viscous fluid motion on the interface between the drops and the suspending fluid. The direction and intensity of the viscous fluid motion depends on the electrical properties of the fluids. Drops more conductive than the suspending fluid exhibit a viscous fluid motion from the equator to the poles, whereas drops less conductive than the suspending fluid exhibit a viscous fluid motion from the poles to the equator. 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 results are presented as a function of the Mason number and the electric capillary number, Mn and Ce. These non-dimensional numbers quantify the strength of the electric forces versus the fluid shear and the capillary forces, respectively. The significance of the electrical field on the viscosity and the normal stress differences will be discussed: At low Mason numbers, $Mn<0.1$, the application of the electric field results in the aggregation of the drops. This aggregation leads to an increase in the effective viscosity of the system and to an increase in the stresses, which result in higher normal stress differences than in hydrodynamic emulsions. At high Mason numbers, $Mn>1.0$, the fluid shear breaks up the aggregated structures and the properties are similar to hydrodynamic emulsions. At $0.1<Mn<1.0$ the properties exhibit an intermediate behavior.

Wednesday 2:45 Alpine West BE12

Drop oscillations under simple shear in a highly viscoelastic matrix

Yuriko Renardy
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We implement a volume-of-fluid algorithm with a paraboloid reconstruction of the interface for the calculation of the surface tension force (VOF-PROST) for three-dimensional direct numerical simulations for a Newtonian drop in an Oldroyd-B liquid near criticalities. Weissenberg numbers up to 1 at viscosity ratio 1 are examined. Critical capillary numbers rise with the Weissenberg number. Just below criticality, drop deformation begins to undergo an overshoot when the Weissenberg number is sufficiently high. The overshoot becomes more pronounced and at higher matrix Weissenberg numbers, such as 0.8, drop deformation undergoes novel oscillations before settling to a stationary shape. Breakup simulations are also described.

Wednesday 3:35 Alpine West BE13

Shape dynamics of droplet/matrix systems with viscoelastic components at bulk and confined conditions: experiments and comparison with 3D simulations

Verhulst Kristof[1], Ruth Cardinaels[1], Paula Moldenaers[1], and Yuriko Renardy[2]
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The influence of matrix and droplet viscoelasticity on steady and transient deformation and orientation of a single droplet, subjected to a homogeneous shear flow is investigated microscopically. The experiments, parametric in both the capillary and "Deborah" number, are performed on a Paar Physica MCR 300 based counter rotating plate-plate device and a Linkam shear cell. Several constant viscosity Boger fluids, as well as a shear thinning viscoelastic fluid, are used. These materials are described by means of an Oldroyd-B, Giesekus or Ellis constitutive equation. When the ratio of droplet diameter to gap spacing (D/H) is small, bulk conditions are obtained. At higher D/H ratios, confinement starts to play a role. It is shown that for bulk conditions droplet elasticity hardly affects the steady droplet deformation and orientation, even at moderate to high capillary and "Deborah" numbers. Nevertheless, close to critical break-up conditions, large oscillations of the droplet deformation and a new break-up mechanism are observed with the Boger fluid droplets. Matrix elasticity has a more pronounced

effect, promoting the orientation towards the flow direction and decreasing droplet deformation. It can also induce an overshoot in drop deformation during start-up flows and slows down droplet retraction upon cessation of flow. All these effects saturate at high "Deborah" numbers, i.e. decreasing droplet radius. Confinement tends to enhance droplet deformation and orientation. The experiments are compared with three-dimensional simulations performed with a VOF-PROST algorithm. The simulations nicely capture the experimentally observed trends and even display quantitative agreement.

Wednesday 4:00 Alpine West BE14

Direct numerical simulations of droplet emulsions in the viscoelastic two-phase fluid system in sliding bi-periodic frames using the level-set method

See Jo Kim[1] and Wook Ryol Hwang[2]

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We present a direct numerical simulation technique for droplet emulsions of the Newtonian/viscoelastic-Newtonian/viscoelastic system in simple shear flows. The sliding bi-periodic domain concept of Lees and Edwards for discrete droplets has been extended to continuous field problems and combined with the DEVSS/DG finite-element method for accurate and stable computation of viscoelastic flows and the level-set method with the continuous surface stress (CSS) formulation has been used for accurate description of the sharp interfaces. Based on the standard velocity-pressure formulation of the finite-element method, we use the mortar element method for the implementation of the sliding periodicity and employ the discontinuous Galerkin (DG) method for the stabilization of the interface advection equation. We present numerical results on the morphological development for a single, two and multiple drops in sliding bi-periodic frames for the demonstration of the feasibility of the present method in investigation of the relationship between the morphology and the bulk material responses for the viscoelastic two-phase system.

Wednesday 4:25 Alpine West BE15

Two-dimensional bubble and droplet motion in a yield-stress fluid

John P. Singh and Morton M. Denn

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We have implemented a finite-element code for a two-phase system consisting of incompressible two-dimensional Newtonian bubbles or droplets moving in a continuous Bingham fluid. The code employs a level-set method to track the deformable interface and a continuously differentiable viscosity function for the dispersed phase that approaches the discontinuous yield-stress fluid as a regularization parameter becomes infinite. Converged solutions for the slow gravitational rising (falling) of single bubbles (droplets) through a Bingham fluid in a large container show the presence of unyielded "ears" on the equatorial axis adjacent to the bubble (droplet) surface. The container boundaries are beyond the outer yield surface, and the flow is independent of the container length scale. Collinear bubble or droplet pairs in a gravitational field interact in a way that is qualitatively similar to the interactions in a Newtonian outer fluid: For two collinear bubbles, for example, fore-aft symmetry is broken, with the formation of a cap on the upper bubble and an inverted teardrop shape on the lower, forming a "shade tree" following coalescence. The dynamics of shape development in the Bingham material differ substantially from those for a Newtonian continuum, however. There is an unyielded region that initially extends between the two equatorial planes, and there is a recirculating flow that causes a precession of the unyielded regions along the bubble interfaces. The teardrop evolves from an intermediate "peanut" shape. With decreasing Bond number (ratio of gravitational to interfacial stresses) the trailing bubble or droplet develops an unusual cusped "fishtail" shape. The buoyant force must exceed the integrated yield stress for any motion to take place. Bubbles or drops that are too small to overcome the yield stress individually can move as pairs when they are sufficiently close. (Supported by the National Science Foundation through the CREST Center for Mesoscopic Modeling and Simulation.)

Wednesday 4:50 Alpine West BE16

Viscoelastic effects on drop deformation in a converging pipe flow

Diwen Zhou, Pengtao Yue, and Jimmy J. Feng

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This talk reports finite-element simulations of drop deformation in converging flows in an axisymmetric conical geometry. The moving interface is captured using a diffuse-interface model and accurate interfacial resolution is ensured by adaptive refinement of the grid. We have explored the effects of viscoelasticity on drop deformation when either the drop or the matrix is a Giesekus fluid. Contrary to the popular belief that viscoelasticity in the drop hinders deformation and that in the matrix enhances deformation, we predict a more complex picture in which viscoelasticity in either component may suppress or promote drop deformation depending on the capillary number Ca and the drop-to-matrix viscosity ratio ß. Smaller Ca and ß are conducive to the behavior mentioned above, while large Ca and ß may produce the opposite effect. Both trends are explained by the reaction of the polymer stress to the inhomogeneous and transient deformation in the converging flow field. Finally, this understanding reconciles contradictory results in the literature as opposite limits in the parameter space.

Symposium SM
Entangled Solutions and Melts

Organizers: Jay Schieber and James Oberhauser

Wednesday 1:30 Canyon B SM8

Stress relaxation of narrow molar mass distribution polystyrene following uniaxial extension

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The stress in startup of uniaxial elongational flow until steady state, followed by stress relaxation has been measured for a narrow molar mass distribution polystyrene melt with a molecular weight of 145kg/mol. The experiments are conducted on a filament stretching rheometer, where a closed loop control of the mid-filament diameter ensures controlled uni-axial extension. The closed loop control algorithm is extended to apply to the stress relaxation part of the experiment. It ensures a constant mid filament diameter, by controlling the motion of the end-plates. By dividing the measured stress with the theoretically predicted stress from the Doi and Edwards model during relaxation, the stretch factors corresponding to each imposed stretch rate are obtained. These stretch factors converge to a unique envelope and eventually converge to unity for long times for all measured elongational rates.

Wednesday 1:55 Canyon B SM9

Hidden (and not so hidden) traps in extensional rheometry of high viscosity systems: the dangers of new generation easy-to-use rheometers

Joao M. Maia
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Over the last 30 years Extensional Rheometry has been continually at the forefront of research in Rheometry for two main reasons; its relevance to real-world flow situations and the difficulty in performing well-controlled, physically relevant experiments. Also, the study of this type of flow allows an insight into the molecular structure of the materials to be obtained, since extensional behavior is very dependent on the particular structure being deformed. Due to this relevance, it is not surprising that a cheap, easy-to-use, reliable technology to perform these experiments has been the subject of intense research over the years. In the early 21st century technological development has reached a point where the simplicity of the current generation of instruments, e.g., the Sentmanat Extensional Rheometer (SER), seems to finally have allowed that goal to be largely achieved and instruments such as the SER are enabling the access of a quickly growing number of researchers to good-quality Extensional Rheometry capabilities. However, the apparent user friendliness of these instruments may mislead the "unaware" rheologist into overlooking the Physics involved in the experiments and believing blindly in the data that is supplied by the instrument and, thus, there is the clear need for researchers to be aware of potential sources of errors or imprecision during the experiments. Thus, the main aim of this presentation will be to present a critical analysis of the most common sources of error in modern extensional rheometers including sample preparation, homogeneity, dimensions and loading, temperature control, supporting media, edge effects, digital analysis of the data and physical significance of the results amongst others and provide correction procedures for these whenever possible.

Wednesday 2:20 Canyon B SM10

Rheological analysis of a system of well-defined sparsely long-chain branched polyethylenes with the McLeish-Larson pom-pom model

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A series of HDPE resins having a relatively narrow molecular weight distribution and a well-defined degree of sparse long-chain branching, LCB, are evaluated to determine if their rheological properties are consistent with the predictions of the McLeish-Larson pom-pom model. Rheological analysis and parameter fitting with a multi-mode McLeish-Larson pom-pom model provides a molecularly sensitive set of model parameters and gives insight to molecular structure. Rheological testing includes small-amplitude oscillatory experiments to extract the backbone orientation relaxation time, tbi, and the corresponding fraction of stress that is relaxing, gi; extensional stress growth experiments to determine the backbone stretch relaxation time, tsi, and the number of dangling branch arms, qi; and jump-strain experiments for the proposition of a new method to determine tsi based on separation in the relaxation modulus curves at short timescales. On short timescales there is a separation of values for the relaxation times associated with the stretch relaxation parameter whereas, on longer timescales the relaxation modulus is observed to be separable in time and strain, which is consistent with the predictions of the model. The new technique for the determination of tsi is verified by the accuracy with which uniaxial extensional data is fit. Rheological analysis provides an opportunity to evaluate the ability of the pom-pom model to describe well-defined systems of materials with minimal differences in LCB concentrations and to determine the consistency of the model to correctly predict the levels of LCB present.

Wednesday 2:45 Canyon B SM11

Atomistic, nonequilibrium molecular dynamic simulations of an H-shaped polyethylene melt under shear

Chunggi Baig[1] and Vlasis G. Mavrantzas[2]

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Considering the growing experimental and theoretical interest in the rheology of branched polymers [1-4], we present results for the structural and dynamical behavior of an H-shaped polyethylene (PE) melt under shear as obtained from nonequilibrium molecular dynamics (NEMD) simulations in atomistic detail. H-shaped polymer, although the simplest type of branched polymers, is considered most important not only from a practical but also from a theoretical viewpoint, taking into account recent theoretical advances in the area [5-6]. The NEMD simulations have been carried out with a model H_78_25 PE melt, containing 78 methylene units along the main chain backbone and 25 ones along each of the four branches. Progressively larger simulation boxes were used in the NEMD runs for the higher shear rates (where chains are likely to be significantly oriented to the flowing direction) in order to avoid any artificial system-size effects. In all cases, the simulations were carried out long enough (in particular, for the lower shear rates) in order to obtain reliable statistics. Results will be presented for a number of structural and dynamical properties and will be thoroughly compared against those corresponding to the linear counterparts of the same total or backbone chain length. Despite the short length of the simulated H_78_25 PE system, detailed physical and theoretical analysis of the NEMD results will be considered in connection with existing state-of-the-art theories for H-polymers, such as the pom-pom model [2].

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Wednesday 3:35 Canyon B SM12

Rheological properties of molten polypropylenes containing supercritical CO_2: effects of long-chain branching, CO_2 concentration, pressure, and temperature

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Supercritical carbon dioxide (SC-CO_2) is of interest as a physical blowing agent in the manufacture of plastic foam and as a plasticizer to reduce melt viscosity during processing. The combined effects of dissolved SC-CO_2, pressure, and temperature on the rheological properties of the melt must be known to achieve optimum processing conditions. In order to achieve good foam products, polymer blends are sometimes used, for example linear polypropylene (PP) with branched polypropylene. Since reliable models for predicting the physical properties of these materials in the presence of a solvent are not available, experimental data are necessary to evaluate candidate resins. Five polypropylenes were chosen for study: one linear and one branched, plus three blends of these two. The pressure-volume-temperature (*PVT*) behavior of the samples was determined to establish their basic phase behavior. To determine the combined effects of blend composition, CO_2 concentration, pressure, and temperature, a high-pressure sliding plate rheometer (HPSPR) and two rotational rheometers were used. In the HPSPR the shear deformation, temperature, pressure, and CO_2 concentration are all uniform. A shear stress transducer senses the stress in the center of the sample to avoid edge effects. It was possible to use shift factors for temperature, pressure and CO_2 concentration to obtain a master curve. While the branched PP is thermorheologically complex, even a small amount of linear PP yields a blend that is thermorheologically simple, and the effect of temperature could be described by the Arrhenius equation. Both the linear and branched PP exhibited nearly piezorheologically simple behavior, and the effect of pressure was described by the Barus equation. The effect of concentration of CO_2 could be modeled using the Fujita-Kishimoto equation. The relative effects of concentration, pressure, and temperature were quantified.

Wednesday 4:00 Canyon B SM13

The nonlinear rheology of entangled linear comb polymer solutions

Keith M. Kirkwood[1], Michael Kapnistos[1], Nikos Hadjichristidis[2], Dimitris Vlassopoulos[3], and Gary Leal[1]

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We report on experimental studies of entangled linear comb polymer solutions (polybutadiene in low MW linear PBd, polyisoprene in squalene, and polystyrene in DEP). The systems that we consider have approximately 5-30 arms, and fall into one of two basic types, depending essentially on the MW of the arms. In the first, the arms are relatively high MW so that the number of entanglements per arm in the solutions ranges from approximately 2-13. In these systems, the backbone MW is such that that they end up being only lightly entangled after the dynamic dilution effect of arm relaxation. In the second class, the combs have relatively short arms (of the order of the entanglement MW or smaller), with relatively large numbers of entanglements per backbone (O(20)). The long-arm systems were previously studied in the linear viscoelastic regime, and comparisons were made with a modified version of the model of Daniels, McLeish and coworkers. Here we present linear viscoelastic data for the short-arm combs, with an emphasis on the departures from LV theories for entangled linear chains. Both classes of comb polymer were then subjected to step shear strain experiments. In the long-arm case, we attempt to separate the contributions of the arm and the backbone to the damping function. In the short-arm case, we focus on dilution studies, and on comparison with linear chains (no arms).

Wednesday 4:25 Canyon B SM14

Linear and nonlinear rheology of model Cayley-tree polymers

Evelyne van Ruymbeke[1], Edwards B. Muliawan[2], Dimitris Vlassopoulos[1], Savvas G. Hatzikiriakos[2], Akira Hirao[3], and Nikos Hadjichristidis[4]
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We investigated the rheology of a series of anionically synthesized, model symmetric Cayley tree polybutadienes and poly(methyl methacrylates) having 2 and 3 generations with branches of varying degree of entanglements. The signature of each layer relaxation was evident in the linear response, both in the plateau modulus and the terminal relaxation as a distinct contribution, well-separated in time. Using a tube-model analysis based on the concept of hierarchy of motion, we described quantitatively the frequency spectra without adjustable parameters. We also performed uniaxial elongation measurements using the SER fixture. The samples tested exhibited significant strain hardening compared to the linear analogues at lower and intermediate Hencky strain rates. The extracted effective steady extensional viscosity scales with the elongational rate with a power exponent of about -0.5, in agreement with earlier findings with linear polystyrenes.

Wednesday 4:50 Canyon B SM15

Correlations between thermorheological properties and molecular structure of long-chain branched polyethylene

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Long-chain branched metallocene catalyzed polyethylenes (LCB-mPE) do show a thermorheological complexity. This presentation gives some detailed correlations between the thermorheological behavior of LCB-mPE and its molecular structure. The analysis of the thermorheological complexity was conducted by shifting relaxation spectra $g(\tau)$ at different relaxation strengths, which give more elusive data than shifting rheological quantities such as $G'(\omega)$, $G''(\omega)$, or $|\eta^*(\omega)|$. As expected, for linear and short-chain branched PE, but also for LDPE, an activation energy independent of the relaxation strength or the relaxation time, respectively, is found. For the long-chain branched metallocene catalyzed PE investigated a significant dependence of the activation energy on the relaxation time is obvious. At shorter relaxation times the activation energy is similar to that of linear PE but it increases with longer times. These findings can be interpreted by assigning the lower values to the linear fraction and the higher ones to different species of long-chain branched molecules within the samples. Thus, the conclusion can be drawn that the LCB-mPE investigated consists of a mixture of PE-molecules with various architectures.

Wednesday 5:15 Canyon B SM16

Linear viscoelastic response and viscosity of ring melts

Miao Hu[1], Gregory B. McKenna[1], Julia A. Kornfield[2], and Robert H. Grubbs[2]
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There is continuing interest in the dynamics of macrocylic polymers or polymer rings. Here we are working with novel polyoctenamer rings synthesized by a ring-insertion metathasis route that precludes linear contamination when pure catalyst is used. While the rings are polydisperse in their molecular weights, the method permits synthesis of extremely high molecular weight entitities. Here we report results on the dynamic moduli and the zero shear rate viscosities of both the cyclic polyoctenamer of Mw up to nearly 400,000 g/mol and the linear analogue. Comparisons will be made with prior literature results on rings made by ring closure methods in dilute solution where contamination with linear chains was problematic.

Symposium BS
Biological and Self-assembled Systems

Organizers: Bob Prud'homme and Pat Doyle

Wednesday 1:30 Canyon A BS10

In vitro optical measurements of the interaction between human lung cells and single-wall carbon nanotubes

Matthew L. Becker, Jeffrey A. Fagan, Jaehun Chun, Barry J. Bauer, and Erik K. Hobbie
NIST, Gaithersburg, MD 20899, United States

The intrinsic band gap fluorescence of individual semiconducting single-wall carbon nanotubes (SWNTs) stabilized with single-stranded DNA and deoxycholate surfactant is exploited to optically measure the interaction between human lung cells and length-fractionated SWNTs. Using near-infrared (NIR) fluorescence microscopy in microfluidic flow platforms, live human lung fibroblasts (IMR-90) are exposed to controlled quantities of length-sorted single wall nanotubes, and the cellular interaction and uptake of the SWNTs is optically monitored in real space-time.

Cell mortality is shown to result from the uptake of shorter nanotubes and is correlated with both SWNT length and concentration. The NIR optical measurements are used to identify potential uptake mechanisms and quantify the kinetics of the interaction.

Wednesday 1:55 Canyon A BS11

Evaluating viscoelastic properties of the cornea and sclera in vitro using elevated intraocular pressure in whole eyes

Matthew S. Mattson[1], Meredith E. Wiseman[2], Changjun Yu[3], Daniel M. Schwartz[4], Robert H. Grubbs[3], and Julia A. Kornfield[3]
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Motivated by ocular diseases such as keratoconus and degenerative myopia in which the cornea and sclera, respectively, gradually elongate, we develop a method to measure the elongational creep of these tissues and use it to screen potential therapeutics. Specifically, we measure the expansion of eyes, enucleated from rabbit kits, that are subjected to approximately four times the normal intraocular pressure. Because the eyes are submersed in a saline bath, monitoring the shape changes over more than 24 hours is possible. In addition to the fast elastic response measured in the initial eye inflation, this method allows measurement of a slow creep that is more characteristic of tissue failure. Photographs indicate that rabbit kit eyes are highly distensible, with a 7.8+/-2.0% change in equatorial diameter and a 17.2+/-8.6% change in axial length after 20 hours of elevated intraocular pressure (85 mmHg). Photoactivated crosslinking initiated by EosinY and triethanolamine within the cornea and sclera reinforces the tissue and slows the creep rates (0.7+/-0.4% change in equatorial diameter; 7.4+/-3.6% change in axial length; 20 hours at 85 mmHg). This technique of examining eye creep may be useful for measuring differences in diseased and healthy tissue that are not evident from traditional techniques that generally use tissue sections instead of whole eyes. In addition, the measurement of corneal and scleral rheological properties provides a screening tool for the selection of promising keratoconus and degenerative myopia drugs that deter creep and prevent tissue degradation.

Wednesday 2:20 Canyon A BS12

Rheological, mechanical and failure properties of biological soft tissues at high strains and rates of deformation

Martin Sentmanat
Xpansion Instruments, LLC, Akron, OH 44303, United States

The rheological, mechanical and failure properties of animal soft tissues were characterized in uniaxial extension at high strains and rates of deformation utilizing a miniature universal testing platform. A variety of biological samples of skeletal, cardiac, and smooth muscle tissues were carefully extracted and prepared from poultry and bovine specimens and evaluated mechanically under a controlled temperature environment. Individual muscle fiber bundles were also evaluated from the sampling of extracted muscle tissues. A variety of tendon, ligament, and cartilage tissue samples were also mechanically evaluated under a controlled temperature environment. The high rate extensional deformation and fracture results revealed clear distinctions in the mechanical properties of the various biological tissues evaluated and provide fundamental insight as to the failure and physiological behaviors of related human soft tissue.

Wednesday 2:45 Canyon A BS13

A new mechanism to explain physiological lubrication

David F. James and Garret M. Fick
Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario M5S 3G8, Canada

Physiological lubrication has defied explanation in terms of standard biofluid mechanics because the viscosity of synovial fluid, the liquid in the joint capsule, is much too low to prevent contact and wear of the articular surfaces under normal physiological loads. The fundamental problem is one of squeeze-film flow under a constant compressive load, for if one models the joint as two coaxial disks and uses standard squeeze-film theory and physiological values, the articular surfaces are predicted to contact in less than 0.1 second. The shear-thinning nature of the fluid aggravates the situation. Contact times must necessarily be much longer to avoid wear and to this end a new mechanism is proposed to explain how the fluid keeps the surfaces apart. The mechanism depends on non-affine motion of the entangled hyaluronic acid chains in synovial fluid, caused by tethering of the chain network to the phospholipid layers lining the articular surfaces. By this mechanism, using the same model of two coaxial disks approaching each other under a constant load, and using the known flow resistance of hyaluronic acid chains, contact times of order 10 minutes are predicted - times which are much more physically reasonable. The effects of surface curvature, network compression, and protein entrapment in the network are investigated.

Wednesday 3:35 Canyon A BS14

Viscoelasticity and conformation kinetics of smart protein bundles "forisomes"

Steve Warmann[1], Amy Shen[1], and William Pickard[2]
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Forisomes, Ca2+-responsive contractile protein bodies, act as flow blocking gates within the phloem of legumes. Microscopic tensile tests (incremental stress-relaxation measurements) on forisomes of Canavalia gladiata and Vicia faba were performed using a microcantilever method. Mechanical properties of forisomes were investigated longitudinally before and after contraction induced with Ca2+, and in the radial direction only before contraction. Forisomes showed viscoelastic properties typical of a biological material with a unidirectional fibrous structure. Creep data were collected in all tensile tests and fit with a three parameter viscoelastic model. The elastic modulus of the forisomes was not differentiable between the species (Vicia 660 +/- 360kPa; Canavalia 600 +/- 360kPa). Both species showed mechanical anisotropy (direction-dependent mechanical response). The elastic modulus was dramatically smaller in the radial direction than in the longitudinal direction, suggesting a weak protein cross-linking amongst longitudinal protein fibers. Activation of forisomes decreases forisome stiffness longitudinally, possibly due to dispersion of the protein structure. Contractile forces generated by forisomes undergoing activation were also measured.

Wednesday 4:00 Canyon A BS15

Rheology of viscoelastic surfactant in heavy brines

Yiyan Chen and Yenny Christanti
Oilfield Chemical Products, Schlumberger, Sugar Land, TX 77478, United States

Viscoelastic surfactants (VES), which can form wormlike micelles and give unique rheology properties, have been used in the oilfield industry as a viscosifying agent in various applications. Sand-control service is a way to prevent production of formation sand that is detrimental to hydrocarbon production. One of these services is gravel packing, where specifically sized gravel is placed in the annulus between a steel screen and openhole wellbore to prevent the passage of formation sand. The gravels must be suspended and transported by a carrier fluid. These fluids typically are high-viscosity, polymer-based fluids. In geopressured wells, high-density brines are required for pressure control. Natural polymers such as guar and xanthan, which are typically used to viscosify water and light brines, have limited solubility in heavy brines, especially divalent brines. One type of VES can form viscoelastic fluid in both monovalent and divalent brines. We will show the steady shear and dynamic oscillatory rheology of this VES gelling various brines. Some of the characteristic shear-induced fluid rheology behavior will also be discussed.

Wednesday 4:25 Canyon A BS16

Phase field models for biofilm flows

Qi Wang and Tianyu Zhang
Mathematics, Florida State University, Tallahassee, FL 32306, United States

We will present a hydrodynamic theory for biofilm flows formulated as a kinetic theory. The fluid is assumed an incompressible mixture consisting of two effective components: extracellular polymeric substance (eps) and solvent. The nutrient is treated as a part of the solvent while the bacteria are modeled as a part of the eps. The eps production by the bacteria leads to a long wave instability to the governing system of equations. The numerical results in 1-D and 2-D geometries will be discussed in various variations of the model.

Wednesday 4:50 Canyon A BS17

Viscoelastic properties of acellular scaffolds for the bioengineering of vocal fold tissues

Roger W. Chan
Otolaryngology, Biomedical Engineering, University of Texas Southwestern Medical Center, Dallas, TX 75390-9035, United States

Tissue replacements for the surgical reconstruction of the human vocal fold lamina propria have been developed in our laboratory. A novel proteolytic enzyme-free, detergent-free saline based protocol was employed to decellularize the bovine vocal fold lamina propria and the human umbilical vein (HUV) into three-dimensional, biodegradable, acellular scaffolds that can be repopulated with human fibroblasts for the replacement of pathological vocal fold tissues. Viscoelastic shear properties of the scaffolds were quantified by a custom-built controlled-strain, linear simple shear rheometer system that is capable of direct empirical measurements of the complex shear modulus of low-modulus biomaterials and soft tissues at frequencies of up to 250Hz. Results showed that the elastic shear modulus, viscous shear modulus and damping ratio of the fibroblast-repopulated scaffolds were comparable to those of native human vocal fold tissues, specifically the superficial layer of the lamina propria that is responsible for vocal fold vibration. These findings supported the biomechanical benefits of the scaffolds for vocal fold reconstruction and regeneration [Work supported by the National Institutes of Health].

Thursday Morning

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Nina Shapley and Erik Hobbie

Thursday 8:05 Alpine East SC41

Brownian motion of germanium nanowires

Bennett D. Marshall[1], Doh C. Lee[2], Brian A. Korgel[2], and Virginia A. Davis[1]
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Determining the fundamental rheological properties of nanorod and nanowire dispersions is an important step in developing liquid based processing techniques for these novel materials. The rotational diffusivities of high aspect ratio germanium nanowires dispersed in organic solvents were experimentally determined using a particle tracking technique. We evaluated the effects of length, confinement, and solvent viscosity on rotational diffusivity. The nanowires ranged in length from 2 to 12 microns with an average aspect ratio of approximately 1000. The experimental data was found to be in good agreement with theoretical values for Brownian rods in spite of the nanowires' high and polydisperse aspect ratios.

Thursday 8:30 Alpine East SC42

Rheological behavior of polyamide-6 based nanocomposites in transient flow

Maryam Sepehr, Kalonji K. Kabanemi, and Leszek A. Utracki
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Rheological behavior of nanocomposites containing polyamide-6 matrix and 2-wt% organoclay (PNC) were studied in simple shear transient flow, using a rate-controlled rheometer with cone-plate geometry. During the stress growth experiments (in forward or reversed flow shearing) the viscosity and normal stress differences have shown stress overshoot. Changing the PNC compounding parameters resulted in different degrees of clay dispersion in samples having the same composition, what in turn resulted in different transient behavior. Next, the experimental behavior was compared with numerical simulation results. The disc shaped particle orientation was modeled using the Advani-Tucker equation of change for the second-order orientation tensor, while the transient rheological properties of the matrix were described by the Giesekus constitutive equation. A coupling parameter between the particles and the matrix has been included in the Giesekus equation. The effect of the matrix type (Newtonian or viscoelastic) has been investigated. An emphasis was also placed on the different types of closure approximations for the fourth-order orientation tensor, as these affect numerical predictions.

Symposium EP
Rheology in Energy Production

Organizers: John Dorgan and Phil Sullivan

Thursday 8:55 Alpine East EP1

Rheology as diagnostic tool in characterizing fluids in energy recovery

Robert K. Prud'homme
Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, United States

Complex fluids arise in a variety of contexts in energy recovery operations. This talk is intended as a survey and introduction to the role rheology can play in oilfield operations and fluids formulation. We will present three examples from our research where rheology is the best diagnostic tool to characterize the microstructure involved in fluids for oil and gas production. Fracture fluids are used to fracture the oil-bearing formation near the wellbore in order to stimulate oil and gas production by increasing the permeability of the formation. The fluids/gels require a careful balance of thinning to flow at low pressures during injection and gel structure to suspend solid "proppants". Dynamic oscillatory measurements can follow the processes of gelation and provide insight concerning the chemistries used to gel polysaccharide polymers. The measurements distinguish between true gels and association fluids with extended lifetimes. In addition, rheology provides information on the self-assembly of surfactant micelles that are also used in fracturing. In pipeline transport of crude oil, gelation of wax components can block flow and cause catastrophic failure of offshore deep sea pipelines. Rheology can be used to assess the effects of polymer additives on wax gel structures.

Thursday 9:20 Alpine East EP2

Complex fluids in flow assurance

Rama Venkatesan and Alberto Montesi
Chevron ETC, Houston, TX 77002, United States

With the ever-increasing demand for energy and ever-improving technology to help produce that energy, the energy companies have been increasingly drilling and producing in offshore and other harsh environments. "Flow Assurance" has thus evolved as an important challenge in the development and production of oil and gas fields. Issues such as heavy oil production, emulsion formation, the formation and deposition of solids such as hydrates, waxes and asphaltenes become more challenging due to the changing nature of both the production environment and the oil chemistry. It is very important to have a proper understanding of these complex fluids and their rheology in dealing with this situation. This talk will focus on some of the challenges faced today in oilfield rheology, including measurement and modeling issues, and some recent developments in this area.

Thursday 10:10 Alpine East EP3

An experimental study of non-Newtonian displacement flows in vertical eccentric annuli

Stefan T. Storey[1], Ian A. Frigaard[2], and Mark D. Martinez[3]
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We present an experimental study of non-Newtonian displacement flows in vertical eccentric annuli. The experiment models the industrial process of oil well cementing and examines interface dynamics during the process of fluid displacement. Interface dynamics are described phenomenologically in terms of three broad classifications, namely steady, unsteady and static. Experiments were devised to study all three interface types and the results are used to analyse the displacement flows in terms of displacement kinematics and also in terms of displacement efficiency. Three main fluids were used in the study. Xanthan and Carbopol solutions were used to simulate cement slurries and drilling muds, with glycerin used as a Newtonian experimental control. The interface dynamics are captured by a simple optical technique and the images post-processed to ascertain interface speed, elongation and displacement efficiency. The results were compared to numerical predictions computed using a simplified 1D model. We discuss the industrial and scientific significance of the results, together with relative merits and limitations of the experimental technique.

Thursday 10:35 Alpine East EP4

Superimposed oscillation and shear: evaluation of static and dynamic sag in drilling fluids

Jason E. Maxey
Global R&D, Baker Hughes Drilling Fluids, Houston, TX 77073, United States

Management of barite sag in a drilling fluid is recognized as a critical problem throughout the drilling industry. While traditional concern is with barite sag, the issue of suspension of all solids is of equal importance. A drilling fluid must be designed to adequately suspend both the large-diameter cuttings and the much smaller weighting agent used. Non-barite weighting materials, such as hematite, ilmenite, and manganese tetraoxide, are now applied in challenging applications. As this occurs traditional fluid formulations must be changed to accommodate their different physical and chemical interactions in the fluid system.

Conventional direct methods for evaluating sag include static aging at elevated temperatures and monitoring density changes under shear in a viscometer or in an annular flow loop. These methods work as an alert to existing problems, but do not aid in predicting potential problems or determining the mechanistic causes of sag. By studying the structural properties of the fluids under oscillatory flow, the structural behavior of drilling fluids under static well conditions may be evaluated. This information can be used to evaluate implications for static sag behavior. Through experimental evaluation of superimposed oscillations on steady shear, the fluid's structural behavior under dynamic well conditions may be studied, allowing inferences for dynamic sag. This presentation will provide an overview of results from viscometry and oscillatory testing, both with and without superposed steady shear, for several types of fluids.

Thursday 11:00 Alpine East EP5

Rheology of model waxy crude oils with relevance to gelled pipeline restart

Kyeongseok Oh, Kesia Guimaraes, Jules J. Magda, and Milind Deo
Chemical Engineering, University of Utah, Salt Lake City, UT, United States

When ambient temperatures are low, crude oils being transported in pipelines from production facilities to refineries sometimes form gels composed of wax crystals. These gels may stop the pipe flow, and make it difficult or even impossible to restart the flow without breaking the pipe. In order to study this problem, we are using rheological techniques to measure the temperature-dependent rheology of model waxy crude oils prepared using known amounts of well-characterized paraffinic waxes. Unlike crude oils, these model oils are also transparent, and thus can be used in model pipeline flow visualization experiments that we are performing concurrently. Results will be presented for the time- and temperature-dependent rheology of the model waxy crude oils. These results show that the model oils exibit many of the rheological features reported for real crude oils, such as three distinct apparent yield stress values.

Thursday 11:25 Alpine East EP6

Rheology of biomass slurries

Tim Scott[1], Max Ehrhardt[2], Jianghui Wang[2], Thatcher W. Root[2], and Daniel J. Klingenberg[2]
[1]USDA Forest Products Laboratory, Madison, WI, United States; [2]Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI, United States

The conversion of biomass to energy is now more promising due to recent advances in the enzymatic hydrolysis of cellulose with subsequent conversion to ethanol. One factor in achieving economic viability will be processing the biomass at high solids concentration, so that the energy required for heating and other processing steps can be minimized, and the concentration of ethanol produced can be increased. However, processing at high concentrations creates challenges for pumping and mixing. While reducing particle size can improve the rheology, with added benefits for reaction kinetics, particle size reduction incurs additional costs. It is therefore important to understand the rheological and mass transfer properties of these slurries in order to design optimal, efficient processes. In this presentation, we report experiments employing various lignocellulosic materials, such as wood pulp and corn stover. Methods for measuring and controlling the particle size distributions will be discussed. Rheological measurements employ torque rheometry, a method commonly employed in the food and polymer industries. We describe the rheology of biomass slurries and its dependence on such variables as solids concentration, deformation rate, particle size and size distribution, and temperature.

Thursday 11:50 Alpine East EP7

Enzo-rheology: investigations of high-solids biomass slurries for bio-refinery applications

Matthew W. Liberatore
Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401, United States

Flow assurance technologies enhance the cost and energy efficiency of the current extractive energy economy. A tremendous technological gap in the area of flow assurance for the growing biofuel industry must also be addressed. The production of cellulosic ethanol involves working with high-solids slurries which are notoriously difficult to transport. Therefore, the overall objective of this work is to manipulate renewable energy fluids, chemically and mechanically, to improve energy efficiency during processing and increase volume and fuel quality of the product streams. High solids cellulosic slurries, like corn stover, require large, powerful pumps for transport due to their high viscosity. Three primary tasks will be discussed: 1. Measurement of the rheology of biomass slurries as a function of the slurry properties, 2. Characterization the rheology of biomass slurries during enzymatic saccharification (enzo-rheology) and 3. Synthesis the rheological measurements into a mathematical model to directly integrated into the operation of a pilot scale biorefinery at the National Renewable Energy Laboratory (NREL).

Symposium BE
Blends, Emulsions and Multiphase Fluids

Organizers: Matt Liberatore and Sachin Velankar

Thursday 8:05 Alpine West BE17

Viscoelasticity and microstructure of PVC-bentonite nanocomposites

Angel Romo-Uribe[1], Maria Eugenia Romero-Guzmán[1], Carlos Cruz-Ramos[2], and Roberto Olayo[3]
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This work will discuss recent results on the microstructure and its correlation with the dynamic rheological properties of layered silicate nanocomposites based on PVC and bentonite. Even though these classes of materials have been intensely studied in recent years, much remains to be understood, especially regarding the derivation of microstructure - property correlation. Molten PVC and nanoclay were mixed using an extrusion process and sheets were produced using the two-roll mill process. The sheets thus produced remained optically transparent and did not show evidence of nanoclay agglomeration. Furthermore, X-ray scattering suggested nanoclay exfoliation. Dynamic mechanical analysis was used to characterize the modes of relaxation in solid state. On the other hand, rheological measurements were carried out in order to characterize the molecular dynamics in the molten state. The results showed that there are changes in modes of relaxation of the molecular chains. Furthermore, the dispersed nanofillers also influenced the rheological properties of the polymeric matrix promoting a rubber-like behavior in the nanocomposite.

Thursday 8:30 Alpine West BE18

The effect of nanoparticles on polymer melt rheology

Jonathan E. Seppala and Michael E. Mackay
Department of Chemical Engineering and Material Science, Michigan State University, East Lansing, MI 48823, United States

Previously we found that nanoparticles reduce the viscosity of polymer melts above a certain concentration which corresponds to the average gap between the particles being smaller than the polymer molecule size (denoted as a confined polymer). Normally this would lead to depletion flocculation with colloidal size systems, however, the thermodynamics on the nanoscale are different leading to nanoparticle dispersion. Since

most polymer systems are polydisperse in size, we investigated how a system behaved when a bidisperse blend was considered. Here we designed the experiment so one component was confined and the other not and found that in some cases the viscosity was not affected at all while in others a viscosity drop occurred. This and other unusual phenomena will be discussed in the oral presentation.

Thursday 8:55 Alpine West BE19

Rheology of polyethyleneoxide in polyisobutylene pickering emulsions

Prachi Thareja[1] and Sachin Velankar[2]

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We present results on emulsions comprised of polyethylene oxide (PEO) drops dispersed in a polyisobutylene (PIB) matrix, with hydrophobic silica particles adsorbed at the interface. It is known that the particles adsorb at the interface of two fluids, when they are *preferentially* wetted by one of the fluids. However an interesting scenario arises when the particle satisfies the same contact angle simultaneously at *two* fluid-fluid interfaces. As a consequence, the film of the preferentially wetting fluid is "bridged" between the two interfaces. This phenomenon is termed as "bridging".

We present the bridging of PEO drops via hydrophobic silica particles in PEO/PIB emulsions. We think that this is an ideal model system for elucidating the effects of particle bridging by microscopy and rheology. These emulsions were subjected to controlled shear flow conditions and studied by optical microscopy in a home built shear cell. We find that the particles can indeed bridge across PEO drops and glue them together. The resulting cluster morphologies include tightly-aggregated drops, loose networks of drops, as well as chains of drops. Not only do the particles glue the drops but also seem to promote the coalescence of the drops. In contrast the emulsions in the absence of the particles did not coalesce substantially under the same shear conditions.

We also studied the rheological properties of such emulsions. Very slow coalescence of PEO drops in the particle free emsulsions was also confirmed by our rheological data. Most importantly, the linear viscoelastic properties of the particle containing emulsions reveal gel-like behavior at low frequencies indicating that particle-induced bridging imparts the emulsion gel-like characteristics.

Thursday 10:10 Alpine West BE21

Small-angle X-ray scattering study of nanoclay flow-induced orientation

Angel Romo-Uribe[1], Patrick T. Mather[2], Timothy Marsh[2], and Carlos Cruz-Ramos[3]

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The influence of flow on nanoclay orientation has been characterized using small-angle X-ray scattering (SAXS). Layered silicate nanocomposites based on PVC and the modified montmorillonite Cloisite 30B were produced through an extrusion process. For comparison, the polymer/nanoclay composites were subjected to a severe flow field (shear and extensional) arising from an injection molding process. The nanostructure thus produced was characterized at the Advanced Photon Source, Argonne National Laboratory using SAXS. Interestingly, the molded bars produced in the manners described were optically transparent and did not show evidence of nanoclay agglomeration. Moreover, the mixing process produced nanoclay intercalation, as evidenced by the SAXS observations. We acquired SAXS patterns along three principle axes (gradient, neutral, and flow) and interpreted them collectively in the form of real-space microstructure. On this basis, it is concluded that the nanoclay sheets were preferentially oriented with their surfaces parallel to (normals perpendicular to) the molded bar wider surface. To our surprise, the quality of the orientation increased with nanoclay concentration while macromolecular orientation was not observed. Complementary rheological measurements revealed retarded relaxation and an enhanced rubber plateau in the nanocomposites when compared with neat PVC.

Thursday 10:35 Alpine West BE22

High rate extensional flow behavior of confectionery products – objectifying “mouthfeel”

Martin Sentmanat

Xpansion Instruments, LLC, Akron, OH 44303, United States

Extensional flows play an important role not only in the processing of confectionery products, but in the mastication and consumption of all foodstuffs. In this study, a number of commercially available confectionery products were physically evaluated in uniaxial extension at high strains and rates of deformation in an attempt to quantify the often subjective measure of food texture referred to as "mouthfeel." Samples of confectionary materials were evaluated under a controlled temperature environment from room temperature up to normal human body temperatures in order to map the window of tensile stress growth behaviors exhibited by these materials during typical mastication conditions. The high rate extensional results revealed the role of temperature on the tensile flow behavior of the confectionary materials and its subsequent impact on the human perception of food texture during mastication otherwise known as "mouthfeel."

Thursday 11:00 Alpine West BE23

Models and experiments to understand physically blown foams

Rekha R. Rao[1], Lisa A. Mondy[1], Thomas A. Baer[2], Edward M. Russick[3], Douglas A. Adolf[3], Anne M. Grillet[4], Ray O. Cote[5], Jeremy B. Lechman[1], and Andrew M. Kraynik[1]
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Foams are ubiquitous low density materials used for a variety of applications including shock, thermal, and vibration isolation of electronic components, disposable containers, and energy production. Despite their many uses, foams are still not well understood at a fundamental level. Two major categories of foam exist: chemically blown foams and physically blown foams. Chemically blown foams expand via reactions that produce a gas phase during polymerization, e.g. polyurethanes, while physical blown foams begin with a dissolved blowing agent that boils, either through increasing the temperature or decreasing the pressure, to produce cells, e.g. thermoplastic foams. For our applications, we are interested in a blown foam that starts of as an emulsion of Fluorinert® blowing agent in epoxy monomer and curative. Once this emulsion is formed, the foam precursor is injected into the mold and inserted into an oven to boil the Fluorinert®, produce foam, and cure the epoxy. The complex interplay between heat transfer, polymerization, boundary conditions and nucleation of Fluorinert® can make predetermination of the final foam density and, therefore, the amount needed to fill the mold, difficult. We are developing a homogenized continuum-level model based on a finite element discretization to help understand and predict the foaming process. This model is based on the equations of motion along with various experiments of discovery, ranging from flow visualization with temperature instrumentation to single droplet nucleation experiments. The final resulting model will be compared to foam self-expansion experiments in thin vessels where the foam is relatively isothermal and in cylindrical geometries where exotherms from the polymerization reaction dominate the physics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Thursday 11:25 Alpine West BE24

Disjoining pressure for non-uniform thin films

Bing Dai[1], Gary Leal[2], Antonio Redondo[1], and Alan Graham[1]
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The effect of the attractive forces originating from van der Waals interactions on the dynamics of thin films (<~ 100 nm) is often approximated as the disjoining pressure between two unbounded parallel interfaces. However, it is known that this concept of the disjoining pressure, as a force per unit area between parallel interfaces cannot generally be extended to films of nonuniform thickness. Based on the analysis of Yeh and coworkers, we derive a formula for the disjoining pressure for a film of non-uniform thickness by minimizing the total Helmholtz free energy for a thin film residing on a solid substrate. Unlike the previous studies, we take into account the excess energy outside the thin film region. This affects the boundary conditions at the common contact lines but not the formula for the disjoining pressure. For the limiting case of interfaces, the disjoining pressure is in agreement with the classical Lifshitz expression for the van der Waals force in this case. The derivation can be readily extended to more general non-uniform films by constructing tangential planes at both interfaces of the films. Because of the steric effects that prevent molecules from overlapping each other, the molecular size cannot be neglected when applying the mesoscopic concept of the disjoining pressure to films of thickness comparable to molecular scales.

Thursday 11:50 Alpine West BE25

ARES-G2: a new generation of separate motor and transducer rheometers

Aloyse J. Franck[1], Russ Ulbrich[2], Ming L. Yao[2], Chris Macosko[3], Ron F. Garritano[4], and John Berting[4]
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The ARES-G2 represents a new concept in rotational rheometry. Fixed test modes do not exist at the instrument level; rather test specific instructions are downloaded into the central processor prior to the start of the test. This freedom to configure a test procedure allows performing tests, unrestricted by the limitations of transient, oscillation, and steady test modes of today's rheometers. The ARES-G2 is based on separate motor and transducer (SMT) technology with a new position independent high-resolution air bearing motor and a rebalance transducer with a dynamic range of over six decades in torque. The instrument features full strain and strain rate as well as stress control capabilities in oscillation and transient experiments.

The unrestricted design of test procedures is made possible with an all-new operating system. All key components of the rheometer are independent intelligent systems orchestrated by a central processor. The data acquisition for transient and oscillation incorporates 5 standard fast data channels. The simultaneous measurement of transducer torque and displacement allows correcting for compliance and non-linear system behavior. The high data-sampling rate (2000 pt/s) in oscillation provides landmark resolution of the magnitude and phase of the measured signals, as well as the evaluation of higher harmonic torque contributions up to the 10th harmonic. Due to the wide transducer range and fast

motor control, controlled stress experiments on complex material systems can be performed with minimum influence of system inertia. The performance of the new rheometer is presented using standard reference samples as well as multiphase materials. This study concentrates on non-linear oscillation and stress controlled experiments of structured fluid systems.

Symposium SM
Entangled Solutions and Melts

Organizers: Jay Schieber and James Oberhauser

Thursday 8:05 Canyon B SM17

What is the size of a ring polymer in a ring-linear blend?

Balaji Iyer[1], Ashish K. Lele[1], and Sachin Shanbhag[2]

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In melts, ring polymers assume more compact conformations compared to linear chains with the same degree of polymerization N_R, i.e. $R_{gR} \sim N_R^{0.4}$, where R_{gR} is the radius of gyration. Upon gradually substituting some of the ring polymers with linear chains, the ring molecules swell. In the limit of infinite dilution, their size scales as $R_{gR} \sim N_R^{0.5}$. We present a scaling argument based on the blob model to capture this transition. Ring-linear blends are modeled as a semi-dilute solution of ring polymers in a "good-solvent" consisting of linear chains. The model predicts that the size of the ring polymer remains unchanged up to the overlap concentration c_R^*. Beyond c_R^* the size of the ring shrinks according to $R_{gR} \sim c_R^{-1/5}$. The overlap concentration depends on the degree of polymerization of the ring according to $c_R^* \sim N^{-1/2}$. These predictions were tested by performing Monte Carlo simulations of ring-linear blends using the bond-fluctuation model. The results of the simulation for N_R =150 and 300, blended at different concentrations with linear chains of the same degree of polymerization validate the scaling mod

Thursday 8:30 Canyon B SM18

A model for predicting linear viscoelastic response of entangled flexible ring polymer melt.

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We present a mean field coarse grained tube model for predicting the linear viscoelastic response of flexible ring polymers in a topologically constrained obstacle environment (such as a ring in a cross-linked gel devoid of solvent or a melt of flexible rings) over a wide frequency range. Following the Rubinstein and Colby[1] arguments, we propose that the dynamic response of a ring chain is composed of a linear superposition of independent modes corresponding to the response of different length scales. We propose a mixing rule, based on our Pom-Pom Ring constitutive equation[2], to capture the amoeba like self-similar dynamics of a ring chain. Our model predicts a power-law dependence of the gain and loss moduli above the crossover frequency in agreement with the Rubinstein and Colby[1] scaling arguments. Furthermore, the predictions of our model are found to be in semi-quantitative agreement with Roovers frequency sweep data for one particular poly(butadiene) ring melt.[3]

[1] Rubinstein, M.; Colby, R. H., *Polymer Physics*; Chap. 9, Oxford University Press: New York, **2004**, 412.
[2] Iyer, B. V. S.; Lele, A. K.; Juvekar, V. A. *Phys. Rev. E* **2006**, 74, 021805 1-12.
[3] Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, 16, 843-849.

Thursday 8:55 Canyon B SM19

Rheology of oligomeric ionomer melts

Robert A. Weiss

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The rheology of low molecular weight PS sulfonated polystyrenes was studied by steady shear and dynamic shear measurements. The molecular weight of the starting PS (Mw ~ 4000/mol) was far below the entanglement molecular weight, and the oligomer behaved extensively as a Newtonian fluid. The introduction of bonded alkali metal sulfonate significantly increased the viscosity of the melt and produced not only non-linear viscosity behavior, but also generated finite elastic effects (i.e., a first normal stress coefficient). The magnitude of the viscosity and elasticity increased as the size of the concentration of the ionic species increased and the size of the cation decreased. The latter quantity is inversely related to the strength of the ion-pair. The ionomer melt rheology can be explained by an ion-hopping mechanism, whereby nanophase separated ionic aggregates behave as labile crosslinks or entanglements. A rubbery plateau typical of a crosslinked polymer was observed in the dynamic measurements, and the magnitude of the plateau modulus was a function only of the ion concentration. The rheological material functions, however, depended on the choice of the cation, which controlled the kinetics of the ion-hopping mechanism. As few as two metal sulfonate groups per chain (on average) increased the zero-shear viscosity, the zero-shear first normal stress coefficient and the terminal relaxation time of PS by as much as 7, 9 and 9 orders of magnitude respectively. In some instances, shear thickening behavior was observed, which is commonly seen in structured solutions or melts.

Thursday 9:20 Canyon B SM20

Probe rheology II: terminal dynamics and glass transition of probe chains in a heterogeneous entangled network

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We systematically investigate the terminal and glassy dynamics of a small fraction of short entangled probe chains in a high MW matrix consisting of a different polymer. The longest relaxation time for the probe chains can be measured as $1/\omega_{peak\_G"}$. Different temperature dependences for the friction coefficients of the components lead to failure of time-temperature superposition. However, the temperature dependence of the terminal peak is in good agreement with the self-concentration model of Lodge and McLeish [1], although the self-concentration effect is found to be even stronger than predicted. On the other hand, the corresponding glassy peak for the probe chains is not observed, because the "effective" Tg is not the temperature of a real material transition.

In the case of immiscible polymer blends, the different phases retain their individual temperature-dependent rheology, so time-temperature superposition also fails. Although the temperature-dependence of the probe chains dynamics is the same as observed in the bulk, the dispersed phase is affected by the matrix and the dynamics is significantly slower than observed for the corresponding pure polymer. This is considered to be a consequence of a confinement effect [2]. The most striking observation is that the Tg of the dispersed phase is higher than the Tg of the bulk polymer. This is the first report of a Tg increase for a polymer dispersed in a matrix at the micrometer scale. A possible explanation is the confinement by the matrix entangled network [2,3], which also leads to a slower terminal relaxation.

[1] TP Lodge and TCB McLeish, Macromolecules 2000 33 5278. [2] R Kausik, C Mattea, N Fatkullin, R Kimmich, J. Chem. Phys. 2006 124 114903. [3] V Thirtha, R Lehman, T Nosker, Polymer 2006 47 5392.

Thursday 10:10 Canyon B SM21

Investigation and modification of the melt rheology of olefin block copolymers

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The melt rheology of novel Olefin Block Copolymers (OBCs), recently developed by The Dow Chemical Company, was investigated. The melt shear rheology of OBCs was found to be similar to that of linear random copolymers of ethylene and alpha olefins. Furthermore, the melt rheology of OBCs can be modified to target certain specific application areas by chemical means or by blending with traditional polyolefins with broader molecular weight distributions or those containing long chain branching. The presentation will discuss the basic modeling of the melt rheology and the results of melt rheology modification by physical blending with high melt streght polymers and by chemcial means involving peroxide/coagent treatment.

Thursday 10:35 Canyon B SM22

Viscoelasticity of polypropylene carbon nanotube composites: effect of functionalization and processing conditions

Vinod K. Radhakrishnan, Brian J. Downs, Dhriti Nepal, and Virginia A. Davis
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We compare the combined effects of processing conditions and nanotube chemistry on the rheological and thermal properties of extruded 12 MF polypropylene (PP) nanocomposites. The PP nanocomposites contained either 0.5 vol% SWNTs, VGCF, or R-SWNTs. Statistically designed experiments were conducted to examine the combined effects of extruder temperature, screw speed, and recirculation time. The range of extruder temperatures, screw speeds and recirculation times were 190 - 230 C, 30 - 80 rpm and 8 - 20 min. respectively. Two preliminary processing techniques were also compared. In the case of dry mixing, functionalization only resulted in higher complex viscosities for the most severe processing conditions. In the case of solvent intercalation using 1,2 dichlorobenzene, complex rheological behaviors indicative of more highly dispersed nanotubes were observed for most processing conditions.

Thursday 11:00 Canyon B SM23

Effect of pressure on shear-induced crystallization of isotactic polypropylene

Jen Shueng Tiang and John M. Dealy
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There have been a number of reports of the effects of shear flow on the crystallization kinetics of molten polymers and on the morphology of the cooled product. One reason for this interest is that in plastics processing, particularly in injection molding, solidification follows immediately after a short period of high-rate shearing. Since the filling of the mold and the solidification that follows occur at high pressure, it is of interest to know how pressure affects shear-induced crystallization. To study this, we used a high-pressure sliding plate rheometer modified by the addition of a bifurcated optical fiber probe to monitor turbidity and shear stress simultaneously. An isotactic polypropylene was studied. In addition to monitoring the kinetics, the crystalline phase and morphology of the cooled samples were characterized using wide angle X-ray scattering and microscopy techniques. Shear rates up to 300 s^{-1} and pressures up to 70 MPa can be generated using the rheometer. The combined effect of these conditions on the enhancement of crystallization kinetics and the formation of certain crystalline phase and morphology were determined.

Thursday 11:25 Canyon B SM24

Experimentally observed criteria for flow induced crystallization in polymers

Deepak Arora[1], Fei Li[2], and H. Henning Winter[3]

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Early stages of crystallization were studied in a new rheo-optical shear rheometer that allows high shear rates on small polymer samples ("on a pellet" of polymer). Shear stress, birefringence, light transmission, small angle light scattering (SALS), and optical microscopy are measured in a single experiment while the crystallization proceeds. Synchronization of these measurements allows comparison of characteristic time scales of crystallization: instant of liquid-to-solid transition from rheology, onset of birefringence due to crystallization, half time of transmission decay, time for maximum density fluctuation from Vv-SALS, growth of crystallinity from Hv-SALS, growth of sperulites from optical microscopy. Dimensionless groups will be defined and evaluated for crystallizing poly 1-butene. For the crystallization experiments, the samples were annealed above their crystallization temperature, then cooled below the crystallization temperature, sheared at large strains, and then crystallized at constant temperature.

Thursday 11:50 Canyon B SM25

Thermoforming wedges

Katie L. Lieg and A. Jeffrey Giacomin

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To make straight edges in rigid plastic packaging, we must thermoform wedges. We think this problem constitutes the simplest relevant problem in thermoforming. Here a thin, nearly flat, sheet of molten plastic stretches by inflation into a straight interior edge of a mold. Analytical solutions for thermoforming wedges from uniformly thin, highly viscous Newtonian polymer sheets are presented including both the free and constrained stages. Free forming is before the melt touches the prismatic mold, and constrained forming, after. Translating cylindrical coordinates are used to find the developing thickness profile, stress, manufacturing time and the wedge's edge sharpness. Finite element simulations of this extensional flow problem, obtained using Polyflow(tm), are compared with our new analytical solution.

Symposium SG
Solids and Glasses

Organizers: Henning Winter and Mataz Alcoutlabi

Thursday 8:05 Canyon A SG1

Impact fatigue of cross-linked rubbers in simple extension

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Fatigue failure of various materials is commonly studied under periodic loading. There are, however, many cases when cross-linked rubbers should work under periodic or random impacts. We call this type of failure impact fatigue. In this report, some results of experimental and theoretical/numerical studies of impact fatigue of cross-linked rubbers under simple extension are presented. Since no commonly accepted theory currently exists for describing large deformations and nonlinear relaxations of rubbers, an experimental program has been developed on the example of simple extension. In these experiments, we attempted to separate nonlinear solid-like viscoelastic effects from the damage accumulated in the rubber. Modeling effort consists of two parts. The first part analytically/numerically describes our experimental data for large deformations and nonlinear relaxations in a medium range of stretching ratios where the rubber damage has not been observed. The second part involves the damage effect into the modeling. Here some modifications of existing damage theories are used to describe large deformations and viscoelastic effects in rubbers. Some molecular interpretations of presented damage results will be made. A 3D extension of the model will also be presented.

Thursday 8:30 Canyon A SG2

Mechanics of rubber shear springs

Alan N. Gent[1], Jong Beom Suh[2], and S. Graham Kelly[2]

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To maintain a simple shear deformation in a rubber block, compressive and shear stresses are needed on the end surfaces as well as on the bonded plates [1]. However, the end surfaces are generally stress-free, and the stress system necessary to maintain a simple shear is thus incomplete. Surprisingly large consequences follow from this failure to apply the requisite stresses on the end surfaces, even when the block is long and thin and the conditions at the ends might be thought unimportant. (We note that boundary conditions differ from an "end effect" that would become small at points far from the ends: they affect the stresses everywhere.) The magnitude of these effects has been studied by FEA for a long thin rubber block, sheared in the length direction [2], and for a long rubber tube, sheared azimuthally and axially [3]. High normal

stresses are generated internally, maintained by restraints at the bonded surfaces. They are generally of second order and thus rise rapidly as the imposed strain increases. Correspondingly high hydrostatic tensions are set up in the interior, sufficient to cause internal fracture in a soft rubbery solid. Fracture energies are determined for bond failure at either end of the bond, but the results are inconclusive - it is not clear where bond failure will occur.

References: [1] R. S. Rivlin, Philos. Trans. Roy. Soc. (Lond.) Ser. A, 241 (1948)379- 397. [2] A. N. Gent, J. B. Suh and S. G. Kelly, III, Internatl. J. Non-Linear Mech.,42, (2007) 241-249. [3] J. B. Suh, A. N. Gent and S. G. Kelly, III, in preparation. [4] A. Wineman, Internatl. J. Non-Linear Mech. 40 (2005) 271-279.

Thursday 8:55 Canyon A SG3

Biodegradable double networks incorporating Polyhedral Oligosilsesquioxane (POSS) moieties

Kyung-Min Lee and Patrick T. Mather
Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

New biodegradable polymer thermosets have been prepared to contain polyhedral oligosilsesquioxane (POSS) moieties and their thermomechanical properties were characterized to revealing surprising behavior. POSS-initiated poly(d,l-lactide-co-glycolic acid) (POSS-PLGA) and POSS-initiated poly(ε-caprolactone) (POSS-PCL) diols featuring a central POSS moiety were prepared by ring opening polymerization and were subsequently terminated with acrylate groups. Such telechelic macromolecules allowed photo-activated addition to a tetrafunctional thiol and covalent network formation. Furthermore, evidence for a superimposed physical network was witnessed, motivating a study of self-assembly in the POSS-initiated macromer itself. Indeed, melts of POSS macromers (POSS-PLGA and POSS-PCL diols) were observed to form supramolecular assemblies that gelled during cooling, as characterized by linear viscoelastic shear moduli obtained while cooling below a critical temperature interpreted as a crystallization temperature for POSS. In covalently crosslinked form, our biodegradable thermosets exhibited two clearly separated rubber plateaus: (1) above Tm for POSS from the covalent crosslink junctions, and (2) below Tm for POSS where the latter is augmented by POSS crystals. With such a structure, "double fixing" shape memory behavior is possible. We will discuss the materials preparation, structure property relationships, and novel shape memory response, while also indicating applications for such materials.

Thursday 9:20 Canyon A SG4

Rheology, thermal transitions and small-angle X-Ray scattering of polyurea elastomers

Jai A. Pathak[1], Peter H. Mott[1], C. M. Roland[1], Derek Ho[2], Eric Lin[2], Mary K. Vukmir[3], and Thomas H. Epps, III[3]
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To elucidate the molecular and physical mechanisms underlying the superior mechanical and impact-resistance of Polyurea elastomers, we have studied their thermal properties by Differential Scanning Calorimetry (DSC), Fourier space microstructure by Small-Angle X-ray scattering (SAXS) and linear viscoelasticity by oscillatory shear and temperature sweep rheometry. DSC on polyurea yields the glass transition temperature, $T_g = -59\,^{o}$ C, the Order-Disorder Transition (ODT) temperature, $T_{ODT} = 155\,^{o}C$ and the melting point, $T_m = 210\,^{o}C$, of the hard segments (based on diisocyanate). The T_{ODT} determined by DSC is in excellent agreement with that determined from dynamic temperature sweep rheometry. SAXS data on Polyurea show a peak in the scattering intensity at non-zero wavevector at room temperature, confirming structure due to both crystallinity and microphase separation. Upon annealing the sample between T_{ODT} and T_m, and then performing SAXS on the quenched sample, the scattering intensity peak shifts to lower wavevectors, indicating growth of the crystal long periods. We have also performed SAXS on Polyurea samples stretched both in an Instron tensile tester (quasi-static conditions), as well as in a home-made high strain-rate tensile tester to study the effect of strain/strain rate (during uniaxial elongation) on microstructure. Slowly deformed Instron samples show pronounced orientation and anisotropy in scattering, while samples deformed at high strain rate show little orientation and isotropic scattering. Current studies are focusing on the linear viscoelasticity of samples annealed in the rheometer just above T_m, followed by quenching to just above T_g, and then measuring the segmental peak in the loss modulus at different temperatures near and above T_g. We will compare these peak times to α relaxation times measured by dielectric spectroscopy.

Thursday 10:10 Canyon A SG5

Connections between the rheology of glassy materials and the mechanical unfolding of proteins

Nathan Duff and Daniel J. Lacks
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Molecular simulations are carried out to address the response to applied stress for both glassy materials and proteins. In both cases the system distorts in response to the stress - the glassy material undergoes plastic flow while the protein is stretched and unfolds. We show that the processes are similar in the two systems, and the behavior is controlled by a dynamic energy landscape that changes as the system is strained: The energy minima and energy barriers move in configuration space, change in depth/height, and are created and destroyed via fold catastrophes. The nature of the response to strain is based on the balance between the rate of the changes of the energy landscape and the rate of thermally activated transitions between energy minima. The underlying basis of stress-induced phenomena such as "rejuvenation" and stress-induced ordering are addressed in these systems.

Thursday 10:35 Canyon A SG6

Pressure relaxation of polystyrene and comparison to the shear response

Yan Meng and Sindee L. Simon

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Isothermal pressure relaxation is measured for a polystyrene after volume jumps as a function of temperature in two pressure ranges using a self-built pressurizable dilatometer. Master curves for pressure relaxation are obtained by time-temperature superposition. Time-pressure superposition is found to exist when the responses are compared at their respective Tgs. The results are compared with those from shear creep compliance measurements made by Plazek for the same material. It is shown that the bulk and shear shift factors have the same (T-Tg) temperature dependence. Furthermore, the retardation spectra for the two functions are identical at short times. However, the long time mechanisms present in the shear response are absent in the pressure relaxation response. The results indicate that Leaderman was incorrect in his supposition that the molecular origin of the bulk and shear relaxation responses differed.

Thursday 11:00 Canyon A SG7

Time-resolved synchrotron study of double yield points in LLDPE

Angel Romo-Uribe[1], Angel Manzur[2], and Roberto Olayo[2]

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Small-angle X-ray scattering (SAXS) patterns and stress-strain traces were obtained simultaneously during in-situ uniaxial deformation of extruded tapes of linear low density polyethylene (LLDPE) at room temperature. Deformation in the elastic region below the first yield point induced an increase in the lamellar long period and in the degree of crystallinity. In the valley region, between the first and second yield points, the lamellae were axially deformed by a slip process towards the tensile direction as reflected by the split of the meridional reflections into off meridional reflections. Further deformation in the second yield point region produced a gradual rotation and thinning of the off-meridional reflections indicating that the lamellae were being destroyed by a shear process. At the same time, intense small-angle amorphous scattering arose due to the production of microvoids. Finally, in the plateau of plastic deformation, after the second yield point, the SAXS pattern showed diamond-like reflections with streaks along the equatorial axis, and new meridional reflections. That is, a semi-crystalline fibrillar morphology was produced with shorter long period, and microvoids oriented along the tensile axis.

Thursday 11:25 Canyon A SG8

Rheology of soft glasses and gels during solidification

H. Henning Winter

Chemical Engineering Dpt. and Polymer Science and Eng Dpt., University of Massachusetts, Amherst, MA 01003, United States

Two (!) material parameters define linear viscoelasticity of materials directly at the transition from liquid to solid ("critical gels"). Even more astoundingly, this same rheological behavior has been observed experimentally for a wide range of materials that solidify by different connectivity mechanisms, some of which connect through attractive forces and others through internal repulsion of their constituents. For this multiplicity of materials (gels and soft glasses), the critical gel dynamics is indistinguishable from one another except for the specific value of the two rheological parameters. These observations raise the question whether the critical gel state is universal or whether other rheological patterns are allowed for the transition. However, even if the critical gel behavior might be universal, large differences have been reported for the dynamics in the vicinity of the liquid-to-solid transition (in so-called "nearly critical gels") when materials approach the transition from either side. Connectivity differences become also apparent when exploring critical gels at large deformations that affect the internal structure ("shear melting", for instance). Experimental observations will be shown for several classes of materials.

Thursday 11:50 Canyon A SG9

Mode-coupling theory for linear viscoelasticity and flow behavior of colloidal suspensions near the glass transition

Jérôme J. Crassous[1], Miriam Siebenbürger[1], Matthias Ballauff[1], Oliver Henrich[2], David Hajnal[2], Matthias Fuchs[2], and Markus Drechsler[3]

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The flow behaviour and the linear viscoelasticity of concentrated thermosensitive core-shell dispersions have been interpreted by a schematic model based on the mode-coupling theory (MCT). To this purpose thermosensitive core-shell particles consisting of a polystyrene core and a crosslinked poly(N- isopropylacrylamide)(PNIPAM) have been synthesized. The particles crystallize for effective volume close to the hard spheres. The effective volume determined from dynamic light scattering, cryogenic transmission electron microscopy and experimental phase diagram has been adjusted varying both concentration and temperature. The reduced flow curves performed in the metastable state were found to be a unique function of the effective volume fraction as well as the reduced loss and elastic moduli from the dynamic measurements. The quantitative analysis of the results supported by microscopic calculations suggests that a theoretical approach biased on the mode coupling theory captures the basics of the dynamics of hard spheres dispersions in stationary flow experiments as well as in the linear viscoelastic domain.

Poster Session

Symposium PO
Poster Session

Organizer: Rajesh Khare

Wednesday 6:00 Grand Ballroom C PO1

Validating phase angles in oscillatory testing

Sachin Velankar[1] and David Giles[2]

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The accuracy of oscillatory measurements hinges critically on the accuracy with which the phase angle, *delta*, can be measured. We have shown that it is the accuracy of *tan delta* that is important for determining G' in the terminal region (and *tan delta* measurements become increasingly inaccurate as *delta* approaches 90 degrees). [Rheology Bulletin, Vol. 76, No. 2, (July 2007)]. Practically, it is difficult to gauge the accuracy of phase angle measurements because rheometer manufacturers generally do not give specifications for phase angle accuracy, and only few viscoelastic standards have been specified for phase angle calibration. We show that linear monodisperse well-entangled melts are excellent standards for validating the phase angle in the terminal region. Such a material has a sharp transition to its terminal region as frequency is reduced, and thus is in the terminal region even when the phase angle is still far from 90 degrees, where *tan delta* is still easy to measure. Phase angles closer to 90 degrees can then be validated by verifying that the rheometer reproduces the expected terminal behavior, (*tan delta* inversely proportional to frequency as frequency approaches zero). Using such a linear monodisperse well-entangled fluid as a viscoelastic standard, we conduct validation tests on a TA AR2000 rheometer and show that the rheometer can measure *tan delta* values on the order of 1000 accurately, provided that the strain is sufficient. We highlight the contributions of angular displacement and torque to errors in phase angle and suggest ways to improve the accuracy of oscillatory measurements in the terminal region.

Wednesday 6:00 Grand Ballroom C PO2

Fast sampling in oscillation mode

Aadil Elmoumni[1], Peter Hodder[2], and Bernard Costello[2]

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Conventional oscillatory rheology requires at least one cycle of data to be analyzed. This limits the rate at which sample points can be acquired to the frequency of oscillation. TA Instruments has therefore developed two methods of increasing the rate of acquisition of sample points. The first method is Fast Oscillation where the analysis is conducted at twice the experimental frequency by running two correlators in parallel, offset by 180 degrees. The second method is using a Raw Signal Data Logger, which operates in real time; fundamental instrument information such as the torque, displacement, normal force and geometry gap can be logged at just under a kilohertz. Detailed information about these two techniques along with experimental data is shown.

Wednesday 6:00 Grand Ballroom C PO3

Response of viscoelastic fluids under combined oscillatory shear and compression flow

Jae Hee Kim, Jun Hee Sung, Jung Gun Nam, Kyung H. Ahn, and Seung J. Lee

School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea

A new rheometer has been designed to investigate the microstructural rearrangement as well as rheological responses by combining two-deformation modes, which are oscillatory shear and compression. Although the realistic flow field is more complicated than the combination of two different flow types, it is useful in understanding the flow behavior of complex fluids in well-defined complicated flow field and overcome the limitation of conventional rheometry which has been confined mostly to shear flow and small deformation. In this sense, this work is expected to contribute to the productivity enhancement as well as to understanding the physics of complex fluid flows. In this presentation we propose a novel method to determine the rheological responses of viscoelastic fluids under combined oscillatory squeezing and mixed-flow field and provided a comprehensive theory for the interpretation of experimental data from the newly developed mixed-flow rheometer. A series of experiments was also carried out with PDMS (Polydimethylsiloxane) to prove its relevance.

Wednesday 6:00 Grand Ballroom C PO4

Yield stress measurement of biofluids

Daniel De Kee and Kyle Frederic
Tulane University, New Orleans, LA, United States

Biofluids such as blood, as well as other structured materials, exhibit rather complex rheological behavior. The material yield stress is one property associated with multiphase systems that involve a three dimensional microstructure with colloidal length scales. Most yield stress determinations rely on the extrapolation of viscometric data to zero shear rate. This causes large errors. In addition, the yield stress of blood (~ 10-3 Pa) is 3-4 orders of magnitude below the yield stress of foodstuffs for example. Experimental techniques that do not rely on extrapolation can measure yield stress values as low as ~ 1 Pa. The purpose of this investigation is to accurately determine the yield stress of blood via our novel slotted-plate technique. Our novel slotted plate apparatus is the only technique that can accurately (without extrapolation) measure the very low yield stress of blood. It is also able to detect changes in blood yield stress due to the presence of medication such as aspirin for example.

Wednesday 6:00 Grand Ballroom C PO5

Twelve years of EC-motors in rotational rheometers

Joerg Laeuger
Anton Paar Germany GmbH, Stuttgart, Germany

The main components of a rotational rheometer are the motor with its supporting bearings systems and the force measurement. In one design, commonly referred as CR (controlled rate or controlled strain), a displacement or speed is applied to the sample by a motor and the resulting torque is measured separately by the use of an additional measuring sensor. In a so-called CS (controlled stress) rheometer, an electrical current is applied and builds up a magnetic field, which produces an electrical torque. In such a design there is no separate torque sensor needed, since the torque signal is calculated from the motor current. The movement of the motor shaft is measured by an angular displacement sensor. Most CS instruments still employ a drag-cup motor like in the first CS instrument, the Deer Rheometer build in 1968. In 1995 Anton Paar introduced a rheometer equipped with an electronically commutated synchronous Motor (EC-Motor) and Digital Signal Processor (DSP) technology. In the meantime the EC-motor technology is now for 12 years and in the third generation of instruments commercially available, making the technology with more than 2000 installations word wide clearly well established. Although the basic principle of a EC-Motor based rheometer has been described earlier, there certainly is still a need for a better explanation of this unique rheometer drive technique and its consequences. In addition since its first introduction significant improvements, due to the use of enhanced electronics, improved materials, and more sophisticated control mechanisms, have been implemented. The aim of the paper is to describe the principle, the properties and the unique features of an EC-Motor and its differences to other rheometer drive systems. The specific configuration and the performance of the EC-motor and air bearing assembly as it is used in current commercial rheometers are discussed on typical experiments relevant for modern research on rheological topics.

Wednesday 6:00 Grand Ballroom C PO6

Characterizing low viscosity material under fast deformation: experiments & frustration

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In IT industry, precise control of coating or chip-on-glass process is becoming one of the key issues for achieving high-quality and robust product, and it requires rheological prospective as in many other process in that field. Coating material or ink in these processes has much lower viscosity compared to pastes or polymer melts, yet they are still complex system with the particle of sub-micron size and its binder material. Moreover, the characteristic length / time scale in the process is very small which makes problem more difficult. How can we evaluate their rheological property properly, duly reflecting the situation they experience in real system? Here we bring two different inks that have similar zero shear viscosity of about 10 cp, and yet show different behavior in inkjet printing process. Conventional rheometry and unconventional measurements are both tried to distinguish them, to find out the way to save the expensive inkjet nozzle from blocking.

Wednesday 6:00 Grand Ballroom C PO7

Rheological analysis of highly shear-thinning shampoo using multiple ranges of Brookfield instruments in cone-plate and coaxial-cylinder geometries

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A commercial shampoo was analyzed at 25 ºC, from 0.04 to 500 s^{-1}, using Brookfield DV-III+CP rheometers having LV, RV and HB spring torque ranges and the CPE-41 cone spindle. Three aliquots were run in each case and the HB-range data comprised three trials per aliquot. Repeatability was very good - all data sets were easily within the ± 1% of Full Scale Range or "FSR" tolerance at each combination of spindle, spring torque range and speed. Narrow-gap, coaxial cylinder geometry experiments were performed at 25 ºC, using the Brookfield DIN Adapter, from 0.026 to 322.5 s^{-1}. The LVDV-III+ rheometer was used with DIN-85 -86 spindles, and the RVDV-III+ rheometer was used with the DIN-85, -86 and -87 spindles. Three aliquots were analyzed by each apparatus; most tests involved three runs per aliquot. Standard deviations and 95% confidence intervals for the data sets were within the ± 1% FSR tolerance, as well. Calibration verifications were performed for all instruments, using certified viscosity standards, thus ensuring measurement accuracy. Apparent viscosities ranged from near-Newtonian plateau values of approximately 10,000 cP at the lowest shear rates for the cone-plate and DIN geometries, to approximately 300 and 400 cP, respectively, at the highest shear rates. Furthermore, the data from the two geometries were in agreement with one another to a few percent. In conclusion, the suitability of these systems - as demonstrated by good precision and accuracy - for viscometric or rheological analyses of highly shear-thinning polymeric solutions was confirmed, over wide shear rate and viscosity ranges.

Wednesday 6:00 Grand Ballroom C PO8

Using capillary break-up to determine the maximum tensile strength of liquids at low stressing rates

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The maximum tensile strength of fluids is an important guide to the onset of cavitation. Being able to predict the onset of cavitation is important in formulation for industries as diverse as printing and automotive industries. A technique has been developed to use break-up in a CaBER to determine the maximum tensile strength, and the technique has been applied to a range of concentrations and molecular weights of polyethylene glycol. The results have been validated by comparison with the values and behaviours observed from the bullet piston apparatus. The advantages of using the CaBER are that it requires significantly less time and material for operation and that it can probe lower stressing rates than the bullet piston apparatus.

Wednesday 6:00 Grand Ballroom C PO9

Accurate temperature control for rotational rheometers

Joerg Laeuger

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Since temperature has a great influence on the rheological behavior, controlling the temperature with a high precision is crucial to receive reliable rheological data. The advance of rheo-optical and other structure probing techniques makes the task of accurate temperature control even more challenging. A temperature control unit has to fulfill three main tasks: 1. Setting and measuring the right absolute temperature, 2. Maintaining a constant temperature without having temperature gradients throughout the sample, 3. Producing no significant temperature overshoots during the control process. In order to design and validate various temperature control units a special method was developed, which employs sensor plates with up to four temperature probes located at different position within the plates. All probes are calibrated against each other and against an external reference probe. These plates are used to measure the absolute temperature and the horizontal and vertical temperature gradients at the sample location for various temperature control systems based on different principles. 1. Peltier temperature control with an actively Peltier controlled bottom plate and an actively Peltier controlled hood. 2. Electric resistance heating systems with electrically heated bottom plate and electrically heated hood. 3. Convection temperature devices based on a combination of radiation heating and forced gas convection. For the later the temperature distribution was determined for parallel-plate geometries, for solid torsion bars, and the SER extensional fixture, respectively. In case of the Peltier and the electrical control units temperature distribution for the standard as well as the various available rheo-optical systems are shown. The temperature measurements presented show that with a proper engineering it is possible to design temperature control units, which do not have any significant temperature gradients and fulfil the requirements for an accurate temperature control.

Wednesday 6:00 Grand Ballroom C PO10

PVT instrument for pressure relaxation measurements

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A pressurizable dilatometer was built for PVT and pressure relaxation measurements at pressures up to 250 MPa and temperatures to 250 C. The instrument consists of a load cell of approximately 1.8 cm^3 in which the sample is surrounded by oil as a pressurizing fluid. The system is pressurized by a piston made of hardened steel whose position is controlled by a stepper motor with a resolution of 3.53×10^{-6} cm per step. Considering the backlash of the gear and the temperature instability, a conservative resolution of 7×10^{-6} cm^3 can be achieved, which is much better than other PVT instruments. The piston position is measured by a linear variable differential transducer mounted at the end of the piston. Temperature stability is better than 0.01 C. The sensitivity and reproducibility of PVT measurements is discussed. In addition, the pressure relaxation response of polystyrene is shown in the vicinity of Tg(P) and measurement linearity is discussed.

Wednesday 6:00 Grand Ballroom C PO11

Real-time determination of the gelling characteristics of time-dependent fluids

David M. Binding[1] and Paul M. Phillips[2]

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When a fluid is subjected to a kinematic history for which the strain is sufficiently small, the theory of linear viscoelasticity provides an unequivocal and complete description of the dynamics. The most convenient technique for determining linear viscoelastic properties is the application of a small-amplitude sinusoidal strain (or stress) at a fixed frequency, repeated for a range of frequencies. Data at low frequencies need longer experimental times, with disadvantageous consequences for time dependent materials. We are concerned with fluids that undergo a chemical reaction resulting in a transition from a low viscosity fluid through a gelling process to a highly elastic solid. Controlled stress rheometers, such as the TA Instruments AR2000, have the facility to apply to a sample a strain profile in the form of a composite wave. The complex modulus is determined at those frequencies simultaneously, using Fourier decomposition techniques. Although its use is not common, the composite wave technique has advantages in the case of time-dependent fluids for which data may be collected at different frequencies simultaneously while the fluid is in the same state. It has the potential to supply data in a very much reduced time scale. This presentation will report on experiments aimed at optimising the determination, in real time, of the gelling characteristics of time-dependent fluids. Using model polymeric solutions for which the characteristic time scales for the gelling process can be controlled through control of the temperature, experiments are performed using multi-wave inputs to determine the most appropriate procedures for obtaining the required information (complex modulus) as accurately and as quickly as possible. On the theoretical side, the fundamental equations controlling the response of a sample to a small-amplitude multi-wave input are analysed to try to determine criteria for the specification of appropriate frequencies and partial amplitudes to enable the required data to be obtained optimally.

Wednesday 6:00 Grand Ballroom C PO12

Preventing wall slip in rheology experiments

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Wall slip is a common problem when testing highly concentrated emulsions or suspensions on a rheometer. It is usually caused by large velocity gradients in a thin region adjacent to the wall. When slip occurs, the measured viscosity can be significantly lower than the actual viscosity of the sample. To overcome the influence, we have introduced a series of roughened surface geometries such as crosshatched or serrated plates, which help significantly improve the contact between geometry and sample to reduce slip. A vane shaped geometry with grooved inner surface cup is also considered to be effective to reduce wall slip. Experimental data have shown the influence of wall slip to rheological test results and the improvement when the crosshatched geometries were used.

Wednesday 6:00 Grand Ballroom C PO13

Ubiquity of domain patterns in sheared viscoelastic fluids

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A universal domain pattern is observed in flowing multi-phase complex fluids that fall within the simple paradigm of interacting soft viscoelastic domains suspended in a less viscoelastic fluid under shear. Specific examples of this effect are presented for three strikingly different complex fluids, all of which exhibit the same shear-induced morphology. We offer a physical argument that relates this phenomenon to the elasticity of the dispersed phase and an approximate internal Weissenberg number, suggesting a physical mechanism of pattern formation. Isolated droplets of the more viscoelastic phase deform under shear and exhibit a rocking motion around the vorticity axis reminiscent of the Jeffery orbits exhibited by rigid rods. The pattern is linked to the combined effects of vorticity elongation and inter-particle repulsion in the flow-gradient plane arising from the local dynamics of individual droplets.

Wednesday 6:00 Grand Ballroom C PO14

A generalized, thermodynamically-founded Giesekus model incorporating chain finite-extensibility and bounded free energy effects

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Guided by the GENERIC [1] and bracket [2] nonequilibrium thermodynamic formalisms, we present a generalized single-conformation tensor based viscoelastic model which reduces to known rheological models, such as the Giesekus, the Phan-Thien/Tanner and the FENE-P ones, under certain limiting conditions. The new model incorporates the dissipation or friction matrix corresponding to anisotropic hydrodynamic effect of the Giesekus model but, in addition, accounts for the finite-extensibility effect as well as for change in the relaxation spectrum in the spirit of the White-Metzner model. Key elements of the new model are the free energy function (associated with the elasticity of the fluid) and the friction matrix (associated with dissipation effects). In essence, the new model extends or corrects the Giesekus model to account for the finite extensibility of the chain at high deformation levels. We test our new model in both simple shear and extensional flows, discuss its capability to fit available rheological data for a number of polymers, and comment on the possibility it offers to accommodate within the constitutive equation more complicated, bounded expressions for the free energy [3] of the deformed liquid such as those proposed for highly elastic materials.

References: 1. Öttinger, H.C. "Beyond equilibrium thermodynamics" (John Wiley & Sons, Hoboken, New Jersey, 2005). 2. Beris, A.N.; Edwards, B.J. "Thermodynamics of Flowing Systems" (Oxford University Press, Oxford, 1994). 3. Housiadas, K.D.; Beris, A.N., J. Non-Newtonian Fluid Mech. 2006, 140, 41-56.

Wednesday 6:00 Grand Ballroom C PO15

High concentration viscosity behavior of light, heavy and bitumous oils: comparison with model polymeric molecules

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Using the analogy of polymer coil overlap concentration were an abrupt change in slope of viscosity versus concentration is seen, oils seem to show a range of concentration dependencies beyond their overlap concentration. Given that the molecular weights of the oils are low, as measured by intrinsic viscosity, the viscosity - concentration behavior of a number of polymers of differing geometries and conformations but having the same or similar molecular weight ranges are compared. Some explanations for this behavior are discussed.

Wednesday 6:00 Grand Ballroom C PO16

3D numerical study of multilayer coextrusion

See Jo Kim[1], Kyung-Hun Lim[1], Patrick C. Lee[2], and Chris Macosko[3]
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It is of great importance to obtain the uniform layer thickness in the multilayer coextrusion processes. In this work, to understand the mechanism of the layer distribution, the 3D FEM was developed and used for the precise 3D flow analysis in the multilayer coextrusion die. The multilayer distribution was numerically visualized and analyzed using the best algorithm of the fluid particle tracking developed in this study at the arbitrary cross-section of the coextrusion die. In addition, numerical results for layer thickness distributions were compared to the corresponding experimental results.

Wednesday 6:00 Grand Ballroom C PO17

Rheology of chocolate seen from a different point of view

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Since the OICCC introduced rheological tests to control the quality of chocolates, measuring the viscosity and the yield stress are a must in the quality assurance of the chocolate industry. An important property for the success of a chocolate, which cannot be predicted using viscosity or yield stress data, is mouthfeel. To better understand how to achieve the desired mouthfeel and other physical properties, more detailed measurements on the basic materials, for example the fat contained in the chocolate, as well as on the final product are needed.

When talking about the recipes of chocolate, the fats used and their complex crystallization behaviour are amongst the most important factors to look at. The different crystalline phases and their individual crystallization points are often difficult to distinguish using a DSC.

With an oscillating rheometer different crystallization points can be observed separately. Using an instrument that combines rheometry and microscopy (RheoScope) the melting or crystallization can be followed with rheological methods while at the same time the growth of the crystals and their individual shapes can be observed.

The hardness of the chocolate and the force needed to break it also have to fulfil certain consumer expectations. With a special designed bending tool, using the normal force sensor and lift drive of a standard rheometer, the compliance of the chocolate as well as the force needed to break the chocolate could be determined accurately.

Selected measurement results on several chocolate samples measured with the HAAKE MARS in combination with the RheoScope module and the bending tool as well as oscillation tests will be presented.

Wednesday 6:00 Grand Ballroom C PO18

Nonlinear dynamics of film process using PLA

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Polylactic acid (PLA) produced from renewable resource like corn is a biodegradable material and able to replace the petroleum-based nondegradable polymers, as advances in technology make biopolymers like PLA more competitive with petroleum-base plastics. The rheological characterizations of PLA, a commercial resin for producing blown or cast film have been investigated by measuring dynamic shear and extensional properties using a rotational and extensional rheometer (AR2000, RME and Rheotens), respectively. Film casting and film blowing experiments have been carried out using PLA. Although the degradation behavior of PLA hinders the normal procedure for observing rheological properties, yet it has been found that PLA has extension thinning nature and high flow activation energy. Based on the rheological background of PLA, blown and cast film experiments were carried out to relate its processability and stability on the system dynamics to the rheological properties.

Wednesday 6:00 Grand Ballroom C PO19

What do we know about chain entanglement in absence of flow?

Shi-Qing Wang
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Many models have been proposed in the past twenty years to account for the onset of chain entanglement, which is known to dictate both linear and nonlinear viscoelastic behavior of a variety of polymers. The specific predictions of these models frequently find agreement with various subsets of experimental data, but have often been regarded to be incompatible with each other because they are derived from different physical considerations. In the present work [1], we compare the theoretical predictions against the extensively available experimental data on both M_e and M_c. The following conclusions emerge from the literature data: (a) It is chain thickness not stiffness that correlates with M_e, in agreement with the packing model for over one hundred flexible linear polymers; (b) several other models appear to provide correlations of lesser quality for M_c, to which the packing model does not apply well. However, uniqueness of the physics controlling M_c cannot be demonstrated since the percolation model, the binary contact model and the orientational correlation model all anticipate some trends in crude agreement with the limited literature data on M_c.

[1] S. Q. Wang, Macromolecules, to be published (2007).

Wednesday 6:00 Grand Ballroom C PO20

Comparison among sliplink simulations on bidisperse linear polymers

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Recent simulations of entangled polymer dynamics were based on sliplink models, first attempted by Hua and Schieber (JCP 109, 10018 (1998)). In this study we compare how different sliplink models predict the linear viscoelasticity of bidisperse linear polymers in order to examine how effectively constraint release is described in the different models. We compare the DT model by Doi and Takimoto (Phil. Trans. Royal Soc. London A. 361, 641 (2003)), the NS model by Nair and Schieber (Macromolecules, 39, 3386 (2006)), and the primitive chain network (PCN) model by Masubuchi et al. (JCP 115, 387 (2001)). It is found that the DT and PCN models show better quantitative agreement with data in the literature than the NS model. This indicates that the role played by the decrease in number of entanglements due to constraint release, accounted for in DT and PCN, is more important than fluctuation of sliplinks in space, taking place in NS and PCN models.

Wednesday 6:00 Grand Ballroom C PO21

Strain affects the solubility of elastomers

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Four environmental factors (temperature, humidity, ultra-violet radiation, and imposed strain) affect modulus change in sealant. Of these, three have demonstrated mechanisms: temperature- Arrhenius affect, humidity- hydrolysis reactions, and UV radiation- photo induced chemical changes. The fourth, imposed strain does not present a clear mechanism for modulus change. The affect of these four elements of the weather on modulus change will be shown. Evidence for strain-induced solubility changes in the sealant will also be shown. If the strain is affecting the solubility, then imposed strain is affecting the moisture present in the sealant. Lastly, the timescale of network reformation to dissipate strain is presented. This viscoelastic response complicates the determination of actual imposed strain on the sealant.

Wednesday 6:00 Grand Ballroom C PO22

Elastic breakup of entangled polymers in uniaxial extension: is there a steady-state at high Weissenberg Numbers?

Yangyang Wang and Shi-Qing Wang
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We carried out step strain, continuous stretching as well as elastic recoil experiments on a series of entangled uncrosslinked SBR melts, using an SER Universal Testing Platform. Our step strain experiments show that after a step Hencky strain in excess of 0.7 these melts yield and break up in a manner similar to that of a crosslinked system.[1] In continuous stretching at high Weissenberg numbers, the tensile force exhibits a maximum (yield point) reminiscent of yield and necking behavior in uniaxial extension of solids such as polyethylene at room temperature. Our strain recovery experiments reveal 100 % recovery up to the yield point, beyond which the sample is unstable against further stretching and breaks apart upon reaching the point of non-uniform extension. Since the recoverable strain does not level off to a constant value before the sample breaks up, steady state is impossible to attain, in contrast to previous reports [2-3]. The origins of yield and subsequent failure reside in a force imbalance between the entropic retraction force and the inter-chain topological interactions that are responsible for the deformation of the entanglement network. [4] These melts are unable to undergo steady-state extension because the buildup of the retraction force exceeds the cohesive strength of the entanglement network that is actually a function of the extension rate.

[1] T. L. Smith and P. J. Stedry, J. Appl. Phys. 11, 1892-1898 (1960). [2] Bhattacharjee et al., Macromolecules 35, 10131-10148 (2002). [3] Bach et al., Macromolecules 36, 5174-5179 (2003). [4] Wang, S. Q.; Ravindranath, S.; Wang, Y.; Boukany, P.; J. Chem. Phys. August issue (2007).

Wednesday 6:00 Grand Ballroom C PO23

Single segment conformation tensor differential toy model with inter-chain tube pressure effect

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In this paper, we develop a "single segment" tube model describing the non-linear behaviour of entangled monodisperse linear polymers. The work is motivated by recent data of Hassager and co-workers [Bach et al. Macromolecules, 36, (2003), Nielsen (PhD Thesis, (2007), Technical University of Denmark)], the concept of interchain tube pressure effects proposed by Marrucci and Ianniruberto [Macromolecules, 37, (2004), Macromolecules, 128, (2005)] and the implementation of these effects by Wagner and co-workers [Rolon-Garrido et al., J. Rheology, 50, (2006)]. Our toy model shows promising quantitative comparisons with the data of Hassager and co-workers, especially for high elongation rates (where the inter-chain tube pressure effects are dominant). We further intend to extend these ideas to a full chain multi-segment model derived from the CRAFT model [Leygue et al. J. Non-Newtonian Fluid Mechanics, 136, (2006)].

Wednesday 6:00 Grand Ballroom C PO24

Influence of die geometry on extrudate swell and concentration defect in the extrusion of polypropylene reinforced with glass fibers

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The influence of die geometry on extrudate swell and concentration defect in the extrusion of polypropylene reinforced with glass fibers was studied in this work. Capillary flow experiments with a polypropylene containing 42 wt % of short glass fibers were carried out at 220 ºC using dies with different diameters and entry angles. The measured extrudate swell was found to be dependent on the die geometry as well as on the concentration defect in the extrudates. On the other hand, the concentration defect was also dependent on the die geometry. Extrudate swell increased with decreasing the die diameter, the entry angle and the concentration defect. The same dependence was observed for the concentration defect on die geometry. A contraction of the extrudates was observed at low shear rates and then an asymptotic value at high shear ones. Via microscopic observations of the extrudates, the results in this work are explained on the basis of changes in distribution, orientation and concentration of the fibers with shear rate and die geometry.

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Wednesday 6:00 Grand Ballroom C PO25

Step shear in entangled polymer melts: from interfacial to bulk failure at large shear deformation.

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Recent experimental evidence based on particle tracking velocimetry (PTV) revealed that entangled polymer solutions yielded both during flow and after cessation of flow in both shear and extension. This yield behavior is associated to elastic breakdown of network [1-3]. Several key questions remained to be addressed: 1) Would well entangled polymer melts show similar shear behavior as seen in solutions? 2) Would the elastic breakdown mechanism apply to describe interfacial wall slip? We attempted to answer such questions in this work by performing startup shear experiments on a model polymer melt using a home-made sliding plate shear rheometer (SDPR) equipped with in situ PTV and flow birefringence observations.

[1] Wang, S. Q.; Ravindranath, S.; Boukany, P.; Olechnowicz, M.; Quirk, R.; Halasa, A.; Mays, J. Phys. Rev. Lett. 2006, 97, 187801. [2] Wang, S. Q.; Ravindranath, S.; Wang, Y.; Boukany, P.; J. Chem. Phys. 2007, August issue. [3] Y. Wang, P. Boukany and S. Q. Wang, Phys. Rev. Lett., under review, 2007.

Wednesday 6:00 Grand Ballroom C PO26

Rheological prorperites of extracellular matrix derived hydrogels

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Extracellular matrix (ECM) bioscaffolds are prepared by decellularization of tissues, and are composed of structural proteins (e.g. collagen) and functional proteins (e.g. growth factors) that characterize the native ECM. Dry ECM scaffolds have been used for tissue-specific constructive remodeling of a variety of tissues. However, for certain applications, the use of dry ECM scaffolds can be limited by the native two-dimensional sheet form in which they are harvested. The current trend towards minimally invasive, outpatient-based surgical procedures has prompted the development of injectable biomaterials. We are evaluating ECM-based hydrogels as injectable scaffolds for tissue regeneration. The objective of the present study was to derive ECM gels from three different porcine tissues - small intestinal submucosa (SIS), urinary bladder matrix (UBM), and liver stroma (LS) - and to characterize their rheological properties.

We conducted in situ gelation experiments of the above three hydrogels. In each case, gelation was induced by bringing aqueous solutions of the ECM from 15^{o}C to 37^{o}C. Gelation kinetics were followed by monitoring by the evolution of the G'. The linear and non-linear viscoelastic properties of the final gel were characterized by frequency-sweep experiments. Finally, the stress and strain to break was measured in creep experiments. All three gels showed qualitatively similar rheology, however, there were significant quantitative differences, especially in their gelation kinetics. These differences likely reflect changes in the collagenous and non-collagenous components of the tissue from which it was derived.

Wednesday 6:00 Grand Ballroom C PO27

New measuring cell for UV assisted thermal curing at elevated temperatures

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In industry thermal curing is used in a wide range of applications like powder coating, adhesives, sealants, soldering materials, inks, etc. Recently there is an increased interest in replacing thermal curing by UV assisted thermal curing in an effort to improve product properties, increase productivity and reduce production costs, for example by reducing the amount of energy needed for initiating the curing reaction, at the same time.

For the development of, and measurements on, such kind of samples a new high temperature UV curing measuring cell was developed for the HAAKE MARS rheometer. The new cell is integrated in the existing CTC oven which has a temperature range from -150 °C up to 600 °C. The lower part of the UV-curing tool is equipped with a light guide that can be attached to a commercial available light source. The light source can be triggered by the measuring and evaluation software of the rheometer. Using the software it possible to program an automatic measuring routine in which the sample is first pre-cured by the UV light and then thermally cured using the CTC oven. The combination of convection and radiant heating guarantees fast temperature changes and an even temperature distribution within the CTC oven.

Selected results of measurements on different samples which were measured using the new UV curing cell integrated in the CTC oven will be presented.

Wednesday 6:00 Grand Ballroom C PO28

What are the origins of stress relaxation behaviors in step shear of entangled polymer solutions?

Sham S. Ravindranath and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

We apply a recently developed particle-tracking velocimetric (PTV) method along with conventional rheometric measurements to elucidate the nature of the simplest nonlinear behavior of entangled polymer solutions under shear. At a fixed degree of chain entanglement, i.e., with the same parent polymer at 10 wt. % concentration, we use different liquid media as the solvent to control the upper-bound magnitude of interfacial wall slip. Contrary to the common perception that these solutions would undergo quiescent relaxation after experiencing a sudden shear strain, we show that they systematically exhibit macroscopic motions either in the sample interior or at the sample/wall interfaces, corresponding to type A, B or type C behavior respectively. These macroscopic motions cause the residual stress to decline faster than relaxation due to quiescent molecular diffusion. We illustrate that a continuous range of relaxation behavior can be observed for solutions of the same level of chain entanglement, with one thing in common that the sufficiently strained polymers (with entanglements per chain higher than ten) do not relax the residual stress quiescently upon shear cessation and yield either at the interfaces or in the sample interior due to the retraction force built by the external strain.

Wednesday 6:00 Grand Ballroom C PO29

Investigation of a thermoset epoxy system

Louis E. Waguespack and Sean Hayes
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A thermoset material goes through a dramatic change in molecular mobility as the system goes through a crosslinking process. This change in mobility will affect many of the materials properties including heat capacity, enthalpy, viscosity, and modulus. Heat capacity and enthalpy can be examined with a DSC while viscosity and modulus can be examined by rheology. In this poster a rheometer is used to characterize a thermosetting epoxy system. A comparison with other techniques will also be shown.

Wednesday 6:00 Grand Ballroom C PO30

Melt blown polymer nanofibers

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Melt blowing is a more than 50 year old polymer processing method for producing polymer fibers, often as nonwovens. It employs a jet of hot air which creates an extensional force on an extruded polymer filament resulting in attenuation of its diameter by more than 1000x in some cases. Traditionally this processing method has been limited to the production of microfibers with average diameter exceeding 1-2 microns. However, we have recently demonstrated (1) the ability to generate nanofibers with average diameters of several hundred nanometers using commercially available melt blowing grades of polypropylene, poly(butylene terephthalate) and a variety of polystyrenes. This was achieved using a custom built laboratory melt blowing apparatus consisting of a modified capillary rheometer and single orifice dies which is capable of processing small quantities of material (less than a few grams) into fibers making it an ideal materials screening platform. This advancement in the production of nanoscale fibers is a step towards closing the gap between electrospinning (which employs solvent to produce nanofibers) and melt blowing technology. Efforts to understand these newly demonstrated capabilities, particularly the role of melt rheology, air and polymer flow rate, temperature and surface tension, through modeling and simulation are underway.

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Wednesday 6:00 Grand Ballroom C PO31

Linear and nonlinear rheological characterization of telechelic polybutadienes with ionic end-groups

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Telechelic apolar polymers with hydrogen-bonded or ionic end-groups are interesting model systems combining topological interactions, i.e.entanglements, and reversible supramolecular linkages. While some rheological characterization of such polymers has been published in literature, no systematic study on the respective influences of topological vs. supramolecular interactions has been reported. This paper presents initial results about the rheological characterization of telechelic polybutadienes (PBD) with carboxylic end groups neutralized with various inorganic and organic bases. A difunctional carboxylic acid polymer shows only a very weak associative behavior with a slightly increased temperature dependence by comparison with unfunctionalized PBD. On the contrary, neutralization of the acid end-groups leads to the formation of a reversible network, whose bonding strength depends very much on the nature of the ion, and to a much higher temperature dependence. An increase of the relaxation time by a factor of more than 10 000 is obtained together with a dramatic change of the plateau modulus by comparison with the reference polymer. For some samples, a very weak gel regime is observed in a "pseudo-terminal" region and thermorheological simplicity fails at intermediate frequencies, presumably where topological and supramolecular interactions together influence relaxation. Besides linear viscoelasticity, behavior in uniaxial elongation has also been studied so far. No strain hardening has been found at low elongational rates, at which the sample can be stretched up to a Hencky stain of 4, while at high strain rates the onset of strain hardening is obvious, but the elongation at break is rather low.

Wednesday 6:00 Grand Ballroom C PO32

Shear modulus and osmotic pressure of glucose- and pH-sensitive hydrogels

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A 'smart' or stimuli-responsive hydrogel is a cross-linked polymer network that absorbs or desorbs water in response to an external stimulus such as change in pH concentration of some analyte such as glucose. Values will be presented for the shear modulus G and osmotic pressure Π of pH-responsive and glucose-responsive hydrogels designed for use in miniature biomedical sensors. According to the Flory-Rehner model, the swelling response of a smart hydrogel is triggered by changes in G and Π with external stimulus.

Wednesday 6:00 Grand Ballroom C PO33

Rheology, morphology and properties of immiscible blends

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A 50 wt percent PS/PP immiscible blend is mixed in an extruder and cast at various draw speeds. The role of extrusion speed and drawing on rheological, thermal and mechanical properties is explored. We see several unexpected trends. For example, we found that elongational viscosity is greater than that of either component, whereas shear viscosity is lower than either component. The crystallinity of the PP is unaffected by drawing, but the modulus and film roughness show a strong increase with drawing. Fundamental mechanisms affecting the properties of this interesting material will be presented for discussion.

Wednesday 6:00 Grand Ballroom C PO34

Viscoelastic properties of blends of hybrid copoy(POSS-PS) nanocomposite and polystyrene

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Polyhedral oligomeric silsesquioxane (POSS) are hybrid nanostructures of about 1.5 nm size. This Si based polyhedral nanostructures are attached to a polystyrene (PS) backbone to produce a polymer nanocomposite. Due to its chemical compatibility, it is suggested that copoly(POSS-PS) can act as a nano-reinforcement to polystyrene. We have solution blended copoly(POSS-PS) with a commercial high molecular weight polystyrene and studied the rheological behavior of the neat polymeric components and the blends. The influence of copoly(POSS-PS) concentration was investigated and the concentration was varied from 3 wt% up to 20 wt%; melt rheology studies were carried out from 100°C up to 180°C. The results showed that the polymeric components and their blends obey the time-temperature superposition principle. The master curves thus produced showed that the macromolecular dynamics of PS is influenced by the polymer nanocomposite copoly(POSS-PS). The microstructure was also investigated by optical and atomic force microscopy in order to establish a structure-property correlation.

Wednesday 6:00 Grand Ballroom C PO35

Confocal microscopy of strained jammed emulsions

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We study polydisperse decane-in-water emulsion droplets stabilized by SDS at volume fractions above jamming. We focus on the droplet dynamics when the emulsion is unperturbed and when an oscillatory strain is posteriorly applied. Confocal microscopy is employed to track the trajectories of single droplets in real space and time. By taking advantage of this technique we characterize reversible and irreversible single droplet reconfigurations as well as the spatial extent of the rearrangements.

Wednesday 6:00 Grand Ballroom C PO36

On the interfacial rheology of inks

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Inks are involved in many free surface processes during printing. Therefore, one of the important material parameters to consider in printing analyses is the surface tension (surface free energy). The determination of surface tension of inks with the methods developed for simple fluids such as the drop-weight, the ring and the Wilhelmy slide methods encounters a major complication. All these methods assume a well defined contact angle between the fluid and the solid surface at the time of the measurements. However, most inks show an apparent yield behavior. It results in a meniscus on the solid surface that has a contact angle other than that assumed in these methods.

An alternative to determine the surface tension of inks is the interfacial rheology. In this work the interfacial rheology of inks are investigated using the AR-G2 rheometer with the interfacial Du Noüy ring feature. It is shown how to locate the position of the ring on the free surface. Then characteristic surface moduli are determined as measures of the surface tension. Comparisons between surface rheology of inks with different additives are presented.

Wednesday 6:00 Grand Ballroom C PO37

Spreading of non-Newtonian droplets on glass surfaces with controlled wettability

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

Wednesday 6:00 Grand Ballroom C PO38

Nanosphere embedment as a method to extract surface rheological and surface adhesive properties

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We are investigating the surface properties of polymers using a nanoparticle embedment method established by Teichroeb and Forrest [1]. An atomic force microscope (AFM) is used to measure the embedment depth as nanoparticles are pulled into the surface by the thermodynamic work of adhesion. Here we describe a viscoelastic contact mechanics solution that includes surface adhesive forces and a time dependent Poisson's ratio. [2] The results show that, with properly designed experiments, both the surface adhesion properties and the surface rheological properties can be extracted from nanosphere embedment rates. We include work on a phase separated copolymer and a commercially available polydimethylsiloxane (PDMS) rubber.

[1] Teichroeb, J. H. and Forrest, J. A., Direct Imaging of Nanoparticle Embedding to Probe Viscoelasticity of Polymer Surfaces, *Phys. Rev. Lett.*, **91**, 1, 016104-1(2003). [2] Hutcheson, S. A. and McKenna, G. B., Nanosphere Embedding into Polymer Surfaces:A Viscoelastic Contact

Mechanics Analysis, *Phys. Rev. Lett.*, **94**, 076103 (2005); Erratum: Nanosphere Embedding into Polymer Surfaces: A Viscoelastic Contact Mechanics Analysis, *Phys. Rev. Lett.*, **94**, 189902 (2005).

Wednesday 6:00 Grand Ballroom C PO39

Structure and diffusion of polyelectrolyte chains in confined spaces of slit micro/nanochannel by Brownian dynamics simulations

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Brownian dynamics (BD) simulations are performed for polyelectrolytes in bulk solution and under confinement between two charged plates. The coarse-grained modeling is based on the nonlinear bead-spring with long-range electrostatic, Lennard-Jones, and hydrodynamic interactions between pairs of beads [1]. We also consider steric and electrostatic interactions between the bead and the confining wall. Relevant model parameters are determined from previous rheology data on the polysaccharide xanthan. The conformational changes induced by confinements and their dependence on the screening effect are characterized. Depending on the intrinsic rigidity and the medium ionic strength, the polyelectrolyte can be classified as flexible, semiflexible, or rigid. Confined flexible and semiflexible chains exhibit a non-monotonic variation in size, as measured by the radius of gyration and end-to-end distance, with changing slit width. The size of confined semiflexible and rigid polyelectrolytes can be well described by the worm-like chain model once the electrostatic effects are taken into account [2]. Since hydrodynamic interactions (HI) play an essential role in the dynamics of polyelectrolyte chains confined in micro/nanochannel environments, we propose a new computational method to describe the HI of confined polyelectrolytes in the context of BD simulations. The method is based on the Green's function for the flow field generated by a point force in the channel. The far-field effect, dominant when the bead-bead and bead-wall separations are large compared to the bead hydrodynamic radius, can be well described with this point force approximation. The mobility of a single sphere modified by the walls is also derived, and then the feasibility of the method is demonstrated by BD simulations of the diffusion

[1] Y.-L. Chen, M.D. Graham, J.J. de Pablo, G.C. Randall. M. Gupta, P.S. Doyle, Phys. Rev. E, 70, 060901R (2004). [2] J. Jeon, M.-S. Chun, J. Chem. Phys., 126, 154904 (2007).

Wednesday 6:00 Grand Ballroom C PO40

Nonlinear rheology of square-well colloidal dispersions

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We present analytical and simulation results for the rheology of colloidal dispersions with short-range square-well attractions both near and far from equilibrium. Brownian dynamics simulation results from the fluid region of the phase diagram are compared to the theoretical behavior predicted by the solution of the pair Smoluchowski equation in the dilute limit. The simplicity of the model enables the efficient rheological characterization of dynamically arrested suspensions such as gels and glasses whose deeper attractive wells and/or tighter packing can be computational and experimental barriers, especially when the systems are strongly perturbed.

Wednesday 6:00 Grand Ballroom C PO41

Sensitivity in slot coating flows using frequency response method

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In slot coating, as in other coating processes, there exist unexpected disturbances that affect the uniformity of the final coating thickness. Sensitivity of slot coating system has been theoretically and experimentally investigated using frequency response method. Sinusoidal variations of the wet film thickness with respect to sinusoidal disturbances at flow rate, web speed, coating gap, bead pressure, etc. have been estimated from both 1D and 2D models. Also, sensitivity results of the wet film thickness on sinusoidal web speed condition has been obtained from slot coating experiments and compared with those by simulations. It has been found that the amplitude ratios of film thickness are decreasing with the frequency of disturbances introduced in web speed and flow rate, whereas those are increasing with the frequency of disturbances at coating gap and bead pressure.

Wednesday 6:00 Grand Ballroom C PO42

Exploring the high frequency behavior of dilute polymer chains in extensional and shear flows using Brownian Dynamics simulation with bending and torsional potentials

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The bead-spring model--used for describing the linear viscoelastic properties of high molecular weight polymers--is justified through a coarse-graining approximation valid at long time and distance scales. At these scales, individual bonds corresponding to a single spring are assumed to relax quickly enough to sample their equilibrium configuration. In fast flows or at high frequency, the number of bonds that can be successfully represented by a spring remains unclear. When we carry out a Brownian dynamics study of a realistic polymer chain in extensional and shear flows and compare our results to experimental observations and predictions using bead-rod simulations and dumb bell models.

Wednesday 6:00 Grand Ballroom C PO43

Fully three-dimensional simulations of viscoelastic flow around a linear periodic array of cylinders

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A parallel finite element method and code has been developed to simulate three dimensional, confined, isothermal viscoelastic flows. The usefulness of the method is demonstrated on the benchmark problem of flow around a linear array of cylinders. The DEVSS-G operator splitting technique is employed on the momentum and continuity equations for three dimensional, incompressible, creeping flow of a fluid following the Giesekus constitutive equation. The equations are discretized with the finite element method; DG elements are used for the polymer contribution to stress to handle upwinding. The vpG and polymer stress sub-problems are solved in separate steps with methods tailored to the character of each sub-problem. Runge Kutta explicit time integration is employed to get to reach the steady state solution. Flow of a Boger fluid around a linear array of cylinders was studied experimentally by Liu. In the configuration with a periodic intercylinder spacing of 2.5 radii, the two dimensional flow undergoes a transition to a three dimensional time periodic flow at a Weissenberg number of 1.53. The onset of the instability was predicted numerically by Smith with a linear stability analysis of axial perturbations to the two dimensional base flow of an Oldroyd-B fluid. We verify our three dimensional code by capturing this flow transition.

Wednesday 6:00 Grand Ballroom C PO44

Estimation of the repulsive force between two interacting Gaussian chains

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It has been reported that osmotic force coming from segment interaction is necessary for sliplink description of entangled polymer network [Y. Masubuchi et al., Slow Dynamics in Complex Systems, 261, M. Tokuyama and I. Oppenheim ed., AIP, New York (2004)] as long as the sliplink is not fixed in space and the elastic force acts between the sliplinks. However, the description of such a force has not yet been fixed. In this study, a force generated by the overlap between two density fields of the segments involved in Gaussian chains is formulated. The overlap of the density fields yields a free energy of the system defined by the volume integral of the product of the density fields. The resulting repulsive force acting on the segments is found from a proper derivative of the derived free energy.

Wednesday 6:00 Grand Ballroom C PO45

Direct calculation of limit cycles and their stability under draw resonance mode

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Draw resonance phenomenon, which is characterized by the self-sustained periodic oscillation of state variables over the onset, has been profoundly investigated as a crucial instability occurring in extensional deformation polymer processes by manifold experiments and theoretical approaches for decades. We have scrutinized more deeply draw resonance instability in fiber spinning process using a bifurcation theory. Time-periodic states or limit cycles under draw resonance have been directly obtained by Newton's method incorporated with pseudo arc-length continuation scheme, and their stability has been determined by Floquet multipliers of monodromy matrix. It has been found that the limit cycle is more stable as drawdown ratio is increasing, supporting that the draw resonance is a stable supercritical Hopf bifurcation.

Wednesday 6:00 Grand Ballroom C PO46

Isotropic-nematic phase transition in a liquid crystal droplet

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We perform experiments to investigate isotropic to nematic phase transition in a liquid crystal droplet by changing the temperature and measuring the growth of the nematic phase within an isotropic phase liquid crystal droplet that is suspended in a silicone oil. The results obtained from this experiment show good agreement with the theoretical model (Stefan type) of the evolution of the nematic phase within the isotropic phase of liquid crystal.

Wednesday 6:00 Grand Ballroom C PO47

Texture orientation correlations and macromolecular alignment in thermotropic liquid crystalline copolyester

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Orientation correlations induced by shear flow and their relaxation were investigated using in-situ small-angle light scattering (SALS) in the thermotropic random copolyester of 60 mol% hydroxybenzoic acid (B) and 40 mol% ethylene terephthalate (ET). B-ET displays a nematic polydomain texture, the SALS and WAXS patterns are amorphous and isotropic. Shear flow produced optical defect multiplication with the consequent reduction of the microdomains size. However, SALS detected long-range spatial correlations within the optically chaotic texture, the SALS patterns showed bimodal orientation of defects. After cessation of shear the orientation correlation rapidly relaxed back to a polydomain and the SALS pattern became again isotropic. Above a threshold shear rate of about ~ 2 s-1 the SALS pattern showed unimodal orientation arising from line defects oriented nearly orthogonal to the velocity axis. Strikingly, the texture relaxation now showed the well known 'banded texture'. The threshold shear rate coincided with a significant increase in the degree of molecular alignment as determined from in-situ X-ray scattering. This technique also showed that shear flow always oriented the molecular chains along the flow direction regardless of the shear rate.

Wednesday 6:00 Grand Ballroom C PO48

Optical texture evolution and viscoelastic properties of liquid crystalline polymers: the effect of chemical composition

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Liquid crystalline polymers (LCPs) based on the random copolymerization of hydroxy-benzoic acid (HBA) and hydroxy-naphthoic acid (HNA), and commercialized by the Celanese Co., belong to the high-performance class of materials. These materials show solid to nematic phase transition at temperatures in the range of 230°C to 290°C, the phase transition temperature being modulated by the chemical composition of the copolymer. A series of low molecular weight copolymers (kindly provided by Celanese Co.) with chemical composition in the ratio HBA:HNA of 1:1, 1:3, 3:1 and 2:1 were studied. We have investigated the influence of chemical composition on the nematic texture using polarized optical microscopy. The influence of thermal annealing on the optical texture coarsening and was also investigated. The viscoelastic properties were investigated by small-strain oscillatory shear rheology. The results showed that the HBA:HNA copolyesters are linearly viscoelastic. The dynamic shear moduli of the 3:1 composition showed a predominantly viscous behavior, whereas the shear moduli of the copolyester with 1:3 composition showed a predominantly elastic behavior. These viscoelastic properties are correlated with the "log-rolling" and "flow-aligning" behavior.

Wednesday 6:00 Grand Ballroom C PO49

Dynamics and rheology of high molar mass polyethylene oxide solutions

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Poly(ethylene oxide)(PEO) is used in wastewater treatment, oil recovery, drilling fluid stabilization, as an additive in pharmaceutical formulations and in drag reduction.Aqueous solutions of PEO are in a state of molecular aggregation, which is hypothesized to be the source of their anomalous rheology and high drag reduction capability. Validation of models for prediction of the viscoelastic behavior of PEO solutions is hindered by the lack of appropriate experimental data. In this work, we have used dynamic light scattering (DLS), microrheology, bulk rheology and fluid mechanics to investigate the structure and dynamics of high molar mass PEO solutions. Steady shear rheology of WSR301 (a high molar mass PEO commonly used for turbulent drag reduction) solutions revealed shear thinning that increased with concentration. The shear thinning is modeled by the FENE-P constitutive equation and relaxation times are estimated. Dynamic light scattering of aqueous solutions of WSR301 revealed two relaxation times (fast and slow mode) by CONTIN (constrained regularization method) deconvolution of the correlation functions in the semi-dilute regime. The fast mode is in agreement with scaling predictions and has a typical q^{-2} dependence consistent with diffusive dynamics, and the slow mode has an approximately q^{-3} dependence reflective of non-diffusive dynamics and consistent with dynamics of large multichain domains, clusters or aggregates. In the dilute regime, polymer centre of mass diffusion theory predicts a q^{-2} dependence of the relaxation times. We report a single peak in the decay time distribution of WSR301 which scales as q^{-3} instead of q^{-2} in the dilute limit. The above results provide molecular level evidence that support earlier rheological inferences (Tirtaatmadja et al., Physics of Fluids, 18, 043101, 2006) that the structure of WSR301 at ~ 10-100 ppm concentrations is not consistent with the picture of a isolated polymer coil in a dilute solution.

Wednesday 6:00 Grand Ballroom C PO50

Characterizing the conformational evolution and diffusion of xanthan in solvent by single molecule imaging

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Understanding the behavior of a polyelectrolyte in confined spaces has direct relevance in design and manipulation of micro/nanofluidic devices, as well as transport in a biological system. Single molecule visualization was performed on fluorescently labeled xanthan polysaccharide using an inverted epi-fluorescence microscope equipped with high-resolution CCD camera. Both the conformation and diffusivity of single xanthan molecules were characterized with variations of the chain confinement and the solution environments such as pH and ionic concentration. Applying the MEMS process, we prepared a suitable chamber consisting of two microslides for the unbounded bulk space, and the polydimethylsiloxane (PDMS)-glass microchannels were fabricated with the widths ranging 2-20 micrometer for the confined system. The center-of-mass displacement is determined as a function of the time elapsed between images, where the radius of gyration can be estimated from a first moment of the intensity distribution [1]. The diffusivity calculated for each individual molecule is an ensemble property of many displacements and lag-times in each Brownian trajectory [2]. It is evident that the diffusion coefficient of confined xanthan is much lower than that in the bulk space. Finally, we will present the scaling predictions originally derived by de Gennes and colleagues to describe the source of the observed free-draining diffusion dynamics.

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Wednesday 6:00 Grand Ballroom C PO51

Effect of surfactants on enhanced oil recovery from kaolin

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Current methods of extracting oil from oilfields employ three stages of recovery. In the first stage, oil is naturally forced out of the reservoir due to the high underground pressure. The second stage extracts more oil by pumping water underground and re-pressurizing the reservoir. However, both the techniques combined can extract only a third of the oil present. The final stage, called enhanced oil recovery (EOR), can recover more oil primarily through chemical flooding. Flooding the reservoir with surfactant solutions reduces the interfacial tension and changes the wettability of the reservoir. In this study, a laboratory scale model has been used to study the dodecane oil recovery from a bed of kaolin powder using SDBS and CTAB surfactant solutions. Experimental data have been analyzed to obtain the effect of amount of oil in the bed as well as the type and concentration of surfactant used on the oil recovery.

Acknowledgements: NSF-REU program.

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Wednesday 6:00 Grand Ballroom C PO52

Flow kinematics of electrospinning and application to the extensional viscometry of semi-dilute polymer solutions

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Polymer electrospinning has received significant attention as a method for the production of a wide array of nanofibrous materials and composites. However, fundamental understanding of the process that would enable control and optimization of electrospun materials is incomplete. We propose an electrohydrodynamic model for stable electrospun jets based on slender body electrohydrodynamic theory that explicitly considers the rheology of polymeric spinning fluids. The model yields predictions for the kinematics of stable electrospun jets and the influence of viscoelasticity on jet dynamics. Experiments employing high speed photography and particle tracking velocimetry on stable jets of aqueous poly(ethylene oxide) are used to critically test the model. The combination of in-situ measurements with the theory enables quantitative measurements of the extensional viscosity of the polymer solutions at rates exceeding the experimental range of conventional techniques. Polymer solutions below the entanglement concentration of the fluid exhibit Newtonian-like behavior, whereas entangled solutions show increased extensional viscosities due to strain hardening. Finally, correlation of the stable jet kinematics with ultimate fiber morphology suggests that the steady-sate extensional rheology of the electrospun fluid sets the scale for the final diameter of electrospun fibers.

Wednesday 6:00 Grand Ballroom C PO53

Self-similar shear thickening behavior in CTAB/NaSal surfactant solutions

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It is well known that certain wormlike surfactant solutions (e.g. CTAB, CTAT) can undergo a phase transition from a solution phase to a gel-like phase upon increasing the shear rate above a critical value [Wunderlich and co-workers (1987), Liu and Pine (1996), Hartmann and Cressely (1997,1998,2000), and Bandyopadhyay and Sood (2001)]. The apparent viscosity of the solution increases (i.e. the solution shear-thickens) as a result of such phase transitions. The critical shear rate and the extent of viscosity enhancement in such systems are very sensitive to salt concentration. In this study, the effect of salt (NaSal) concentration on surfactant (CTAB) solution rheology has been investigated in the shear thickening regime. Experimental data have been analyzed to obtain power-law relationships for the critical shear rate and apparent relaxation time of the shear-thickened solution as a function of salt concentration CS. Effect of CS on the elastic properties of the shear-thickened solutions is discussed for different surfactant concentrations. Finally, a procedure has been developed to collapse viscosity vs. shear rate data at various values of CS into a single master curve indicating the self-similarity of the shear-thickening system.

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Wednesday 6:00 Grand Ballroom C PO54

The rheological properties of high volume fly ash cement paste

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The rheological behavior of a cementitious matr ix in fresh state is identified by the yield stress and the plastic viscosity of the medium characterized by the consistency and the physicochemical properties of the cementitious/binder material. A laboratory research program was carried out to investigate the relationship between the yield stress, viscosity and the consistency of fly ash, cement and fly ash-cement pastes (4:1 by weight, respectively) in terms of the experimental results obtained by rheometer of cone and plate geometry, and slump, flow table. All pastes were investigated for low, medium and high consistencies (corresponding to 50, 150 and 250 mm slump values respectively) for various time intervals ranging between 0 - 1 hr, 15 min after mixing at room temperature. The experimental results indicate that the rheological behavior of cement paste is highly correlated to the consistency and the physicochemical properties of the cementitious/ binder material.

Wednesday 6:00 Grand Ballroom C PO55

Rheology and shear-induced alignment of PP/MWCNT dispersions

Saswati Pujari and Wesley R. Burghardt
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We have prepared dispersions of multiwall carbon nanotubes in polypropylene via conventional melt batch mixing and via solid-state shear pulverization. The degree of dispersion is assessed via viscoelastic measurements in small-amplitude oscillatory shear, scanning electron micrscopy and polypropylene crystallization kinetics as probed by differential scanning calorimetry. Increasing either the intensity or the duration of the melt mixing leads to higher degrees of dispersion, evidenced by progressive increases in a low-frequency elastic plateau and accelerated PP crystallization kinetics attributed to more effective heterogeneous nucleation. The sample prepared by pulverization exhibits faster crystallization kinetics than any of the melt blended samples, but in contrast shows no measurable low frequency elastic plateau. This may be attributable to scission of the nanotubes during pulverization, such that even well dispersed tubes can not form an entangled network at a given concentration. We also report on preliminary studies of shear induced alignment in these samples using in situ x-ray scattering.

Wednesday 6:00 Grand Ballroom C PO56

Investigating retardation time behavior of ageing suspensions of laponite

Yogesh M. Joshi, Ranjith Reddy, Ajit L. Kulkarni, and Raj P. Chhabra
Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, UP 208016, India

We investigate the ageing behavior of suspensions of laponite with varying salt concentration using rheological tools. It is observed that the ageing behavior of these suspensions after rejuvenation is independent of minor differences in rejuvenation protocol if strong stress field is used to rejuvenate the system. Immediately after rejuvenation, the increase in the complex viscosity was found to be very fast which slowed down eventually and followed a power- law type behavior at sufficiently high age. Corresponding power law exponent showed a decrease with an increase in the salt concentration. The succeeding creep experiments performed at various ages showed damped oscillations in the strain due to a coupling of the instrument inertia and the viscoelastic nature of the suspension, the behavior which was predicted very well by a single mode Kelvin-Voigt model. The characteristic time-scale of the Kelvin-Voigt model, also known as retardation time, was observed to be independent of applied stress. Retardation time showed a prominent decrease with the age of the system; however, it became weaker with an increase in the salt concentration. A decrease in retardation time can be represented as decrease in friction that opposes elastic deformation of the system and hence is related to the viscosity (friction) of the dissipative environment surrounding the arrested entities. These results are analyzed from a perspective of the ageing dynamics of laponite suspensions.

Wednesday 6:00 Grand Ballroom C PO57

Universal ageing phenomena in soft glassy materials

Yogesh M. Joshi and Reddy Ranjith
Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, UP 208016, India

Ageing and rejuvenation of soft solids of laponite is studied to investigate underlying universal behavior. It is observed that the relaxation time of the system has a power law dependence on age, and it decreases with application of stress. Irrespective of state of ageing, normalization of time by dominating relaxation mode gives a universal master curve, thus showing time superposition with respect to various system variables, the behavior that may be generic in variety of soft materials.

Wednesday 6:00 Grand Ballroom C PO58

Nanosilver particle suspension for Drop-on-Demand (DOD) inkjet printing

Jun Hee Sung, Ayoung Lee, Kyung H. Ahn, and Seung J. Lee
School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea

Inkjet printing is familiar as a method of printing text and images onto substrates such as paper or glass. Recently, it has been explored as a way of printing the electrical and optical devices with the use of special inks. For successful inkjet printing, high resolution patternability should be achieved, and it is essential to understand the mechanism of ink drop deformation and to reduce the satellite drop which can cause defect in printing. In this presentation, we report the drop formation of nanosilver particles suspended in low viscous Newtonian fluid, with the effect of imposed pulse shape as a function of dwell time and frequency on Drop-On-Demand (DOD) inkjet printing. We also investigated the effect of electric field on the motion of metal inks which are suspensions with different viscosity and surface tension under the electric field from 0 to 100V.

Wednesday 6:00 Grand Ballroom C PO59

Heterogeneity on stress development in suspension coating process

Sunhyung Kim, Jun Hee Sung, Kyung H. Ahn, and Seung J. Lee
School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea

Coating materials which contain particles, binder, and additives can be considered as complex fluids from the rheological point of view. They show complicated behavior under high shear coating flow and form heterogeneous microstructure due to non-uniform distribution of binder and solvent, particle aggregation and so forth. Heterogeneity influences stress of coating layer during film formation resulting in unexpected coating failure like crack, curling and deformation etc. Therefore, evaluating the heterogeneity and understanding its effect on stress development is highly desired to achieve defect-free coating. We investigated heterogeneity of coating materials and its effect on stress development of films formed from poly(vinyl alcohol)(PVA) solution, pure silica and PVA/silica suspension of varying composition and concentration. The heterogeneity of coating materials is characterized with particle tracking microrheology technique and the stress history of coating films was measured in situ during drying with cantilever deflection method. Our approach is expected to explain stress development of coating process with heterogeneity of coating material which is dependent upon both concentration and composition of PVA-silica suspension.

Wednesday 6:00 Grand Ballroom C PO60

Structural transitions of MR fluids in microgravity

Paula A. Vasquez[1], Eric M. Furst[1], and Juan Agui[2]
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Magnetorheological (MR) fluids are a class of smart materials capable of changing their viscoleastic properties in response to an applied magnetic field. These materials have many advantages in applications that require fast response, strength, tunability, and physical flexibility such as feedback controlled devices like shock absorbers and high-performance suspension systems. In this poster we present and analyze microgravity data obtained from a NASA study called InSPACE that was carried out on the International Space Station. In this project the performance of MR fluids was studied under steady and intermittent (pulsed) magnetic fields. Here we present an analysis of the formation of low-energy structures of such suspensions. The aim of this study is understanding the competing forces responsible for the aggregate microstructure: the demagnetizing field, the surface energy, and the effects of inter-aggregate repulsion.

Wednesday 6:00 Grand Ballroom C PO61

Drying of particle laden non-Newtonian fluids

Jeong In Han and Chongyoup Kim
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The drying of particle-laden sessile drops is examined experimentally. Although the flow inside the drop and heat transfer characteristics of Newtonian fluids with colloidal particles are well understood, the flow and heat transfer characteristics of other kinds of suspensions are poorly understood, particularly particle-laden non-Newtonian fluids and fluids with non-colloidal particles. We investigated the suspensions of various particle diameters in rheologically complex fluids. It has been found that the drying characteristics are dependent on particle size as well as the rheological properties of fluids: The typical 'coffee ring' of colloidal particles is not always observed in the case of non-colloidal particles in a Newtonian fluid and large particles (10 micron in diameter) move toward the center. Marangoni effect does not appear to be responsible for this movement. In an aqueous solution of xanthan gum, however, the particles move toward the edge and form a ring stain regardless of particle size. In aqueous solutions of polyethylene oxide and polyacrylamide, the colloidal particles moved toward the contact line while there is a competition of inward and outward movements of non-colloidal particles with the increasing inward movement of larger particles.

Wednesday 6:00 Grand Ballroom C PO62

Self organization of granular chains

Xialing Zhang and Amy Shen
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The freely jointed chain model is commonly applied to the study of flexible macromolecules like polymeric fluids, DNA strands, and soybean stalks. To date, most experimental studies of the dynamical influences of chain structure have been involved single chains. Here, we report results concerning on the dynamical behavior of collections of beaded chains in a two-dimensional rotating cylinder under gravity. Our primary focus is on the conformation of granular chains, the porosity of flow region, and the mean square end-to-end distance of single chains with varying experimental conditions. Scaling analysis of experimental results shows that, (1) the porosity in granular flow increases as the increase of rotation speed and the decrease of filling percentage; (2)the mean square end-to-end distance of single chains is related to the number of chain links, which basically agrees with the results from self-avoiding walk theory.

Wednesday 6:00 Grand Ballroom C PO63

A rapid method to predict particle sedimentation of charge-stabilized coatings

Charles Rohn[1] and Fred Mazzeo[2]
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Experimental rheology is capable of identifying the important material functions that control the stability of charge stabilized coating dispersions providing their viscoelastic spectrum covers both the terminal and plateau regions. This can be accomplished by producing valid master curves. Two charge stabilized coating samples that have different sedimentation stability as observed after being stored in test tubes for over one year were tested using a rotational rheometer. Frequency master curves covering the terminal and plateau regions were produced. Particle size and zeta-potential measurements were made on these samples. Agreement is found between their plateau moduli, zeta-potential and long term sedimentation stability.

Wednesday 6:00 Grand Ballroom C PO64

Rheology of glass fibers suspensions in viscoelastic media

Benjamín M. Marín-Santibáñez, José Pérez-González, and Lourdes de Vargas
Lab. de Reología, Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, México D.F. 07730, Mexico

In this work the rheological behavior of two series of model suspensions of glass fibers in Newtonian and Boger fluids, respectively, has been investigated by rotational rheometry and flow visualization. The steady-state shear viscosity increased with the fiber content and different flow behaviors were observed depending of the concentration regime. In the semidilute regime, both type of fiber suspensions became slightly shear thinning; while in the concentrated regime, just above of the semidilute regime, the suspensions exhibited shear thickening at low shear rates and shear thinning at high shear rates. In the concentrated regime for both suspensions, flow visualization allowed the detection of bundles of fibers randomly distributed across the flow region, which are suggested as the origin of the shear thickening behavior at low shear rates. The formation of these bundles may be due to mechanical contacts and adhesive forces between fibers. Finally, both types of model suspensions exhibited shear and normal stress overshoots in stress growth experiments. The shape and the magnitude of these overshoots were dependent on the fiber content, the distribution of lengths as well as on the viscoelasticity of the matrix.

*This work was supported by CONACYT-CIAM 51837K and SIP-IPN 20071010. B.M. M.-S. had CONACYT and PIFI-IPN scholarships.

Wednesday 6:00 Grand Ballroom C PO65

Particle interaction measurements using laser tweezer optical trapping

Matthew D. Reichert[1], Christopher M. Brotherton[2], Sunil Sainis[3], Eric Dufresne[3], and Anne M. Grillet[2]
[1]Chemical Engineering, University of Delaware, Newark, DE 19716, United States; [2]Microscale Science and Technology Department, Sandia National Laboratories, Albuquerque, NM 87185-0834, United States; [3]Chemical Engineering, Yale University, New Haven, CT 06511, United States

Laser tweezers optical trapping provides a unique noninvasive capability to accurately measure interaction forces between colloidal particles as small as 10 femtoNewtons. Understanding interactions forces is critical for predicting the behavior of particle dispersions including dispersion stability and flow rheology. We measure the interactions of colloidal silica particles and examine the effect of grafted polymer coatings on the particles. Using a new analysis method, we can simultaneously calculate the interparticle velocity and particle diffusivity which allows direct calculation of the interparticle potential for the particles.

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 6:00 Grand Ballroom C PO66

Rheological characterization of concentrated pharmaceutical protein solutions

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Rheological characterization of protein solutions is an emerging field in the biotechnology industry. In the past, most protein pharmaceuticals were formulated at low concentrations. These low concentration solutions have water-like rheological properties. However, some recent protein formulations and newly developed antibody therapeutics require higher doses and are thus formulated at high concentrations. The techniques currently used to characterize protein solutions typically require low concentration. Unfortunately, higher concentration protein solutions may behave differently from dilute solutions. These concentrated formulations pose great challenges to protein pharmaceutical formulation, down-stream manufacturing, and drug administration. Rheological characterization of the concentrated protein solutions may provide unique and crucial information for drug development. We examined the rheological properties of Kineret (anakinra protein concentration of 150 mg/mL) and a monoclonal antibody solution at 105 mg/mL. These solutions are shear thinning; however, at low concentrations they exhibit Newtonian behavior. We also report the oscillation tests performed to understand the mechanical stability of these solutions.

Wednesday 6:00 Grand Ballroom C PO67

High speed micro-measurements of dynamic interaction of red blood cell and platelet-sized particles in sudden expansion

Rui Zhao[1], Fangjun Shu[2], Joie Marhefka[2], Marina V. Kameneva[3], and James F. Antaki[1]

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Thrombosis is a common complication associated with mechanical circulatory support devices. Steps and crevices within these devices serve as a nidus for thrombus development. The geometry design in these areas is crucial to the occurrence rate of post-surgical thrombosis. However, the basic mechanism and the dynamical features of the thrombi formation are not clear yet. In this project, microscopic blood flow dynamics was studied in a 100um:200um flow expansion using a high speed camera with a frame rate up to 2000/s. The study aimed to determine the relationship between red cell/platelet dynamics and platelet transport phenomenon in order to further the understanding of thrombi formation mechanism in this area. A suspension of red blood cells (RBCs) and platelet-sized fluorescent particles (PLTs) was driven through a polydimethyl siloxane (PDMS) microchannel. Images with 100× magnification were recorded. Detailed RBC and PLT flow behavior was tracked and quantified. An RBC free area formed in the corner of the expansion under all experimental conditions but dramatically decreased as the hematocrit (Ht) increased. The dimension of the cell free area was about the size of several RBCs when Ht was equal or greater than 40%. In this case, the PLTs were excluded by the larger RBCs to the corner, resulting in an elevated PLT concentration that may be responsible for the preferable occurrence of thrombi in the flow separation in the real devices. The exclusion effects were not obvious in diluted samples of RBC suspension. RBCs and PLTs recirculated within cell free area when flow rate was above certain critical values. They circulated for a longer time at higher Ht due to a smaller drag force from the main flow caused by to the smaller size of the recirculation zone. We conclude that cell-cell interaction and the drag force, which are varied at varying flow rates and Hts, play important roles on the thrombi formation in flow expansion.

Wednesday 6:00 Grand Ballroom C PO68

Slip detection of biocompatible materials under oscillatory shear conditions

Sarah A. Klemuk and Ingo R. Titze

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The viscoelastic environment of cells affects cell shape and overall behavior. For this reason, accurate viscoelastic measurement of biomaterials used for implantation or for in vitro modeling is crucial. The aim of the present investigation was to study sample to hard surface adhesion of three biocompatible materials, during oscillatory shear measurement across frequency. Slip was tested by varying gap and surface conditions. Indications of slip were gap-dependency, surface-dependency, or some combination. A total of 4 materials were evaluated. Biocompatible materials included a pliable, porous, three dimensional polyurethane made from Tecoflex(tm), and two commercially produced collagen suspensions, Zyderm II and Cymetra. The fourth material was non-Newtonian standard fluid, NIST SRM-2490. Roughness of 5 parallel plate surface conditions and the polyurethane substrate were quantified using scanning electron microscopy and imaging analysis software. The least rheologic variability of the substrate across frequency occurred when using 220grit-covered surfaces or smooth surfaces, the two extreme conditions according to surface data. A trade-off between rms height and mean spacing between irregularities may account for this result. SRM-2490 proved to be a control condition, where accuracy and precision of G' and G" were within 8% over three gap settings and two surface conditions, for frequencies 0.04-15.9 Hz. G' and G" values at any given frequency, for the collagen suspensions using a standard stainless steel base and parallel plate, varied by an order of magnitude for three gap conditions. The least variability in viscoelastic measurement, 11-25%, occurred when surfaces were covered with 220grit sandpaper, but accuracy is still unconfirmed. In general, slip is a potentially large source of error in rheologic measurements. Detecting slip and improving adhesion remains a trial and error process.

Work supported by NIH-NIDCD (grant F31 DC 008047 and grant 2 R01-DC004224)

Wednesday 6:00 Grand Ballroom C PO69

Tuning of tissue engineering hydrogel material properties

Janssen L. Vanderhooft[1] and Glenn D. Prestwich[2]
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Synthetic extracellular matrix hydrogels can be used for three-dimensional cell culture, wound repair, and tissue engineering. Thiol-modified hyaluronic acid and thiol-modified gelatin can be cross-linked into biocompatible materials and used to aid the development and repair of cells and tissues. The material properties of these hydrogels contribute to their usefulness in a given application. For example, the stiffness of a gel used to aid in bone reconstruction must be much higher than that of a gel used to prevent abdominal tissue adhesions. In addition, the physical properties of materials used as tissue engineering scaffolds help determine cell phenotype and stem cell differentiation. Hydrogels with a wide range of stiffness have been synthesized from a few components in variable concentrations and characterized rheologically. The dependence of oscillatory shear modulus on these composition variables will be discussed.

Wednesday 6:00 Grand Ballroom C PO70

Viscoelastic behavior of ocular lens soluble proteins

Matthew A. Reilly and Nathan Ravi
Department of Veterans Affairs Medical Center, Washington University in St. Louis, St. Louis, MO, United States

Purpose: To elucidate the rheological behavior of lens soluble proteins and infer their role in the dynamics of vision.

Methods: Fresh porcine lenses were decapsulated. The lenses were homogenized using a dounce homogenizer. This homogenate was centrifuged to separate the soluble and insoluble proteins. The viscoelastic behavior of the lens soluble proteins were characterized using capillary and cone-and-plate rheometers at 37°C in steady shear, creep, and dynamic protocols.

Results: The lens soluble proteins exhibit significant shear thinning. Viscous behavior dominated under all conditions, exhibiting a minimum loss tangent of 4.67 at a frequency of 0.65 Hz in the capillary rheometer, and 3.44 at a frequency of 0.63 Hz in the cone-and-plate rheometer. Elastic behavior vanished as shear rate increased. Reversible degradation of fluid structure was observed with respect to strain level and shear rate.

Conclusions: The lens soluble proteins contribute to the viscous portion of the lens' viscoelastic behavior. Shear thinning behavior allows large changes in accommodation to occur with less force than would be necessary if the fluid behaved as a Newtonian fluid. High viscosity at low shear rates resist physiological perturbations to accommodation caused by heartbeat (~0.54 Hz) and neurological activities. Previous efforts using finite element analysis have indicated that the stresses that develop in the lens fiber during accommodation are concentrated within the cell membrane's structural proteins. Thus, the cell membranes contribute the solid-like behavior while the soluble proteins contribute a viscous damping behavior that gives the lens a proper dynamic response to accommodation demand, allowing neural control of accommodation to remain stable.

Wednesday 6:00 Grand Ballroom C PO71

Optimized design of in situ forming vitreous substitutes

Katelyn E. Swindle[1], Scott S. Dobson[2], and Nathan Ravi[3]
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Purpose: To use a statistically designed experimental plan for the development of a biomimetic hydrogel vitreous substitute that forms in situ under physiological conditions.

Methods: Various polyacrylamide hydrogel formulations were synthesized containing a reversible disulfide crosslinker and a hydrophobic comonomer. The hydrophobic comonomer, crosslinker, and hydrogel concentrations were varied. The concentration effects ascertained via preliminary testing were used to design an optimal formulation with viscoelastic and refractive properties similar to the natural vitreous humor. The values from natural porcine vitreous were used as a model for optimizing the hydrogel formulation. The storage and loss moduli of the hydrogels were determined using a Vilastic 3 capillary rheometer (Houston, TX) holding frequency or shear rate constant. The refractive indices of the hydrogels were determined using an Abbe refractometer.

Results: The optimal formulation's viscoelasticity and refractive index were very similar to those of the natural young porcine vitreous. The polymer concentration in the hydrogel had the greatest effect on the viscoelastic properties while the hydrophobic monomer concentration had the least significant effect. Additionally, the variations in the hydrogel composition impacted the viscoelastic properties more significantly than the refractive indices.

Conclusions: The porcine vitreous is a loosely formed viscoelastic biological hydrogel with low storage and loss moduli. We therefore hypothesize that generating a synthetic hydrogel that acts as a viscoelastic solid will be more capable of dampening eye oscillations and tamponading the retina. Preliminary studies in vivo in rabbits have indicated that this hydrogel is extremely biocompatible. Matching the viscoelastic and refractive properties while maintaining this biocompatibility will allow rapid clinical development of an artificial vitreous substitute.

Wednesday 6:00 Grand Ballroom C PO72

Experimental and theoretical studies of the microstructure of incipient and mature blood clots

Phylip R. Williams, Rhodri L. Williams, Karl M. Hawkins, Paul Rees, and Martin R. Brown
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We report experimental and theoretical work involving viscoelastic measurements and NMR diffusion measurements on coagulating blood. Together, the viscoelastic and NMR measurements provide, for the first time, a detailed static and dynamic fractal description of the microstructure of incipient and mature clots. We have conducted complementary modelling and simulation work in this area and, to date, have developed a numerical technique that stochastically generates a representation of both incipient and mature clots with fractal and spectral dimensions commensurate with those characterised in experiments. In this technique the generation of the clot microstructure is mediated by a series of random walks within a 3D space. The clot backbone is first generated by a random walk biased in one direction to ensure the clot spans the whole sample space. This is an important aspect of the simulation as our rheological studies have established that the incipient clot is a space-filling, self-similar object: such objects are appropriately characterised using fractal parameters. Variation of the various fractal parameters is accomplished by randomly choosing points on the sample-spanning incipient clot backbone to launch both random and self-avoiding random walkers. The number of steps each walker takes is a function of the fractal dimensions that are to be achieved. This numerical approach yields information on clot formation and assembly during the interval between incipient and mature clot stages. The potential of this work for developing a diagnostic tool for a range of coagulation disorders alongside rheological and NMR measurements are discussed.

Wednesday 6:00 Grand Ballroom C PO73

Non-linear rheology and ageing of hard and soft sphere glasses

Arnaud Le Grand[1], George Petekidis[1], and Matthias Ballauff[2]
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In colloidal suspensions at very high concentration, the particles are trapped in cages formed by their neighbours and show a very slow structural rearrangement. These systems present characteristics common to molecular glasses: they are non-ergodic, out of equilibrium systems and they show ageing properties. Moreover, colloidal glasses are weak solids that can yield - or be fluidized - under the application of a relatively small stress. We investigated the yielding and ageing behaviour of two different colloidal glasses - hard spheres (PMMA) and soft spheres (thermosensitive core-shell PS-PNIPAM particles) - by dynamic strain sweeps, FT measurements, flow curves and transient stress experiments. We discuss and compare the results obtained in these two systems. In both samples the linear viscoelastic properties evolve with waiting time after a shear induced rejuvenation revealing a progressive stiffening of the vitrified state. The role of particle interactions is assessed comparing the volume fraction dependence of the elastic modulus, the yield strain and stress.

Wednesday 6:00 Grand Ballroom C PO74

Rheology and relaxation of an aging soft colloidal glass

Eko H. Purnomo, Siva A. Vanapalli, Dirk van den Ende, Jorrit Mellema, and Frieder Mugele
Physics of Complex Fluids, University of Twente, Enschede, The Netherlands

We report the linear, non-linear rheological and relaxation behavior of thermoreversible microgel suspensions for which the degree of hindrance (volume fraction) of the suspension is controlled by tuning the temperature. All measurements clearly display an age dependence. The experimental data is in good agreement with the soft glassy rheology (SGR) model. From the evolution of the dynamic moduli (G' and G") with age obtained from linear measurements, we extract a normalized effective noise temperature X/Xg ~ 0.6, i.e. much smaller than unity, as expected for aging systems. The creep compliance J(t-tw, tw), obtained from step stress experiments, for the short time regime ((t-tw)<tw) are consistent with this finding (tw being the sample age). More over, the elasticity of the compressed particles increases with increasing degree of hindrance in agreement with the increasing bulk elasticity (G' and 1/J). We find that the characteristic relaxation time typically lies outside the experimentally accessible frequency window of oscillatory rheological experiments. By applying the recently proposed strain rate frequency superposition technique we determine the characteristic relaxation time. The characteristic relaxation time was found to increase with the sample age with a slope that is consistent with the effective noise temperature extracted from the linear oscillatory measurements.

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Plenary Lectures

8:30 AM Grand Ballroom C

Monday, October 8	**Exact coherent states: controlling turbulence and transition** Fabian Waleffe *Department of Mathematics, University of Wisconsin*
Tuesday, October 9 *Bingham Lecture*	**Single particle motion in colloids: from microrheology to osmotic propulsion** John F. Brady *Department of Chemical Engineering, California Institute of Technology*
Wednesday, October 10	**Novel ink designs for direct writing in three dimensions** Jennifer A. Lewis *Department of Materials Science and Engineering, University of Illinois*

Social Program

Sunday, October 7	**Welcoming Reception** 6:00 PM – 8:00 PM	 Alpine Ballroom
Tuesday, October 9	**Society Business Meeting** 5:30 PM	 Canyon A
	Awards Reception 7:00 PM *Sponsored by a generous contribution from Xpansion Instruments*	 Grand Ballroom C
	Awards Banquet 8:00 PM	 Grand Ballroom C
Wednesday, October 10	**Poster Session Reception** 6:00 PM – 8:00 PM *Sponsored by a generous contribution from Anton-Paar USA*	 Grand Ballroom C

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