THE SOCIETY OF RHEOLOGY

73RD ANNUAL MEETING
PROGRAM AND ABSTRACTS

Hyatt Regency Bethesda
Bethesda, Maryland
October 21-25, 2001

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## Session Codes

- **CA** = Polymers With Complex Architecture
- **CF** = Quantifying Microstructure In Complex Fluids*
- **FI** = Flow Instabilities
- **GP** = General Papers
- **LS** = Probes of Local Rheology and Structure
- **ML** = Molecular Level Modeling and Theory
- **PL** = Plenary Lectures
- **SB** = Phenomena Near Solid Boundaries
- **SM** = Viscoelasticity In Polymer Solutions and Melts*
- **SR** = Solid Rheology From Glasses To Gels*
- **SS** = Simple Fluids To Suspensions
- **TS** = Two Phase Systems: Emulsions, Blends and Suspensions*

* Sessions intended to highlight the contributions of NIST/NBS to the field of rheology
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Nonequilibrium thermodynamics applications in rheology
Antony N. Beris

Chemical Engineering, University of Delaware, Newark, DE 19716

In the last decade significant progress has taken place within non-equilibrium thermodynamics resulting in several formulations for coupled transport phenomena that allowed for an extension and a more systematic application of continuum mechanics to continua endowed with an internal microstructure. A particular fruitful area for applications has been the rheology of complex systems where nonequilibrium thermodynamics has been used to connect the modeling for the mechanical behavior to a description of the internal microstructure. Nonequilibrium thermodynamics can place constraints on model admissibility through the requirement of non-negative entropy production and establish links between various parts of the governing equations linking terms in the expression for the stress tensor to others appearing in the evolution of the internal structure or in mass transfer. Moreover, thermodynamic phase transitions and surface-induced effects can now be consistently described under nonequilibrium conditions. Finally, the connection between various levels of description (for example, microscopic versus macroscopic) can more consistently be made. A particular example in polymer rheology is the nonequilibrium casting of kinetic theory models that has allowed for a more systematic handling of heat and mass transfer effects.

In this presentation we will first outline the general modern approach that involves the merging of the more traditional approach of modeling dissipative phenomena through Linear Irreversible Thermodynamics (and its nonlinear generalizations) with the most general Poisson-bracket description of conservative dynamics. Then, we will overview illustrative examples to rheology with particular emphasis to the study of polymer systems under flow. New phenomena are observed due to the coupling between various transport and relaxation processes with important consequences as far as the understanding of the nonlinear dynamics and the rheology of complex systems.
Monday Morning

community, since they probably represent Schowalter's first experimental study in rheology. We showed for a solution of polyisobutylene in decalin that the radial distribution of normal stresses in a 25 cm-diameter (!) cone-and-plate rheometer is linear in the logarithm of the radius. Inertial effects were shown to be negligible.

Monday 10:10 Cabinet SS2

**Dynamic simulation of sheared suspensions of non-Brownian spheres**

Andreas Acrivos¹, German Drazer¹, Boris Khusid², Joel Koplik¹, and Marco Marchiorò³

¹The Levich Institute, The City College of the City University of New York, New York, NY 10031;
²Department of Mechanical Engineering, New Jersey Institute of Technology, Newark, NJ 07102;
³RiskMap SpA, Milan, Milan, Italy

We studied the flow of a monodisperse suspension of non-Brownian spheres in a simple shear flow, using Stokesian dynamics simulations. We showed that the evolution of the system in phase space is chaotic, leading to a diffusive behavior at long times, and evaluated the particle tracer diffusion coefficient in both transverse directions as a function of the volume fraction. This diffusivity was computed for particle volume fractions up to 0.45 both from the slope of the mean square particle displacements as well as by integrating the corresponding velocity autocorrelation function. We also studied how the presence of an interparticle non-hydrodynamic force affects the scaling of the diffusion coefficient at very low volume fractions and we showed that, as \( \phi \) goes to zero and in the absence of non-hydrodynamic forces, this coefficient scales as \( \phi^2 \), whereas for large interparticle repulsive forces, a linear dependence on \( \phi \) is observed.

Monday 10:35 Cabinet SS3

**Large scale hydrodynamic simulations of Brownian suspensions**

Jonathan L. Higdon and Marc N. Viera

Chemical Engineering, University of Illinois, Urbana, IL 61801

Recently, a method was developed for efficient computation of hydrodynamic interactions in concentrated suspensions. This method followed the classic Stokesian dynamics approach with a far field multipole expansion for the many body effects combined with an exact two body near field lubrication correction. The new algorithm is based on a particle mesh Ewald approach whereby near field interactions are evaluated directly and far field interactions are computed using a grid based velocity computed with FFT's. This yields an \( O(N \ln N) \) algorithm where \( N \) is the number of particles. Simulation results have been presented for dynamic simulations with up to 64,000 particles and Monte Carlo realizations with up to 1 million particles.

In the present paper, we extend the fast Stokesian dynamics algorithm to include the effects of Brownian motion. In the simplest Brownian dynamics simulations, one body hydrodynamic resistance functions are employed, and the stochastic Brownian forces may be modelled with simple uncorrelated random forces or displacements. When accurate hydrodynamic interactions are included, the fluctuation dissipation theorem requires that the individual Brownian forces or displacements satisfy a correlation equation based on the N body resistance tensor \( R \). In practice, the calculation of these forces/displacements requires the computation of a matrix square root \( R^{1/2} \). The cost of this operation via direct methods or traditional iterative methods would be prohibitive. We present a novel iterative approach which exploits the particle mesh Ewald formulation and yields the Brownian forces/displacements with a computational effort approximately equal to that of the non-Brownian hydrodynamic computation.

Numerical results will be presented for the rheology of concentrated Brownian suspensions based on dynamic simulations with up to 64,000 particles.

Monday 11:00 Cabinet SS4

**Suspensions in extensional flow**

Saud Smai and John F. Brady

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Stokesian Dynamics simulations of mono-disperse hard-sphere colloidal dispersions in planar extensional flow are carried out over a wide range of volume fractions and shear rates (or Peclet numbers). Results are presented for the first and second extensional viscosities, the long-time self-diffusivities, and the suspension microstructure from the
Brownian dominated regime at low Peclet number to the hydrodynamically dominated regime at high Peclet number. Comparison to theory and experiment and to the behavior in simple shear flow is made.

Monday 11:25 Cabinet

**Inertial influence on the rheology of a dilute suspension of spheres**

Jeffrey E. Morris and Duane R. Mikulencak

*School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100*

The influence of weak inertia on the rheology of a dilute simply-sheared suspension of spheres was studied by Lin, Peery and Schowalter (1970 JFM 44, 1); the work used asymptotic methods to examine the stresses generated by the particles at small Reynolds number, Re. Despite rapid advances in numerical solution of fluid flows, a thorough study of the role of inertia on dilute suspension rheology at elevated Reynolds numbers has not been presented to date. Here, results of a study of the simple-shear rheology of a dilute suspension are presented for $10^6 < Re < 100$, using flow field information for simple shear flow around an isolated sphere computed by finite-element algorithms tailored to provide high accuracy. The particle surface traction moment, or stresslet, and volumetric Reynolds stress contributions to the bulk stress resulting from a force- and torque-free, as well as a fixed, sphere will be presented. It is observed that the particle contribution to the stresses shear thicken in the sense of increasing as the value of Re increases; the inertial flow results in asymmetries in the stress and fluctuational velocity fields leading to normal stress differences which are found to be consistent with theoretical predictions of the noted work of Lin et al at small Re. Selected flow fields from which the computed stresses were determined will also be presented, and the vortex stretching field -- that is, $w e$ as a function of position, with $w$ the vorticity and $e$ the rate of strain -- generated by the presence of a suspended particle at finite Reynolds number will be presented.

**Symposium FI**

**Flow Instabilities**

Organizers: Michael Graham and Peter D. Olmsted

Monday 9:45 Old Georgetown

**Influence of fiber additives on the stability of Taylor-Couette flow**

Vijay Gupta¹, Radhakrishna Sureshkrumar¹, Bamin Khomami¹, and J Azaiez²

¹Washington University, Saint Louis, MO; ²University of Calgary, Calgary, Alberta, Canada

Small amount of additives such as polymers, surfactants and fibers to shear flows can modify their linear and nonlinear stability characteristics depending on the flow geometry (e.g. free vs. wall-bounded, curved streamlines) and the interaction of the additive with the flow to yield normal stresses. In this work, we investigate the influence of non-Brownian fiber additives on the linear stability of Taylor-Couette (TC) flow of a Newtonian fluid. The constitutive model is similar to that used by Azaiez (JFM 2000) but with hybrid or quadratic closure approximation for the higher moments of the fiber orientation. This model predicts shear thinning of the first and the second normal stresses that arise from the non-planar steady state fiber orientation field. It is found that fiber additives provide moderate stabilization to the TC flow. The onset of instability is governed by three parameters: the volume fraction and the aspect ratio of the fiber additives and an interaction coefficient that accounts for hydrodynamic interactions. A parametric study reveals that enhanced inter-fiber interactions can induce significant stabilization of the flow in the semi-dilute regime. The stabilizing effect arises from the favorable negative fiber normal stress. The most dangerous eigenvalue is real, corresponding to a stationary and mode of instability, as in the case of the Newtonian TC flow. These results will be evaluated in the light of a kinetic energy budget associated with the secondary flow. We will also compare the effect of fiber additives with those caused by soluble polymers. Influence of the closure approximation on the linear stability analysis predictions will also be discussed.
Finite-amplitude waves in plane channel flow of viscoelastic fluids
Kunt Atalik and Roland Keunings
Cesame, Universite Catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

A non-linear analysis of the temporal evolution of finite, two-dimensional disturbances is conducted for plane Poiseuille and Couette flows of viscoelastic fluids. A fully-spectral method of solution is used with a stream-function formulation of the problem. The upper-convected Maxwell (UCM), Oldroyd-B and Giesekus models are considered. The bifurcation of solutions for increasing elasticity is investigated both in the high and low Reynolds number regimes. The transition mechanism is discussed in terms of both the transient linear growth of misfit disturbances due to non-normality, and their possible saturation into finite-amplitude periodic solutions due to non-linear effects.

Toward a structural understanding of turbulent drag reduction: Nonlinear coherent states in viscoelastic shear flows
Philip A. Stone and Michael D. Graham
Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706

Recently discovered "exact coherent states" in Newtonian plane shear flows provide an opportunity to study the behavior of polymers in steady flows that retain many of the important properties of turbulent velocity fields, such as exponentially stretching material lines and a (Lagrangian) spectrum of time scales. Perhaps most importantly, these states arise near the experimentally observed transition Reynolds number and exhibit a streamwise "streaky" structure clearly related to that observed in the turbulent buffer layer. First, the FENE-P dumbbell constitutive equation is coupled to the momentum balance equation to determine how the elasticity and maximum extensibility of the polymer model affect these exact coherent states. For low values of the elasticity, El = We/Re, a minimum is seen in the critical Reynolds number for the appearance of the coherent states. When the Weissenberg number based on the largest Liapunov exponent for the velocity field becomes greater than 0.5, the three-dimensionality of the solution decreases compared to the Newtonian case. Accompanying this decrease in three-dimensionality is an increase in the average streamwise velocity, i.e., drag reduction occurs. The relationship between polymer and vortex stretching in the flow is also analyzed. Second, the behavior of passive stochastic polymer chains is investigated in these model flows. A Brownian dynamics simulation of bead-spring polymer models with finitely extensible connectors calculates the polymer configuration. The effects of chain length and flexibility, hydrodynamic interactions, and excluded volume on the polymer configuration are examined. Results from the Brownian dynamics simulations allow us to assess the utility of the FENE-P model used for the full fluid dynamics calculations.

Location of the continuous spectrum in complex flows of the UCM fluid
Michael Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

In contrast to the Newtonian case, linear stability problems for viscoelastic flows involve continuous as well as discrete spectra, even if the flow domain is bounded. Numerical methods approximate these continuous spectra poorly, and incorrect claims of instability have been published as a result of this on more than one occasion. In this paper, we shall derive some analytical results on the location of the continuous spectrum for linear stability of flows of the upper convected Maxwell fluid. In general, we shall show that in "subsonic" flows where the fluid speed is always slower than the speed of shear wave propagation, there are only three possible contributions to the continuous spectrum: 1. A part on the line Re(\(\lambda\)) = -1/W, where W is the relaxation time of the fluid. 2. A part associated with the short wave limit of wall modes that has real parts confined between -1/W and -1/(2W). 3. A part associated with the integration of stresses in a given velocity field. If the flow is two-dimensional and has no stagnation points, then the latter part also has real part on the line Re(\(\lambda\)) = -1/W, and hence the continuous spectrum is always stable.
Monday 11:25 Old Georgetown

**Linear stability of periodic channel flow: Local and non-local analyses**

Balraj Sadanandan and Radhakrishna Sureshkumar

*Washington University, Saint Louis, MO*

Periodic geometries have served as rigorous benchmarks for viscoelastic flow modeling due to their ability to represent different flow types, e.g. open vs. closed streamlines, streamline curvature, separation effects, and periodic modulation of the flow cross section. However, the present picture of the mechanisms that cause flow instabilities in such flows is far from complete. To a great extent, this is due to the computational challenges presented by the stability analysis of such flows arising from lack of closed-form base flow solutions and the large dimension of the associated generalized eigenvalue problem (GEVP). Localized normal mode expansions have been used to reduce computational complexity. However, the local approximation limits the range of perturbation wavenumbers that can be imposed: in general, \( \text{We} \ (n/a) \ll 1 \) where \( \text{We} \), \( n \) and \( a \) denote the Weissenberg number, the frequency of the geometry and the streamwise wavenumber of the perturbation respectively. In this work, we develop a mixed spectral method that will enable us to perform a global (non-local) stability analysis of periodic flows with no internal stagnation points. This method uses pseudo-spectral Chebyshev collocation in the wall-normal direction and a Fourier Galerkin projection in the streamwise direction. The flow is mapped from the periodic domain to a standard rectangular domain in which the computations are performed. The Jacobian of the mapping is represented as data corresponding to a Fourier series expansion in the streamwise variable. This scheme allows for the resolution of the continuum set of eigenvalues corresponding to each Fourier mode. This is particularly advantageous since the continuum set of eigenvalues often causes erroneous predictions of instability. The results obtained from the non-local stability analysis will be compared with those obtained from the local analysis (Sureshkumar, JNNFM, 97: 125-148 (2001)).

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**Symposium CF**

**Quantifying Microstructure In Complex Fluids**

Organizers: Norman Wagner and Alan I. Nakatani

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Monday 9:45 Judiciary

**Structure and rheology of polymer blends under shear flow**

Charles C. Han\(^1\), Alan I. Nakatani\(^2\), Erik K. Hobbie\(^1\), and Hyun S. Jeon\(^3\)

\(^1\)Polymers, NIST, Gaithersburg, MD 20899; \(^2\)Rohm and Haas Company, Spring House, PA; \(^3\)Dept. of Petroleum and Chemical Engineering, New Mexico Tech, Socorro, NM 87801

For symmetrical low molecular mass polymer blends, the phase diagram shift and the structure formation and mixing under shear flow has been studied by the combination of Small Angle Neutron Scattering (SANS), dynamic light scattering and shear light scattering microscopy techniques. The shear suppression of critical temperature and the droplet deformation, breakup and string formation can be explained by the theoretical predication of Onuki and Kawasaki, which is based on a mode-coupling renormalization-group (MCRG) calculation together with the classical Taylor-Tomotika theory. For high molecular mass and viscoelastic blends of polyutadiene (PB) and polyisoprene (PI), the viscoelastic effect plays an important role. For a near critical low vinyl PB (LPB) and a low vinyl PI (LPI) blend, the terminal loss modulus above and below the LCST is well described by means of a log additive mixing rule. A single master curve in the loss modulus was obtained above and below the LCST by using the empirical time temperature superposition (tTS) principle. However, the storage modulus above the LCST deviates from both the tTS principle and the log additive mixing rule. The discontinuity caused by this deviation in the \( G' \) vs temperature plot depends on the frequency used and it extrapolates in the limit of zero frequency to the cloud point measured under quiescent condition. The droplet breakup and string formation and mixing for this LPB/LPI blends is very similar to the low molecular mass blends. For blends with large viscosity mismatch, such as a low vinyl PB (LPB) and a high vinyl PI (HPI) blend used in this study, we find that a coexisting structure (apparent as a “walnut-like” light-scattering pattern) develops probably due to a shear-induced phase inversion at a fixed composition (\( j_{\text{HPI}} = 0.8 \)) and constant temperature. The relaxation processes after cessation of shear depends on the shear history. The influence of hydrodynamic instability, diffusion, and the spinodal decomposition will be demonstrated.
Shear induced demixing of temperature sensitive microgel suspensions

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Temperature sensitive polymers are termed "smart materials" because they allow to strongly influence flow properties by simple temperature variation. A well studied system is water soluble poly-(N-isopropylacrylamide) (PNiPAM) which is known to undergo a temperature induced phase transition (LCST) at around 32-34°C. Chemically crosslinked PNiPAM microgels were obtained by emulsion polymerization using N,N\textsuperscript{-}methylenebisacrylamide as a crosslinker. The swelling and deswelling of the thermosensitive microgel particles was monitored by means of static and dynamic light scattering (LS). With increasing temperature the hydrodynamic radius of the particles first decreased slightly but a strong volume transition occurred at the LCST. The effective volume fraction $\phi_{\text{eff.}}$ was determined in dilute solution using an expression derived by Batchelor relating the relative viscosity $\eta_{\text{rel.}}$ to $\phi_{\text{eff.}}$. The rheological properties of concentrated solutions of the microgel particles were investigated at different temperatures and concentrations. The shrinking of the microgel particles with increasing temperature resulted in a strong dependence of shear viscosity $\eta_\tau$, moduli $G',G''$ and yield stress on temperature. Online measurements of the rheological properties were carried out simultaneously with birefringence or transmission experiments using a rheo-optical setup. Shear induced phase separation was observed for the PNiPAM microgel suspensions. The cloud point temperature $T_c$ decreased under shear. Additional small angle neutron scattering (SANS) studies at rest and under shear were conducted at temperatures near the LCST. In concentrated solution at temperatures below the LCST the microgel particles were close to contact thus a structure factor was obtained. Increasing the temperature induced deswelling of the particles so that the structure factor vanished.

Shear-induced tilt order in viscoelastic emulsions

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Light scattering and optical microscopy are used to measure the domain morphology as a function of shear rate and composition in polymer blends with viscoelastic asymmetry in the melt components. The blends studied are immiscible mixtures of low-vinyl polybutadiene (PB) and high-vinyl polyisoprene (PI), where the vinyl content strongly influences the rheological properties of the melt. At 130°C, where the measurements were performed, the PI exhibits dramatic shear thinning and a relatively large first normal stress difference, while the PB exhibits a viscosity that is independent of shear rate and a negligible first normal stress difference. The disparate rheology of the two components leads to a rich variety of domain shapes and droplet orientations in the flow-vorticity plane as the shear rate and composition are varied. For PI volume fractions between 0 and 0.4, the minority (PI) phase forms domains that acquire a component of elongation along the direction of vorticity at moderate to high shear rates. In the strong-shear limit, these mixtures exhibit long-range correlation in the tilt angle between the axis of elongation and the vorticity axis. At a fixed composition, this tilt angle decreases with increasing shear rate. At a fixed shear rate, the tilt angle increases with increasing composition. Accompanying this orientational order is weak liquid-like order in the two-point correlation function along the direction perpendicular to the axis of mean elongation. The importance of droplet-droplet interactions and the internal elasticity of the domains will be discussed.

Shear-induced phase separation in wormlike micellar fluids

Srinivasa R. Raghavan, Beth A. Schubert, and Eric W. Kaler
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Polymer solutions in the vicinity of the theta-point are known to phase-separate when subjected to shear. Recent studies in our laboratory show that the same phenomenon also occurs for certain wormlike micellar solutions. Wormlike micelles are the self-assembled counterparts of polymers, characterized by their ability to reversibly break and recombine. In the system of interest, the micelles are formed by the cationic surfactant, erucyl bis(hydroxyethyl)methyl ammonium chloride (EHAC), in conjunction with a salt such as sodium chloride (NaCl) or sodium salicylate (NaSal). Those solutions that become turbid under shear are distinguished by their proximity to a
upper- or lower-consolute phase boundary. Once the shear is stopped, the turbidity disappears slowly with time and the homogeneous state is eventually recovered. Rheo-optics and flow-SANS are used to probe the microstructure under shear. These studies suggest that the turbidity is due to shear-enhanced concentration fluctuations manifesting as anisotropic domains large enough to scatter light.

Symposium ML
Molecular Level Modeling and Theory
Organizers: David Morse and Jimmy Feng

Monday 9:45 Diplomat/Ambassador ML1
Brownian dynamics simulations with hydrodynamic interaction for polystyrene solutions in extensional flow
Chih-Chen Hsieh, Lei Li, and Ronald G. Larson
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Taking advantage of recent improvements in simulation methods (Jendrejack, Graham and de Pablo, 2000), full hydrodynamic interactions have been included in bead-spring Brownian dynamic simulations for up to 70 beads. We performed the simulations for dilute polystyrene solutions in extensional flow and focus on the transient behavior of the stress. The hydrodynamic interaction parameter in our simulation is obtained a priori by matching the drag force from a fully extended bead-spring model with that from Batchelor’s theory for cylindrical rods. This method gives us a reasonable estimation of hydrodynamic interaction parameter so that the simulation can be done without fitting experimental data. We will present the results for polystyrene of molecular weight 2 million simulated with different number of beads, and discuss the influence of the HI parameter. The simulation results with HI for polystyrene will also be compared with those without HI and with experimental results. We conclude that for accurate simulation of HI for high-molecular-weight polymers, the use of large numbers of beads (> 100) is unavoidable.


Monday 10:10 Diplomat/Ambassador ML2
Transient and steady behavior of semiflexible bead-rod chains in shear flow
Alberto Montesi and Matteo Pasquali
Department of Chemical Engineering, Rice University, Houston, TX 77005

We are studying transient and steady behavior of dilute solutions of linear polymer in shear flow. The polymer molecules are modeled as freely-draining, non-interacting semiflexible bead-rod chains. The dynamics of the chains are simulated with the Brownian Dynamics mid-step algorithm of Grassia & Hinch, modified by Pasquali et al. to compute efficiently metric and bending forces. Variance reduction techniques are introduced to compute statistically meaningful average properties at reasonable computational cost. Molecular visualization techniques are used to provide further insight into the dynamics of single chains. The effects of contour length and persistence length (chain stiffness) on the conformational and material properties is being studied. Preliminary results show that stiffer molecules expands less in flow, as expected.

Monday 10:35 Diplomat/Ambassador ML3
Modeling of dilute polymer solutions by Dissipative Particle Dynamics
Guoai Pan and Charles W. Manke
Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Dissipative Particle Dynamics (DPD) is employed to model the dynamics of a dilute polymer solution in steady shear flow. The polymer molecules are represented by 10-bead FENE chains, and the surrounding solvent is modeled by free DPD particles. Thermodynamic interactions between the polymer and solvent are modeled by a solvent quality parameter that modifies the repulsive forces between the polymer and solvent species. The simulations successfully predict the expansion of the polymer chains in a good solvent environment and the
attendant enhancement of intrinsic viscosity and other rheological properties. Like previous Brownian dynamics simulations for FENE chains, the DPD simulations predict realistic shear-thinning behavior for both the viscosity and the first normal stress coefficient. Unlike previous simulations, which typically overpredict macromolecular extension ratios, the DPD simulations predict macromolecular extension ratios and orientation angles that are in excellent agreement with experimental data.

Monday 11:00 Diplomat/Ambassador ML4

Use of an Adaptive Length Scale model in the simulation of flow of a viscoelastic fluid through an axisymmetric contraction-expansion
Yong L. Joo1, Scott D. Phillips2, Jonathan P. Rothstein3, Gareth H. McKinley4, Robert C. Armstrong2, and Robert A. Brown2
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Recent experimental and numerical studies have shown that the dynamical behavior of dilute polymer solutions in strong extensional flow is far more complex than the qualitative description given by a simple elastic dumbbell undergoing uniaxial stretching. For example, experimental measurements of the pressure drop for dilute polymer solutions flowing through axisymmetric contraction-expansions have shown a substantial enhancement of the pressure drop with increasing Deborah number. In contrast, existing steady-state or transient numerical computations with simple elastic dumbbell models predict a significant decrease in the pressure drop with increasing Deborah number. One possible source of the disagreement between experiment and simulation is the poor description of the transient extensional behavior of a polymer chain by the simple elastic dumbbell models. We examine viscoelastic flow through axisymmetric contraction-expansions with the new Adaptive Length Scale (ALS) model developed by Ghosh et al. (2001). This model provides a better description of the transient extensional rheology of a dilute polymer solution than either the Oldroyd-B or FENE dumbbell models. In the new closed constitutive equation, referred to as the ALS-C model, the polymer molecule is viewed as a set of identical segments that are each short enough to be stretched reversibly. The calculations are performed by discretizing in space with the finite element method coupled with a fourth-order Runge-Kutta method for time integration. Our results show that the ALS-C model predicts an enhanced pressure drop with increasing Deborah number, as is observed experimentally. The effects of re-entrant corner curvature and contraction ratio on the pressure drop, vortex structure, and birefringence patterns are investigated and compared with recent experiments by Rothstein and McKinley (1999, 2001).

Monday 11:25 Diplomat/Ambassador ML5

Brownian dynamics simulation of a full-chain temporary network model with sliplinks
Jay Schieber1 and Jesper Neergaard2
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A recently proposed full-chain, temporary network model for the nonlinear flows of linear, entangled polymeric liquids is presented. The model is inspired by the success of a recent, full-chain reptation model [1, 2, and references therein], but contains no tubes. Instead, each chain uses a different (and smaller) set of dynamic variables: the location of each entanglement, and the number of Kuhn steps in chain strands between entanglements. However, the model requires only a single phenomenological parameter that is fit by linear viscoelasticity. The entanglements are assumed to move affinely, whereas the number of Kuhn steps varies stochastically from tension imbalances and Brownian forces. In the language of reptation, the model exhibits chain connectivity, chain-length fluctuations, chain stretching, and tube dilation. Predictions of the new model by means of Brownian dynamics simulations are compared with those of the full-chain reptation model. In particular, the successes and limitations of the reptation model are addressed, including overshoot in both shear and first normal stresses, strain-rate dependence of the strain magnitude at maximum stress, steady-state viscosity and first-normal-stress coefficient as functions of shear rate, and transient and steady-state behavior of the extinction angle.

Monday Afternoon

Symposium SS
Simple Fluids To Suspensions
A Symposium in Honor of William R. Schowalter
Organizers: Andrew M. Kraynik and William B. Russel

Monday 1:30 Cabinet SS6
Two-dimensional suspensions: Dynamics and rheology
Gerald G. Fuller1, Alex Laschitsch1, Martin Widenbrant1, Ed Stancik1, and Jan Vermant2
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Colloidal particles are often used to stabilize emulsions. Commonly referred to as "Pickering" emulsions, these systems are employed to handle systems that are otherwise difficult to stabilize, such as water-in-oil emulsions. These particles are attracted to the liquid/liquid interfaces and form viscoelastic films that retard coalescence. This paper discusses the fluid dynamics and interfacial rheology of monolayers of model, colloidal spheres. The spheres (monosized polystyrene particles with diameters of 3 microns) assemble at the interface between air and water or oil and water to form 2-dimensional, structured monolayers characterized by complex interparticle potentials with multiple minima. Under most circumstances long range order in the form of 2-dimensional crystals is observed. Flow microscopy has been used to following flow induced structure within the monolayers subject to both simple shear and extensonal flows. Fourier transformation of the images reveal transitions in the monolayer microstructure that include melting and recrystallization. The rheology of these monolayers has been examined using an interfacial stress rheometer (ISR). This instrument reveals a strong dependence by the complex interfacial moduli on the area fraction of the particles. These material functions strongly diverge at a critical value of the area fraction that depends on the strength of electrostatic repulsive forces.

Monday 1:55 Cabinet SS7
Apparent viscosity of the non-colloidal suspension under the influence of particles spin
Shihai Feng1, Alan L. Graham1, James R. Abbott1, and Howard Brenner2
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The influence of particles spin on the apparent viscosity of non-colloidal suspension is investigated using a boundary element method. The results are compared with various theoretical predictions of fluids with asymmetric stress tensors. Results will be presented for various concentrations and asymmetry of the stress tensor. The numerical results reveal that particles spin has a pronounced affect on apparent viscosity of the suspension. Varying the spin gradient from positive to negative, the apparent viscosity changes from close to zero to infinite with asymptotic change to apparent negative viscosity. The effects of the spin field are independent of the effects of the pressure-induced field. The spin viscosity determined by the numerical calculation agrees well with dilute suspension predictions.
Normal stresses and free surface deformation in concentrated suspensions of noncolloidal spheres in a viscoelastic fluid

Isidro E. Zarraga, Davide A. Hill, and David T. Leighton

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The rheology of concentrated suspensions of noncolloidal spheres in a constant viscosity elastic fluid were characterized using rotating plate viscometers and profilometry of the suspension surface deflection near a rotating rod. It was found that the relative viscosity was quantitatively consistent with a previously determined correlation for suspensions based on Newtonian fluids. Moreover, the first normal stress difference $N_1$ was found to be positive and the second normal stress difference $N_2$ negative. Although the magnitude of $N_1$ and $N_2$ increased with the solids concentration $c$, in general the ratio $|N_1/N_2|$ decreased as loading increased. Analysis of the normal stress data suggests that the rheological contribution of the solids microstructure was approximately decoupled from that of the dissolved polymers at high solids loading ($c < 0.3$).

Measurements of the surface deformation of the suspension near a rotating rod exhibited three different types of deflection: pure rod-climbing, pure rod-dipping, and combination of the two, with an upward climb near the rod and a downward deflection further away from the rod. These observations were found to be qualitatively consistent with the rheological measurements conducted in rotating plate viscometers, with $N_2$ becoming increasingly more important than $N_1$ with solids loading. It is proposed that the phenomenon responsible for this behavior is the "isotropic-rendering" of the stretched polymer molecules in the interstices of the solids and the dominant influence of the solid particle microstructure on the bulk rheology as $c$ increases.

Keywords: suspension, noncolloidal, rheology, osmotic pressure

Flow of particulate suspensions through porous media subjected to resonant acoustic fields

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Acoustic methods offer an enormous potential for the rapid, effective, and energy efficient manipulation of fine particles (1-100 micron) suspended in fluids. We have developed a particle-fluid separation process that involves application of a resonant acoustic field to a highly porous medium positioned within a flowing suspension. The acoustic excitation enables the porous medium to entrap suspended particles up to 100 times smaller than its nominal pore size. The process requires low acoustic power, typically results in 90% collection efficiency, and the entrapment is reversible.

Detailed observations of the motion of the suspended particles within an acoustically excited porous medium reveal various types of flow phenomena that affect the particle-retention phenomena. In some instances, particle streamlines are focussed along preferred pathways resulting in the formation of chains of particles sequentially deposited at fixed positions within the porous medium. In other cases, collections of particles, which remain levitated and unattached to the elements of the porous medium, are observed. In some instances these collections follow stable closed orbits. Lastly, we observed that particles encounter strong accelerations away from certain positions within the porous medium.

To elucidate the origins of the flow phenomena described above, we have completed a trajectory analysis of particles within an acoustically excited porous medium. The analysis accounts for hydrodynamic effects in the vicinity of the elements of the porous medium and the forces resulting from the scattering of the acoustic field by the porous medium. The analysis accounts for the material properties of the suspended particles and the porous medium, the intensity of the acoustic and flow fields, and pertinent geometric characteristics of the porous medium. The results of the trajectory analysis provide rationale for the three categories of flow phenomena described above.
Shear thickening and shear thinning in concentrated suspensions
Richard L. Hoffman
Retired (Monsanto/University of New Hampshire), Wilbraham, MA 01095

Considerable insight into the process of shear thickening can be obtained by comparing the flow behavior of suspensions stabilized in various ways with one another and with similar suspensions that are flocculated. For example, by comparing the flow behavior of concentrated shear thickening cornstarch suspensions in glycerin with the flow behavior of monosized PVC in dioctyl phthalate at the same concentrations, we obtain some flow curves that superimpose. From this we infer that layered flow can occur in the starch suspensions, even though light diffraction gives no evidence of ordered flow. This conclusion follows because the monosized PVC suspensions, which match the flow response of the starch suspensions, give pronounced diffraction patterns showing layered flow at low shear.

Another comparison involves the flow behavior of stabilized, shear thickening suspensions of cornstarch with flocculated suspensions of the same particles at equal concentrations. Before shear thickening occurs in the stabilized suspensions, the flow curves lie well below those of the flocculated suspensions at the same concentrations. But, in the shear thinning region that follows shear thickening, the flow curves for the stabilized suspensions show a telling response relative to the flow behavior of the flocculated suspensions. At the highest particle concentration tested, the curves superimpose. Then, as the concentration of particles is reduced, the flow curves for the stabilized suspensions overshoot the curves for the flocculated suspensions. Finally, at yet lower concentrations, the flow curves for the stabilized suspensions fall below the curves for the flocculated suspensions. Taking the view that flocculated suspensions should represent an upper bound on the flow response of suspensions which shear thicken through hydrodynamic clustering, we suggest that hydrodynamic clustering is an unclear and unlikely mechanism at high particle concentrations, but it may have validity at lower particle concentrations.

Reversible shear thickening in concentrated colloidal dispersions
Norman J. Wagner¹ and Brent J. Maranzano²
University of Delaware, Newark, DE 19716; Chemical Engineering, PPG Industries, Inc, Pittsburgh, PA 15230

Shear thickening is of concern in the processing, coating, and formulation of numerous industrial and commercial products that contain colloidal dispersions. A decade of research by numerous laboratories using simulation, theory, rheology and rheo-optics has elucidated the basic mechanism to be consistent with the formation of a "hydro-clustered" microstructure. In this presentation, a large data set on model, stable colloidal dispersions is analyzed within the framework of a scaling model that connects the bulk rheology to the particle and solvent properties, particle interactions, and particle concentration. The scaling model considers both the balance of forces and timescales for the incipient formation of the "hydro-cluster" microstructure. Hard-sphere, charge stabilized, and polymer stabilized latices, as well as weakly flocculated systems are considered in the analysis and comparison with data. Further, small angle neutron scattering experiments elucidating the detailed three-dimensional microstructure in the shear-thickened state are compared quantitatively with theory and simulation.

Scaling relations for suspensions of soft spheres
Jan J. Mewis¹ and Gary Biebaut²
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The scaling laws for the rheological properties of suspensions with Brownian hard spheres are well documented. They have been extended to systems in which the particle interactions are not "hard", an approach which obviously has its limitations. Here, the applicability of the hard sphere scaling is investigated for suspensions of different types of sterically stabilized suspensions. In these systems the range of interaction as well as the steepness of the interaction potential is varied by using particles with different grafting density and molecular weight of the stabiliser polymer. In addition, the molecular configuration of the stabiliser layer is modified by changing the solubility of the medium for the grafted molecules. The interparticle potentials are derived from data of the dynamic moduli.
Monday Afternoon

Procedures are evaluated that incorporate a concentration-dependent softness without introducing additional parameters. They are used to scale low and high shear Newtonian viscosities. Scaling relations for the apparent yield stress and the high frequency dynamic moduli are also considered. One cause of deviation from general behaviour for the concentrated systems is the hydrodynamics on close contact, this is demonstrated with data on shear thickening.

Monday  4:50       Cabinet  SS13
Rheology of hairy particle suspensions
Michael H. Duits, Paul A. Nommensen, Dirk Van den Ende, and Jorrit Mellema
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We studied the linear and nonlinear rheological behavior of suspensions of polymerically stabilized colloidal particles. The particles consisted of a spherical silica core, onto which poly (dimethyl-siloxane, PDMS) chains were endgrafted. Both the core radius and the layer thickness had a size of approximately 40 nm. In good solvents like heptane, the polymer chains assume a brush-like structure. Flow curve measurements showed a low-shear viscosity plateau that increased five orders of magnitude with increasing concentration in a very narrow range around a critical concentration. Below this critical concentration, the dependence of the low-shear viscosity on concentration differs significantly from hard sphere behavior. Above the critical concentration, low-shear viscosity plateaus were observed, too, followed by an extreme shear-thinning in which the shear stress was virtually constant. In this concentration range hysteresis was observed. The behavior at high shear rates was captured with lubrication based modeling. Viscoelastic behavior could only be measured at concentrations above the transition. The observed storage moduli were virtually frequency independent. Their concentration dependence was satisfactorily described with a model based on the work of Elliott and Russel [S.L. Elliott and W.B. Russel., J. Rheology 1998, 42, 361]. Essential ingredients of this model are the particle pair potential and the associated radial pair distribution function, g(r12). The pair potential was calculated with theories from polymer physics, using the results of the chemical particle characterization as input. g(r12) was calculated using Monte Carlo simulations. Both ordered and disordered structures were found above a concentration close to the critical concentration found in the flow curves. Remarkably, these structure differences caused only a marginal difference in calculated values for the storage modulus.

Monday  5:15       Cabinet  SS14
A two-fluid model for electro- and magnetorheological fluids
Karl von Pfeil1, Michael D. Graham1, Jeffrey E. Morris2, and Daniel J. Klingenberg1
1Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706; 2School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100

Mesoscopic models of ER and MR suspensions are very popular for investigating these complex materials. Here, the suspensions are modeled as interacting particles in a continuum. Unfortunately, these methods cannot presently be utilized to simulate the entire suspension volume of an experiment or a device. Modeling such large volumes can be important, for example, to describe devices where the applied fields are not uniform, or to describe large-scale particle migration (e.g., shear-induced diffusion and stripe formation). As an alternative approach, we have developed macroscopic, continuum-level models for describing the behavior of ER and MR suspensions. Here, the media are treated as continua, and the magnetic field strength and the conservation of mass, momentum and energy are described by just a few macroscopic balance equations. These balance equations can easily be solved to describe the entire suspension volume. The challenge is to include appropriate models for the constitutive behavior, such as the relationship between the stress and such variables as the strain rate, field strength, concentration, etc. In this presentation, we will describe a macroscopic, two-fluid model for ER and MR suspensions, wherein the suspension stress is described in terms of electrostriction and magnetostriiction coefficients, respectively. We will show that this approach recovers various features observed in ER and MR suspensions, such as the formation of particulate columns in quiescent suspensions, and the formation of particulate stripes in shear flow.
Monday Afternoon

Symposium FI
Flow Instabilities
Organizers: Michael Graham and Peter D. Olmsted

Monday 1:30 Old Georgetown  
**Linear stability of homogeneous shear flow of linear and branched polymer melts**  
Vijayalakshmi Ganesan and Bamin Khomami  
*Chemical Engineering, Washington University, St. Louis, MO 63130*

In this work, we examine the dynamics of both linear and branched polymer melts in homogeneous shear flows. The evolution of the microstructure in branched and linear polymers is described by the Pompom and the Marucci, Greco and Ianniruberto models respectively. Our overall goal is to study the linear stability characteristics of these models as well as examining their continuous and discrete spectra in order to develop efficient time-dependent algorithms for complex flow simulations. In order to accomplish this goal, we have adopted two of the classical methods namely, the generalized eigenvalue problem and time integration of the linearized equations. Specifically, we have obtained results regarding the continuous and discrete spectra for these models which clearly demonstrate that a highly accurate and self consistent solution to the stress and velocity fields are required at each time step in order to obtain accurate dynamic information for dependencies on the stretch and orientation of the polymer molecule.

Monday 1:55 Old Georgetown  
**Pseudospectral simulation of three-dimensional viscoelastic flow in undulating channel geometries**  
Peter Wapperom and Antony N. Beris  
*Chemical Engineering, University of Delaware, Newark, DE 19716*

We examine the development of three-dimensional secondary flows for a viscoelastic fluid in an undulating channel geometry. To ensure a high accuracy we use as a framework a pseudospectral method proposed for two-dimensional flow in [1]. To preserve computational efficiency we use a conformal mapping to map the undulating channel on to a rectangular domain. The resulting nonseparable elliptic equations are solved using a spectrally preconditioned biconjugate gradient algorithm BICGstab [2]. The method parallelizes trivially, except for the transforms from spectral to physical space and vice versa. To allow for a high degree of parallelization, a new transpose split method has been developed which splits the data along two dimensions over the processors.

With the above numerical framework, we examine the flow instability against three-dimensional disturbances for viscoelastic fluids as the Weissenberg number increases. Results are presented varying from small to moderate amplitude undulations for both zero and non-zero Reynolds numbers.


Monday 2:20 Old Georgetown  
**Controlling the end plate instability in the filament stretching rheometer**  
Anders Bach¹, Henrik K. Rasmussen², and Ole Hassager²  
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²IPT, Technical University of Denmark, Kgs. Lyngby 2800, Denmark

The endplate instability observed in the transient filament stretching rheometer is investigated both experimentally and numerically. For the experiments we use a 12 wt% solution of high molecular weight PS ($M_w = 2.0 \times 10^6$ g/mol, $M_w/M_n =1.2$) in Tricresyl phosphate (TCP) as a model polymer melt. The observations of the evolution of the instability is done by using a technique developed by Spiegelberg and McKinley, where a glass rod is used as bottom plate and a camera is placed under the rod. We control the initial disturbance at the endplates, responsible for the evolution of the instability, by grinding equally distributed linear cuts in the bottom glass cylinder. The relatively
large disturbance applied on the bottom disc suppresses the random disturbances, and ensures that the instability evolves in a completely reproducible way. We show that 3 and 4 equally distributed disturbances (modes) results in 3 and 4 symmetrical planes in the produced instability. On the other hand 8 equally distributed disturbances results in 4 symmetrical planes, and a geometry similar to the one observed in experiments with 4 disturbances.

In the numerical simulations we describe the fluid by the K-BKZ constitutive equation and use a time dependent 3D Lagrangian Integral Method. Good agreement between experiments and simulations are achieved, although simulations stopped before the entire time evolution of the experiments ends. Simulations show that the instability develops faster when a small number of disturbances are applied, than a larger. This explains the mechanism of mode reduction observed in experiments — an overlaying 4 mode perturbation develops faster than the higher 8 mode disturbance. At the same time the low mode instability develops at the expense of the high mode instability, essentially driving the experiment against a low mode instability.

Monday 2:45 Old Georgetown FI9
Non linear behaviour of viscoelastic micellar solutions
Jean-Paul F. Decruppe and Sandra Lerouge
Laboratoire de Physique des Liquides et Interfaces, University of Metz, Metz 57070, France

Wormlike micelles are long flexible cylinders built with self-assembling molecules of surfactants. In a solution, they continuously break and recombine and thus, have their own particular dynamics.

By combining these processes with the chains reptation, Cates worked out a microscopic model which, in the case of fast reaction kinetics leads to a relaxation profil with a single relaxation time. This model predicts a non monotonous variation of the shear stress with the shear rate $\gamma$ in the non linear domain. For a critical shear rate, the laminar homogeneous flow becomes unstable, the liquid separates in two bands which shows different rheooptical properties.

The solutions we report on are quasi-perfect Maxwell fluids with a plateau in the curve $\sigma(\gamma)$. This behaviour, typical of a system showing a phase transition with shear bands is also seen in flow birefringence experiments.

The spatial distribution of the angle of extinction $\chi$ in the gap of a Couette cell indicates that the average orientation profil is formed by two well distinct domains separated by an interfacial zone.

The relaxation of the shear stress towards its steady value happens on two different time scales : the first one, at short time just after starting the flow, is the purely mechanical response of the system; it is followed by a sigmo-dal decrease towards the steady state plateau value; the second relaxation mode is typical of a nucleation growth process of the induced phase. The optical measurements of the birefringence $\Delta n$ and of the orientation angle $\chi$ confirm this time evolution and are related to the rheological profilis. The direct observation in the gap also allows to follow the kinetics of the evolution of the induced structure.

Monday 3:35 Old Georgetown FI10
The effect of salt valency and micelle surface charge on the shear thickening of dilute worm-like micellar solutions
Jennifer M. Politsch and David J. Pine
Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106

We investigate the shear thickening of dilute worm-like micellar solutions at concentrations ranging from the CMC to the micelle overlap concentration. The systems studied consist of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) and a complex salt, the salycilate ion (Sal‘) salted with either a monovalent counterion, sodium ($Na^+$), or a divalent counterion, magnesium ($Mg^{++}$). The salycilate ion acts as a salt and as a small co-surfactant in these solutions. Comparisons between the two salts ($Na^+$ and $Mg^{++}$) are made by maintaining a constant CTAB:Sal‘ ratio. While significant shear thickening is observed in solutions containing either salt, the shear thickening is much stronger in those samples containing the divalent counterion. For the samples containing the $Na^+$ counterion the critical shear rate increases with increasing surfactant concentration. The opposite behavior of decreasing critical shear rate with increasing surfactant concentration is observed for solutions containing the $Mg^{++}$ counterion. To compare the micelle surface charge, we vary the CTAB:Sal‘ ratio in the solution. For a given surfactant concentration, changing the CTAB:Sal‘ ratio results in large shifts in the critical shear rate, zero shear viscosity, and
magnitude of the shear thickening. For a given surfactant concentration, there are upper and lower limits for this ratio beyond which no shear thickening occurs, and within these limits, the critical shear rate exhibits a minimum. This suggests that Coulombic interactions and polyelectrolyte effects play a crucial role in controlling shear thickening in these systems.

Monday  4:00   Old Georgetown

Flow instabilities in the non-local Johnson-Segalman model with concentration coupling: A linear analysis
Suzanne M. Fielding and Peter D. Olmsted

Physics, University of Leeds, Leeds LS29JT, United Kingdom

Complex fluids such as wormlike micelles, polymer solutions and liquid crystals can, when subject to shear, exhibit instabilities that are analogous to the familiar phase transition phenomena of equilibrium systems. Such flow instabilities fall into two basic categories: i) those arising from a coupling between concentration and shear stress, and ii) those of purely mechanical origin. Type i) instabilities occur in multi-component systems such as polymer solutions in which the different components have widely separated relaxation times. The slow component (polymer) tends to migrate to regions of high stress; if viscosity increases with polymer concentration, positive feedback occurs and the system is thus unstable to concentration inhomogeneities. Type ii) instabilities occur in systems such as wormlike micelles for which the “underlying” (homogeneous) flow curve has an unstable branch of negative slope. Separation occurs primarily in the mechanical variables (strain rate and stress), resulting in “shear bands” of different strain rate co-existing at common stress. Within any constitutive model, one can show that this banded state has a steady, unique stress provided that the model includes non-local terms to allow for the band interfaces.

In this work, inspired by recent experiments on wormlike micelles (0.3M CTAB in NaNO3+H2O), we perform a theoretical linear stability analysis (analogous to that for spinodal decomposition in conventional phase transitions) for the initial stage of the separation. By combining the non-local Johnson Segalman model for the polymer stress with a two-fluid model for the relative motion of polymer and solvent, our approach is capable of capturing both type i) and type ii) instabilities. We discuss the conditions under which each instability (or a combination of both) occurs, giving results for the time-scale, wave-vector and eigenvector (strain-rate, stress, concentration) of the fastest growing mode. Our results qualitatively agree with experiment.

Monday  4:25   Old Georgetown

Vorticity versus gradient banding in complex fluids
Jacqueline L. Goveas1 and Peter D. Olmsted2

1Chemical Engineering, Rice University, Houston, TX 77005; 2Physics, University of Leeds, Leeds LS29JT, United Kingdom

Experiments on various complex fluids show that shear flow can induce the formation of new phases. It has also been observed that sharp interfaces between two or more phases or “bands” can be stable in a shear flow. In some systems, the bands lie in the flow gradient direction, and in others they lie in the flow vorticity direction. We present a general phenomenological model to describe these phenomena. The model consists of a reaction-diffusion equation of motion for a non-conserved composition variable, coupled to Newtonian stress relations for the reactant and product species. Depending on the shape of the stress constitutive curve and the magnitude of the diffusion coefficient, banding in both the gradient and vorticity directions is produced.

Monday  4:50   Old Georgetown

Stress-induced polymer migration effects in the Taylor-Couette flow: Numerical simulation of the stress-concentration coupling
Vlasis G. Mavrantzas1, Michalis V. Apostolakis1, and Antony N. Beris2

1ICE/HT-FORTH, Institute of Chemical Engineering, Patras GR 26500, Greece; 2Chemical Engineering, University of Delaware, Newark, DE 19716

Stress-induced polymer migration effects, first observed by Shafer et al.1 and Dill and Zimm2 who reported convincing evidence about the radial migration of high MW DNA molecules in solutions subject to flow between concentric cylinders or cones for times up to many hours, are analyzed in the Taylor-Couette device. The underlying
molecular model employed is a two-fluid Hamiltonian model, consisting of two components, one of which is viscoelastic and obeys the Oldroyd-B constitutive equation. The two components of the mixture are considered to be in thermal but not mechanical equilibrium interacting with each other through a drag coefficient tensor. The solution to the steady-state purely azimuthal flow is first addressed with a spectral collocation method and an adaptive mesh formulation to track the steep changes of the concentration in the flow domain. The numerical results show substantial migration of polymer from the outer to the inner cylinder in agreement with the experimental data. The migration is enhanced for decreasing gap thickness values and increasing Deborah numbers. In this case, the concentration can change by several orders of magnitude, resulting in a dramatic depletion of the area near the outer cylinder in polymeric material. This depletion is accompanied by significant deviations in the velocity profile from its form corresponding to a uniform concentration. To cast additional light on the coupling between the momentum and the concentration equations, a linear stability analysis of the inhomogeneous steady-state profiles corresponding to various wavenumbers in the $\theta$ and $z$ direction has been performed, from which representative results will be reported. The role of the Peclet number on the identification of the stable and unstable branches of solutions will also be elucidated.


Monday 5:15 Old Georgetown FI14
Extrusion of linear polyethylenes using dies constructed from copper alloys: New findings and their relevance for slip and flow instabilities
Leonor Pérez-Trejo¹, José Pérez-González², and Lourdes de Vargas²
¹Metalurgia y Materiales, ESIQIE, Instituto Politécnico Nacional, Mexico, D. F., México D. F. 07300, Mexico; ²Física, ESFM, Instituto Politécnico Nacional, México D. F., México D. F. 07300, Mexico

A study of the influence of die materials on slip and flow instabilities during the continuous extrusion of linear polyethylenes is presented in this work. The study is mainly focused on the effects of copper alloys. The experiments were carried out in a single screw extruder at a temperature of 200 °C, using capillaries of different materials. Different flow conditions, including strong slip, were induced for a given polymer in order to compare the effects of the materials of construction of the dies. Slip and flow instabilities were characterized by measurements of electrostatic charges and die swell on the melts, as well as through the external morphology of the extrudates. Important conclusions are drawn in relation to the flow enhancement, elimination of extrudate distortions and stick-slip behavior when using dies constructed from copper alloys.

Symposium CF
Quantifying Microstructure In Complex Fluids
Organizers: Norman Wagner and Alan I. Nakatani

Monday 1:30 Judiciary CF5
Shear-induced displacement of isotropic-nematic spinodals
Tjerk Lenstra, Zvonimir Dogic, and Jan Dhont
Institut für Festkörperforschung/Weiche Materie, Forschungszentrum Jülich, Jülich 52425, Germany

Phase coexistence in systems of rigid rod like colloids, in the absence of shear flow, have already been understood for quite a number of years. Experimental observations of isotropic-nematic phase coexistence in systems of rod-like colloidal particles were made by Zocher and Bernal in the 1920’s. Theoretical predictions for the isotropic-nematic phase boundaries for very long and thin, rigid rods with excluded volume interactions were obtained some 50 years ago by Onsager. Phase coexistence and phase separation kinetics in systems of lyotropic rigid rods under shear flow conditions are less well understood. Shear flow tends to align rod shaped colloids along the fluid flow direction and therefore possibly enhance the stability of the nematic phase. We will present a study of the shear dependent location of the isotropic-nematic spinodals in suspensions of bacteriophage fd rods. The phase diagram under shear flow is studied and determined by means of time resolved birefringence experiments. The hysteresis in the birefringence on increasing and subsequently decreasing the shear-rate allows the determination of the location of
points in the shear-rate versus concentration phase diagram between the isotropic-to-nematic and the nematic-to-isotropic spinodals. These experimental hysteresis curves are interpreted on the basis of an equation of motion for the orientational order parameter tensor, as derived from the N-particle Smoluchowski equation. The spinodals are found to shift to lower concentrations on increasing the shear-rate. Above a critical shear-rate, where shear forces dominate over thermodynamic forces, no spinodal instability could be detected.

Monday 1:55 Judiciary

Pathway from planar lamellae to multilamellar vesicles
Florian Nettesheim¹, Johannes Zipfel², Peter Lindner², Ulf Ollson³, and Walter Richtering¹
¹Physical Chemistry, Christian-Albrechts-University of Kiel, Kiel, Schleswig-Holstein 24098, Germany; ²Large-Scale-Structures, Institute Laue-Langevin, Grenoble 38042, France; ³University of Lund, Lund 22100, Sweden

Structural transitions in lamellar phases induced by shear have been subject to many studies and show different structural features, such as the flipping of lamellae from a parallel to a perpendicular orientation as well as the formation of multilamellar vesicles (MLVs). Despite of the effort that has been taken the formation of MLVs is not fully understood. Non-ionic surfactant systems like tetraethyleneglycol mono dodecylether (C₁₂E₄) or triethyleneglycol mono decylether (C₁₀E₃) display a lamellar phase in water over a broad concentration and temperature range. Small angle neutron scattering experiments (SANS) were conducted, establishing that the transition from MLVs to planar lamellae is reversible, when scanning the temperature up or down. The structures are in both directions coupled to the shear flow. Hence it is possible to study the transition from planar lamellae to MLVs starting from reproducible conditions in so called start up experiments. Time resolved SANS was used to study the evolution of the scattering simultaneously to shearing. An intermediate state with cylindrical symmetry was found, an indication for multilamellar cylinders. The concentration and temperature dependence of this process were studied as well as the stability of the intermediate structures. In addition the formfactor of the three different structures present during the start up experiment was recorded. Supplementary this transition was studied with a rheo-optical set-up, yielding rheological simultaneously to small angle light scattering data (SALS). From these measurements the size of the MLVs could be estimated to be of a few microns, depending on the shear rate. Within the range of moderate shear rates (1-30s⁻¹) the transition seems to be controlled by the total strain.

Monday 2:20 Judiciary

Flow of temperature sensitive hydrogel suspensions
Prashant Mullick and Charles F. Zukoski
Chemical Engineering Department, University of Illinois at Urbana Champaign, Urbana, IL 61801

Rheological properties of temperature sensitive microgel particles are investigated as a function of temperature and concentration. The microgel particles consist of cross-linked poly N-Isopropylacrylamide (PNIPAM), chemically cross-linked using N,N’-methylenebisacrylamide (BIS). Dynamic light scattering indicates that the particle diameter ranges from 300 nm to 150 nm as the temperature increases 20°C to 32°C. For a fixed number density of particles, this change in size results in a volume fraction alteration of almost an order of magnitude allowing for very precise control of packing fraction. In this investigation we characterize suspension thermodynamic and mechanical behavior as a function of temperature and concentration. Transitions from fluids with well-defined zero shear rate viscosities to suspensions with well-defined zero frequency elasticities accompany the onset of iridescence suggesting an order-disorder transition. We compare the flow properties of these materials with those of other suspensions that order upon increasing volume fraction. In agreement with previous work we find that up to volume fractions on the order of 0.5, suspension flow behavior is independent of temperature if the particle concentration is converted to volume fraction using the intrinsic viscosity. However, as packing fractions in excess of unity are readily achievable, this approach results in unphysical predications at low temperatures and high concentrations. For these dense suspensions we compare our studies with those of other deformable gel particle suspensions.
Microstructure evolution through the shear thickening transition for concentrated colloidal dispersions by flow SANS measurements
Norman J. Wagner¹ and Brent J. Maranzano²
¹University of Delaware, Newark, DE 19716; ²Chemical Engineering, PPG Industries, Inc, Pittsburgh, PA 15230

The shear induced microstructures for electrostatic and Brownian suspensions are compared using in-situ small angle neutron scattering (SANS). The dispersions consist of 75 nm Stober silica coated with TPM and have a zeta potential of -42.6 mV. Neutralizing the surface charge with 0.066 M nitric acid yields stable hard-sphere dispersions. SANS is conducted over a range of shear rates on the charge-stabilized and Brownian suspensions to test the order-disorder transition (ODT) and hydrocluster mechanisms for shear thickening, and demonstrate the influence of stabilizing forces on the shear induced microstructure evolution. Shear induced changes in the microstructure are correlated to the hydrodynamic component of the shear stress and the thermodynamic component of the normal stress to demonstrate that hydrocluster formation drives the shear thickening transition. Finally, similar tests and analyses are performed on a bimodal mixture to examine the effects of polydispersity on the shear induced microstructure evolution.

Controlling structure and rheology of wormlike micelles through hydrophobicity of homopolymer and copolymer architecture
My Hang T. Truong and Lynn M. Walker
Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15232

The diverse rheological behavior of wormlike micelles, which is dictated by micellar structure, has led to many proposed applications. For practical usage, controlling the structure, and, hence, the rheology of these systems is critical. In this work, both rheometric and small-angle scattering techniques show that nonionic triblock copolymers can effectively control the flow-induced structure of aqueous systems of cetyltrimethylammonium p-toluenesulfonate (CTAT), while the homopolymer analogs have little effect on such a structural transition. These copolymers have distinct effects on the critical shear rate required for the transition, while small-angle neutron scattering (SANS) reveals dramatic changes to quiescent micellar structure at multiple length scales even with subtle changes in polymer microstructure. These drastic changes indicate the coupling between the sensitive structure of wormlike micelles and macroscopic rheology. The hypothesis that drives our present research is that the size and position of hydrophobic moieties of a nonionic polymer alter local micellar structure and interactions, consequently leading to changes in the rheology.

Drag reduction, rheological properties and microstructures of mixed cationic surfactants with different alkyl chain configurations
Yunying Qi¹, David J. Hart², Yeshayahu Talmon³, and Jacques L. Zakin¹
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Many dilute solutions of quaternary ammonium surfactants with appropriate counterions are effective drag reducing additives. However, drag reduction effectiveness is determined by many factors such as temperature, pH, chemical structure of the cationic surfactant (both headgroup and alkyl chain tail) and its concentration, counterion chemical structure and counterion/surfactant concentration ratio. The effective temperature range of any surfactant-counterion system is determined by the variables noted above. Mixed surfactant systems such as mixed catanionic surfactants, zwitterionic/anionic surfactant mixtures and cationic surfactant systems with different alkyl chain lengths are receiving more and more interest to tailor-make surfactant solutions for different drag reduction and other applications.

In this study, cationic surfactant solutions with different saturated alkyl chains length mixed with unsaturated C₁₈ isomer chains (cis- and trans-), are examined. Pure (cis) Oleyl ((Z)-9- octadecenyl) and (trans) Elaidyl ((E)-9-
octadecenyl} trimethyl ammonium salts which are not commercially available were synthesized. The differences in the geometry of the alkyl chain tails causes different packing of the tails inside the micelles and therefore, different microstructures and rheological properties. The effect of cis- and trans- unsaturated alkyl chain configuration and counterions (sodium salicylate) ratios on their micelle microstructures and rheological properties will be discussed and compared with their mixtures with saturated alkyl chain quaternary ammonium salts.

Monday 4:25 Judiciary

**Scaling behavior of shear-induced sponge to lamellar transformations**

Lionel Porcar\(^1\), William A. Hamilton\(^1\), Paul D. Butler\(^1\), and Greg G. Warr\(^2\)

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We report here complementary rheological and small angle neutron scattering (SANS) structural measurements showing in detail clear evidence of shear-induced sponge to lamellar phase transformations in Cetylpyridinium chloride (CPCl)-hexanol-brine-sugar systems. To ensure the reproducibility of the scattering measurements it was necessary to perform them using a Couette shear cell specially designed to limit evaporation to which the sponge phase is extremely sensitive. Our measurements show well-defined shear response that proceeds in three steps characterized by two critical shear rates: \(G_{1c}\) and \(G_{2c}\). Below \(G_{1c}\), no shear effect was observed. For \(G_{1c}<G<G_{2c}\), the systems shear thin and SANS measurements show that the sponge phase is progressively transformed into a lamellar phase with the membrane normals aligned parallel to the shear gradient. The critical shear for this sponge to lamellar phase transformation follows the scaling behavior first expressed by Cates and Milner [1]: \(G_{1c}\) is proportional to \(\Phi/\eta^3\), where \(\Phi\) is the membrane volume fraction and \(\eta\) the viscosity of the brine-sugar solvent. Above \(G_{2c}\), the induced lamellar phase apparently collapses and new large scale structure forms. This higher critical shear shows the same scaling behavior as \(G_{1c}\) and is appears to be related to membrane diffusion processes. From neutron scattering and rheological measurements we extracted master curves giving a universal phase response for these systems under shear flow. These results disagree with results obtained previously by others [2].


Monday 4:50 Judiciary

**Visualization of conformational properties of single DNA molecules under shear flow**

Connie K. Smith\(^1\), Rajat Duggal\(^1\), and Matteo Pasquali\(^2\)

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Polymers are among the most used materials in todays society playing a central role in the chemical industries such as coatings as well as the biological sciences with applications in gene therapy and drug delivery. Many applications involve the use of dilute solutions of polymers in viscous solvents. The long, flexible chains of polymers in solution are normally in a coiled state at rest. The configuration of the polymer molecules due to the applied flow conditions, determines the properties of the final product. To study these conformational properties, we observe single DNA molecules under shear flows, using fluorescence microscopy. Previously the molecules have been viewed in the plane of motion but our apparatus allows analysis of the molecules conformation in the vorticity plane. The dilute polymer solution is forced to flow through a rectangular channel. We study the effect of the channel dimensions on the conformation of the DNA molecules. Another flow studied is a shear flow due to parallel plates moving in opposite directions. The apparatus allows for the study of transient conformation dynamics of single DNA molecules.

Monday 5:15 Judiciary

**Extensional Flow of DNA solutions: Simultaneous measurement of conformation and stress**

Rudy Dubbelboer, Duc A. Nguyen, and Tam Sridhar

Department of Chemical Engineering, Moansh University, Clayton, Victoria, Australia

The technique of Fluorescence microscopy applied to the study of DNA solutions has been developed by Chu and coworkers. These papers showed the extraordinary diversity of molecular conformation adopted by DNA molecules under deformation. Concurrently, the development of the filament stretching rheometer has matured such that routine measurements of the fluid stress under carefully controlled extensional deformation is now possible. These
two developments address two fundamental and intimately linked issues in rheology—microscopic conformation and macroscopic stress. Hence we have a strong motivation to integrate these two techniques so that one can obtain both stress and conformation under identical conditions. This paper addresses this issue and discusses some of the experimental difficulties and presents some preliminary data on dilute DNA solutions.

Symposium ML
Molecular Level Modeling and Theory
Organizers: David Morse and Jimmy Feng

Monday 1:30 Diplomat/Ambassador ML6
On the strain measure tensor in entangled polymeric liquids
Francesco Greco
Institute for Composite Materials Technology (ITMC), CNR, Naples 80125, Italy

Concentrated polymeric liquids and melts are non-Newtonian fluids, hence a constitutive equation for the stress tensor must be found to afford the description of their rheological behaviour. In step deformations, the "tensorial response" of the material defines a Strain Measure, which can thereafter be used for calculating the stress in other deformation histories.

Advanced molecular models for the rheology of entangled polymeric liquids are all based on reptation theory, with a "test-chain" moving inside a mesh made up of other chains. The Strain Measure tensor which arises from this "chain-in-a-cage" theory was calculated many years ago by Doi and Edwards, by means of equilibrium statistical mechanics. The ensuing Damping Function (e.g., in step shear) nicely agrees with data, with no adjustable parameters, a result which strongly supports the theory. However, the calculations by Doi and Edwards are (perforce) based on some simplifying assumptions, and some discrepancies with experiments are therefore also found.

In revisiting the theory, we succeeded in deducing a new Strain Measure with less simplifying hypotheses than Doi and Edwards made. Specifically, we have shown how to avoid the hypothesis of constant tension along the polymeric chains. The new predictions favourably compare to experiments, e.g., in step shear deformations. In particular, the predicted ratio of second to first normal stress difference turns out to be larger (ca. +20% up to strain values of order 10) than that previously calculated, and in better agreement with recent accurate data, without introducing new parameters. The small strain limit is calculated as \(-N_2/N_1 = 0.17\), hence correctly predicting the Weissenberg effect.

Monday 1:55 Diplomat/Ambassador ML7
Elasticity of polymer networks
Michael Rubinstein\(^1\) and Sergei Panyukov\(^2\)
\(^1\)Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290; \(^2\)P.N. Lebedev Physics Institute, Moscow 117924, Russia

We develop and solve a new molecular model for nonlinear elasticity of entangled polymer networks. This model combines and generalizes several successful ideas introduced over the years in the field of rubber elasticity. The topological constraints imposed by neighboring network chains on a given one are represented by the confining potential, that changes upon network deformation. This topological potential restricts fluctuations of the network chains to the nonaffinely deformed confining tube. Network chains are allowed to fluctuate and redistribute their length along the contour of their confining tubes. The dependence of the stress \(\sigma\) on the elongation \(\lambda\) is usually represented in the form of the Mooney stress \(f(1/\lambda) = \sigma/(\lambda - 1/\lambda^2)\). We find a simple expression for the Mooney stress \(f(1/\lambda) = G_0 + 1.84 G_e/(\lambda + 0.84 \lambda^{-1/2})\) where \(G_0\) and \(G_e\) are phantom and entangled network moduli. This allows to analyze the experimental data in the form of the universal plot and to obtain the two moduli \(G_0\) and \(G_e\) related to the densities of the cross-links and entanglements of the individual networks. The predictions of our new model are in good agreement with experimental data for uniaxially deformed polybutadiene, polydimethylsiloxane, and natural rubber networks.
Local rheology, microstructure and chain stretching in a lattice model of polymer fluids under shear
Yitzhak Shnidman and Maja Mihajlovic
Department of Chemical Engineering and Chemistry, Polytechnic University, Brooklyn, NY 11201

We present a novel method for computing the time evolution of local rheology, microstructure and chain stretching exhibited by polymer fluids in sheared channels. In our model, polymer segments are restricted to the sites of a discrete cubic lattice. Similarly to the equilibrium self-consistent field (SCF) lattice theory of Scheutjens and Fleer, segmental site probabilities are related to polymer volume fractions at other by means of a Markovian matrix propagator. However, out of thermodynamic equilibrium, segmental probabilities cannot be identified with a canonical probability distribution in a self-consistent field. Instead, we use the lattice unit cell as the control volume, to derive a set of microscopic convective-diffusive transport equations. The rates of diffusive transport in our model depend on a local self-consistent field representing inter-segmental interactions, kinetic energies, and entropic chain stretching related to the local stress tensor.

The present study focuses on melts and blends of homo and block co-polymer chains below entanglement molecular weight. The polymer contribution to the stress thus follows either the dumbbell, or the Rouse model, and evolves in accordance with an upper-convected Maxwell model. This results in a closed system of ordinary differential equations (ODE) describing the time evolution of segmental probabilities, momenta, the stress tensor, and the matrix propagator at each lattice site. The resulting ODE system is stiff, since momentum diffusivity is controlled by the kinematic shear viscosity, and is much faster than either the chain relaxation or the center-of-mass self-diffusion. We will present numerical solutions of these equations, and will discuss the resulting time evolution of the local shear and normal stresses, chain stretching, the interfacial microstructure, and velocity slip, in a variety of sheared polymers fluids below the entanglement molecular weight.
Colloidal states of carbon black suspension in polymer melt

Vaclav Bouda¹, Jiri Chladek¹, and Jana Mikesova²
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The growth of the self-assembled structure of carbon black (CB) colloidal aggregates has been studied. To induce different states of CB self-assembly in the polyethylene melt, the samples of composites were annealed in electrical field between tinned electrodes for time periods up to several days. AC conductivity and permittivity of samples in situ and in real time were measured during the process to investigate the state of the clusters of CB-aggregates. The tin concentration in the samples was checked. AFM and TEM were used as well. Annealing experiments in air were also conducted in the Rheometrics SYS4 rotational rheometer at 190 °C to study the effect of polymer matrix oxidation. As high stability of the matrix in nitrogen was proved, it was assumed that the observed complex increase in elastic modulus indicates the thermal oxidative degradation of the polymer without direct relation to the observed behavior of conductivity. The changes of conductivity are very complex. Colloid theory is the best tool for interpreting them effectively. Oxidation of CB-particles induces surface potential on CB-colloidal aggregates presumably. The appearance of the same charge results in repulsion of the aggregates. Oxidation of the electrode material results in a gradual increase in the concentration of charged counter-ions of electrode material in the atmosphere adjoining a charged surface of CB-particles. The counter-ions atmosphere screens the electrostatic repulsive forces to a variable extent. According to the applied DLVO theory, the state of kinetic stability of CB-dispersion is between the critical dispersion concentration and the critical coagulation concentration of the counter-ions. Four possible internal processes influence the states of the carbon black assembly: soft axial order generation, soft lateral order generation, axial condensation, and lateral condensation of carbon black particles. The gradual increase of ionic concentration controls the rates of the processes.

Microstructure and defects in liquid crystals induced by spherical drops or particles

Olga V. Sozinova and Davide A. Hill

Chemical Engineering, University of Notre Dame du Lac, Notre Dame, IN 46556

Recent studies on thermally-induced phase separation of mixtures of isotropic liquids and liquid crystals (prevalent phase) have revealed the possibility of producing minute, monodisperse droplets of the guest compound. Furthermore, the particles are seen to self-assemble into highly coherent structures without coalescing. These phenomena may be of interest for production of monodisperse polymer particles, formulation of advanced electro-rheological fluids, micro-encapsulation, as well as novel microfabrication techniques. Both the drop-size-selection and self-assembly mechanisms are controlled by anisotropic interactions induced by Frank elasticity, and by stable, "companion" defects anchored near the drops. Because of the crucial role played by disclinations, an advanced description of molecular order is necessary for analysis. As a first step towards tackling multiparticle systems, we analyze the equilibrium structure of a nematic liquid in the neighborhood of an isolated sphere. The chosen boundary conditions are of uniform far-field alignment and homeotropic anchoring at the particle surface. The free energy density is modeled as the sum of a molecular term of the Doi-type and a Landau-de Gennes distortional component. The order-parameter-tensor field is obtained numerically through minimization of the global free energy of the system. Because of the non-linearity of the equations, multiple solutions with markedly distinct topologies and defect patterns are possible. Competing attractors are successfully resolved through the use of a relaxation method whereby the systems is gradually "annealed" beginning from different initial states. Results will be presented to illustrate the possible topologies and defect structures, as well as the feasibility of the chosen algorithm.

Hydrodynamic theory for mixtures of liquid crystalline polymers and flexible polymers

Qi Wang

Mathematics, Florida State University, Tallahassee, FL 32306

I will present a hydrodynamic theory for mixtures of liquid crystalline polymers (LCPs) and flexible polymers, in which the LCP molecular configurations are taken into account. The theory is based on a density functional
approach. I will also address the extension of the theory to nanocomposites of inorganic nanoparticles in a polymer matrix. Finally, I will briefly discuss the application of the theory in simple flows such as simple shear and elongation flows.

Monday     5:15     Diplomat/Ambassador     ML14
Effects of elastic anisotropy on sheared nematic polymers
Jianjun Tao and Jimmy Feng
City College of CUNY, Levich Institute, New York, NY 10031

Nematic polymers undergo a series of instabilities when sheared, leading to counter-rotating rolls along the flow direction. Recent simulations showed cell breakup at higher shear rates to be a pathway to the creation of thick disclinations. Most of the prior theoretical work was based on the so-called one-constant approximation, i.e., assuming elastic isotropy. On the other hand, nematic polymers possess strongly disparate elastic constants for the splay, twist and bend modes. The effects of elastic anisotropy on the various transitions in the flow and orientation of sheared nematics have not been systematically studied. We use a finite-difference code to simulate the shear flow of nematics based on the Leslie-Ericksen theory, and investigate how the formation, oscillation and eventual breakup of roll cells depend on each elastic constant. Results show that K3, corresponding to bend, is by far the most important of the three K's. Increasing K3 stabilizes the shear flow against the formation of rolls, and postpones the onset of cell oscillation and breakup. K1 has similar effects but to a much less extent. K2 tends to destabilize the flow, lowering the critical Ericksen number for the onset of roll cells. The conformation of disclinations are also modified by elastic anisotropy. Finally, we seek to explain the results in terms of the free energy penalty incurred by each mode in the orientational field. Not surprisingly, bend turns out to be the dominant mode of distortion in roll cells.
Tuesday Morning

Symposium PL
Plenary Lectures
Sponsored by a generous contribution from NIST Polymers Division

Bingham Lecture

Tuesday 8:30 Crystal Ballroom PL2
Modeling of entanglement – past and present
Masao Doi
Department of Computational Science and Engineering, Nagoya University, Nagoya, Japan

Molecular entanglement in polymers is a very old notion. When Kuhn made a statistical theory for Staudinger's macromolecule in 1930's, he was aware that these molecules do entangle and should play an important role in their mechanical properties. Theoretical development of the entanglement effect, however, was very slow since "entanglement interaction" is quite different from the usual potential interaction. In 1946 Green and Tobolsky modeled the entanglement by temporary junctions, and set up the first "molecular" theory for the viscoelasticity of polymeric fluids. This work lead to many successful constitutive equations for polymer melts. Theories along this line, however, could not relate the rheological parameters with molecular characteristics.

In the 1970's, new types of modeling started by the "tube model" which model the entanglement effect by "tubes" surrounding each polymer. The tube model was successful for monodisperse polymers, but failed for polydisperse polymers.

Recently a third generation of the entanglement model started: it is called the "Dual slip-link model." It is an extension of the tube model, and seems to resolve some of the drawbacks of the original reptation model. The model looks very much like the grand parents, the networked polymers.

Symposium SS
Simple Fluids To Suspensions
A Symposium in Honor of William R. Schowalter

Organizers: Andrew M. Kraynik and William B. Russel

Tuesday 9:45 Cabinet SS15
Evolution of stresses during latex film formation
William B. Russel
Department of Chemical Engineering, Princeton University, Princeton, NJ 08544-5263

The process of latex film formation, for example from aqueous paints, involves the evaporation of water from an initially fluid dispersion, deformation and then fusion of polymeric particles, and the elimination of voids to create a solid film. At some temperatures the film cracks during drying. The mechanism for this remains debatable with both air-water surface tension and sintering stresses generating the requisite tensile stresses in the plane of the film. However, very few measurements offer guidance on the magnitudes. Recently we have undertaken experiments that involve drying films of varying thickness and polymer glass transition temperatures on a cantilever and deducing the stresses in the plane of the film from the deflection. The dependence of the stress on time, temperature, and the
thickness of the film offers some insight into the origin of the stresses, possibly implicating an interfacial tension that is dramatically enhanced by the particles.

Tuesday 10:10 Cabinet SS16

**Experimental studies on aggregated suspensions in drying**
Charles F. Zukoski and Lloyd A. Brown
*Chemical Engineering, University of Illinois at Urbana Champaign, Urbana, IL 61801*

We present an experimental test of a recently proposed model of drying consolidation. Key compressive rheological parameters that are required by the model are measured using centrifugation and pressure filtration techniques. The volume fraction of particles within the suspensions as a function of drying time is determined experimentally and compared to model predictions. We find that the model predictions are extremely accurate and that the results are somewhat insensitive to the form chosen to represent the permeability. We are able to describe drying behavior in these systems in terms of a single parameter. We also present qualitative results on studies of crack formation in these systems and link this information to the interaction forces in our system as characterized by yield stress measurements.

Tuesday 10:35 Cabinet SS17

**Self-similar behavior in coagulating systems**
Hassan Aref and Dmitri Pushkin
*Department of Theoretical and Applied Mechanics, University of Illinois at Urbana-Champaign, Urbana, IL 61801*

As one of the simplest examples of a self-assembling system, coagulation is omnipresent - aggregating colloids; coalescing droplets in clouds; coagulating smoke, smog, and dust particles in aerosols; growing polymers; and the formation of planets and stars - all belong to this realm. A number of experiments and computer simulations of coagulating systems have reported power-law cluster size distributions. This indicates emerging self-similarity. We discuss the origin of self-similarity, and the conditions required for it to emerge, and we establish a connection between the power-law exponent of the self-similar cluster size distribution and the homogeneity index of the coagulation kernel. Various non-traditional examples of coagulation have also appeared in the literature in recent years: the linkages of random networks, including the world wide web; the scaling of genetic algorithms; and the merging of banks. The theory of emerging self-similarity is illustrated by the asset size distribution of U.S. banks produced by an unprecedented wave of bank mergers during the 1980s and 1990s.

As Dean of the College of Engineering at University of Illinois, Urbana-Champaign, Bill Schowalter repeatedly stressed that engineering students also needed a firm understanding of economic and business issues. It is, therefore, particularly pleasing to be able to present an economic application of the scientific subject to which he made such important contributions.

Tuesday 11:00 Cabinet SS18

**Flow-induced structure and the yielding of colloidal particulate gels: Scattering and direct visualization studies**
Priya Varadan and Michael J. Solomon
*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109*

Under certain conditions of volume fraction and interaction potential, the aggregation of colloidal particles can result in gelation, the onset of solid-like linear viscoelasticity and the development of an apparent yield stress. In this paper, we report a study of the structural properties of such colloidal particulate gels as determined by flow small-angle light scattering (FSALS) and confocal laser scanning microscopy (CLSM). The materials studied are monodisperse colloidal silica stabilized with surface grafted aliphatic chains. The particles undergo reversible gelation below a critical temperature in the solvent hexadecane. For intermediate volume fractions (0.01 > φ > 0.10), the suspensions adopt a fractal cluster structure upon gelation. As characterized by FSALS in the flow-vorticity plane, upon the start-up of steady shear flow, structural anisotropy is observed. Shear flow also results in the structural rearrangement of the suspension into large, dense clusters with low number density. To further probe the possibility of long length scale structural heterogeneity and anisotropy in these gels, a direct visualization study by
CLSM was undertaken. Materials were prepared that were analogous to those studied by light scattering except for the incorporation of a fluorescent dye into the core of silica core/shell particles. The CLSM studies for $\phi > 0.10$ extend the characterization of the gel structure into the non-fractal regime.

Tuesday 11:25 Cabinet SS19
Material instability with stress localization
Joe D. Goddard
Dept. Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093-0411

The most familiar form of material or constitutive instability involves the spontaneous transition from spatially homogeneous states to patterned states involving strain localization (shear bands and necks) arising from non-monotone behavior such as shear thinning, strain softening or "dissipative clustering" [1]. Another type of instability, involving "blowup" in the field equations with stress localization, conceivably could arise from singular "strain hardening" with nonunique stress states. Possible examples include "coil-stretch" transitions in polymer fluids [2], stress multiplicity ("ignition-extinction") in gas-solid dispersions [3], "micro-arching" or force chains in granular media [4] and "discontinuous-dilatant" behavior [5] or force-percolation clusters in sheared suspensions [6]. This article provides a review and synthesis of related literature, together with an analysis of certain quasi-static bifurcations of steady-state stress fields for some special deformations of elastic solids and viscoelastic fluids. In particular, it is shown that heterogeneous stress states with lamellar or filamentary structures may exist in pure stretching motions.


Symposium SB Phenomena Near Solid Boundaries
Organizers: Radhakrishna Sureshkumar and Lynden Archer

Tuesday 9:45 Old Georgetown SB1
Transient networks at high shear rates: Solid like friction, constitutive instability and slippage at the walls
Eric Michel, Mohammed Filali, Jean Kieffer, Francois Molino, Jacqueline Appell, and Gregoire Porte
GDPC, Université Montpellier II, Montpellier cedex 05 F-34095, France

We report on the flow behaviour of transient physical gels that form spontaneously in aqueous solutions of "telechelic polymers" and surfactants. The polymers consist of a hydrophilic chain at both ends of which is grafted a hydrophobic "sticker". The hydrophobic stickers assemble and incorporate into the spherical micelles connected to one another by the hydrosoluble chains. Since the average residence time of the stickers in the micelles is finite, the network has the viscoelastic properties of a physical gel. The flow behaviour shows up an unexpectedly rich sequence of events upon increasing rates: At low rates, shear thickening is first observed followed by an abrupt drop of the stress at a critical rate which corresponds to the onset of inhomogeneous flow: a sliding layer forms, presumably at the wall of the shear cell. At intermediate rates, the stress becomes unstable and wanders erratically around a constant value independent of the rate. At high rates, a steady homogeneous flow pattern is recovered which has an intriguing Bingham like signature. We compare this complex flow behaviour with those of other systems exhibiting constitutive instabilities. In particular, the balance of pinning and snapping of the stickers determines a non-monotonic constitutive equation qualitatively similar to that of wormlike micelles: the stress plateau is however not seen with telechelic systems and is replaced by the random fluctuations of the stress. This behaviour may arise from strongly non-affine distribution of the strain concentrating on weaker parts of the network: fractures constantly initiate, propagate and heal at a steady rate.
A tube model for dynamics of tethered chains
Ashish K. Lele1 and Yogesh M. Joshi2
1Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, United Kingdom; 2Chemical Engineering Division, National Chemical Laboratory, Pune, Maharashtra 411 008, India

We present a tube model for describing the dynamics of linear tethered chains near a solid wall and discuss its implications on the stick-slip instability in highly entangled melts. We consider three different surface coverage regimes for the tethered chains: mushroom regime, cooperative regime and overlap regime. It is shown that the critical wall shear stress (and critical shear rate) increases with surface coverage in the mushroom and cooperative regimes, while it decreases with surface coverage in the dry brush regime. The scaling laws for other slip parameters are similarly derived in the three regimes and are in general agreement with experimental data in the literature.

Stick-slip flow and molecular relaxation dynamics near surfaces
Tien T. Dao1 and Lynden A. Archer2
1Chemical Engineering, Texas A&M University, College Station, TX; 2School of Chemical Engineering, Cornell University, Ithaca, NY

We investigate relaxation dynamics and apparent slip violations in entangled 1,4-polybutadiene (PBD) melts near attractive glass and metallic substrates. Narrow molecular weight distribution and bidisperse PBD melts were used to determine the effect of molecular weight and polydispersity on stick-slip dynamics near rigid substrates. A new experimental method, "Evanescent Wave Laser Polarimetry" (EWLP), was also developed to investigate near-surface relaxation dynamics in these materials. The method relies on total internal reflection of phase-modulated laser light at an interface between a high refractive index transparent hemisphere and the polymer liquid to probe shear-induced changes in molecular orientation in a fluid layer within approximately 80 nm. of the polymer/substrate interface. A characteristic near-surface relaxation time determined from step shear EWLP relaxation experiments suggest that constraint release between bulk and surface adsorbed molecules dominate dynamics near rigid surfaces. These experimental results are discussed in terms of slip models for entangled polymer liquids.

Visualization studies of polymer flow at boundary discontinuities: Sharkskin and extrudate swell
Zhiyong Zhu and Shi-Qing Wang
Dept. of Polymer Science, University of Akron, Akron, OH 44325-3909

Despite a great deal of efforts our understanding of viscoelastic flow at a boundary discontinuity remains rather incomplete. Two leading phenomena are associated with exit flow of entangled polymers: sharkskin and extrudate swell. We have measured the local surface velocity near the die exit by tracing, with a microscopic lens attached to a videocamera, the particle motion on the die wall inside the die and on the extrudate surface. Using linear polybutadiene as a model, it is found that the extrudate surface velocity V, at the exit attains a significant value relative to the average velocity V of the extrudate, i.e., suggesting presence of plug-like flow immediately outside the exit. This feature is examined in detail as a function of viscoelastic parameters that are determined by the molecular weight, its distribution, temperature and shear rate/stress in an attempt to correlate with the sharkskin and extrudate swell behavior. Specifically, we found that (a) V/V is around 0.4 about 50 microns from the exit below the onset of sharkskin; (b) the surface roughness (i.e., sharkskin) occurs via two different modes, a peeling/rolling mode and a fast/slow mode; (c) in the fast/slow mode, V/V is found to split from 0.4 reaching nearly 1.0 during the fast period. In a related context, extrudate swell measurements are carried out in real time to determine how viscoelastic properties of polymers influence the value of the extrudate swell ratio.
Flow-split of polymer melts during capillary extrusion: Gaining insight into a new flow instability

Anton Santamaría¹, Merche Fernández¹, Antonio Muñoz-Escalona², and Luis Méndez³

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Recently we have reported a new hydrodynamic effect that takes place in very elastic polyethylene melts: under certain conditions, capillary extrusion provokes the scission of the jet, giving rise to two distorted branches which rotate at the exit [1]. We have used the term "flow-split" to define this new flow instability. Here we present a new set of data of a series of ten high molecular weight polyethylenes, with very similar molecular architecture, six of which develop flow-split at the exit of the capillary.

Allegedly, the presence of very small amount of long chain branching produces a viscoelastic behavior characterized by $G' > G''$, in all the considered frequency range. A value of $G' > 10^5$ Pa at 190°C all over the range $10^{-2}$ - $10$ Hz. appears as a necessary condition for the existence of flow-split phenomenon. The influence of temperature, diameter and length of the capillary die, and diameter of the barrel are analyzed. A tentative model, which takes into account rotational entry instability, slip-stick and exit stretching, is presented to explain the origin of this striking effect.


Symposium CF
Quantifying Microstructure In Complex Fluids
Organizers: Norman Wagner and Alan I. Nakatani
Novel rheological properties in polymer-organoclay composites
Mikhail Y. Gelfer¹, Lizhi Liu¹, Benjamin Hsiao¹, Benjamin Chu¹, Hyun H. Song², Carlos Avila-Orta¹, Christian Burger¹, Mayu Si³, and Mariam Rafailovich³
¹Chemistry Dept., SUNY Stony Brook, Stony Brook, NY 11794; ²Polymer Science and Engineering Department, Hannam University, Daejon, Republic of Korea; ³Materials Science and Engineering Dept., SUNY Stony Brook, Stony Brook, NY 11794

A series of nanocomposites prepared by melt-blending of cloisite(r) organoclays with polyethylene-vinylacetate (PEVA)/neutralized ethylene-methacrylic acid (PEMA) co-polymers were investigated using in situ SAXS (small-angle X-ray scattering), TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), TEM (transition electron microscopy) and advanced rheological techniques.

SAXS and TEM data proved high degree of clay exfoliation in all tested nanocomposites. In PEMA and in PEVA both melting temperature Tm and bulk crystallinity were not significantly affected by the presence of organoclays indicating that clay particles are predominantly confined to the amorphous phase in the final morphology. Rheological properties above Tm (determined by DSC) were drastically different in PEVA and PEMA nanocomposites. PEVA-clay systems demonstrated solid-like rheological behavior in small-strain oscillatory shear experiments, yet they were able to flow under a steady shear that is characteristic of physical cross-linking. Also the addition of organoclays to PEVA caused drastic reduction in apparent flow activation energy Ea. In contrast, PEMA-clay composites always exhibited melt-like rheological behavior; Ea variation with clay content in PEMA systems was insignificant. TGA results showed higher thermal stability in all tested composites as compared to the pure polymers. The increase in degradation temperature was more pronounced in PEVA than in PEMA.

We propose that carbonyl groups of vinylacetate interact with hydroxyls present on the clay surface resulting in strong physical cross-linking in PEVA-based materials. On the other hand the interaction between PEMA and clay is weak due to the repulsion between carboxyl anions and negatively charged clay surface, so the physical cross-linking does not occur in PEMA composites.

Structure and rheology of goethite suspensions
David F. James¹ and Brian C. Blakey²
¹Mechanical & Industrial Engineering, University of Toronto, Toronto, Ontario M5S 3G8, Canada; ²Chemical Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

The viscous behaviour of synthetic goethite suspensions was studied in steady shear and for step changes in shear rate, as part of a program to understand the flow behaviour of goethite-dominant laterite slurries. The goethite suspensions were prepared with solid volume fractions between 0.01 and 0.08, and viscometric tests show that these fluids have high viscosities - up to 10 Pa.s at shear rates below 10 1/s - and that they are severely shear-thinning, with power-law exponents (n) as low as 0.1. The fluids also exhibit time-dependency after large step changes in shear rate, with relaxation times of the order of minutes. The viscosity was found to depend on pH, with the maximum occurring at about pH 9, and not to depend on NaCl concentration for levels between 0.001 and 0.1M. Microscopic observations of the suspension revealed a flocculated structure, with floc size depending on pH but not on ionic concentration, like the viscosity. Comparisons with the viscosity data show that the viscosity increases with floc size. Because of this correlation, measurements of surface charge and zeta potential were made for various ionic conditions, and the same strong dependence on pH and weak dependence on NaCl amount were found. To further investigate charge effects, goethite particles were mixed with negatively and positively charged latex spheres. Electron micrographs of the combined populations indicate that the surface charge on goethite particles is not uniform, appearing to be negative in some locations and positive in others. These observations suggest a possible mechanism for the observed flocculation.
Modelling viscosity of suspensions of alumina and kaolin as a function of volumetric concentration of solids
Agenor De Noni Jr, Daniel E. Garcia, and Dachamir Hotza
EQA, UFSC, Florianopolis, SC 88040-900, Brazil

The variation of viscosity in function of concentration of solids in suspension and of shear rate was studied. Understanding viscosity as being a macroscopic manifestation of internal attritions of particles in suspension, as a result of mechanical and electromagnetic interactions, a model of viscosity as function of volumetric concentration of solids is presented. The theoretical model was compared with experimental data accomplished with a double concentric cylinders rheometer. The volumetric concentration of solids in alumina and kaolin suspensions was varied from 2 to 24%. With some simplifications and adapting the experimental conditions in order to reproduce them, a good correlation of the proposed model with the measured data could be verified in the studied systems. The forces of mechanical origin that cause restrictions to the rotation and translation of particles influence the variation of viscosity in the analyzed system remarkably.

Simulations of inhomogeneous kinetic theory of liquid crystalline polymers
Jason K. Suen, Robert A. Brown, and Robert C. Armstrong
Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Liquid crystalline polymers are complex fluid systems that are technologically and industrially important, yet fundamentally poorly understood. A major challenge lies in the inhomogeneous nature of the liquid crystalline polymers, which introduces structures such as disclination and defects. This makes experimental data difficult to interpret and molecular models difficult to derive. We have recently developed a self-consistent molecular model by using a configuration space kinetic theory. The key features of this model include translational diffusion and an inhomogeneous polymeric stress contribution.

To explore the behavior of this model, we developed a novel, coupled wavelet-finite element method for simulating molecular evolution in a complex flow field. The numerical method is built on the local discontinuous Galerkin discretization for the physical space and a scaling function expansion for the configuration space. A semi-implicit time integration algorithm is implemented to improve the stability of the overall scheme.

We simulate the behavior of this model in two different flow systems: rectilinear flow through a planar channel and flow around periodic array of cylinders confined in a planar channel. Comparisons are made between the new inhomogeneous model and the Doi model. For the planar channel flow, we find that the new model stabilizes the hydrodynamics and induces disclination formation and refinement. The new model and the wavelet-finite element method provide new tools for understanding the dynamics and rheology of liquid crystalline polymers.

Hydrodynamic coefficients for dynamic mean-field models of LCPs
David C. Morse
Chemical Eng. and Materials Sci., University of Minnesota, Minneapolis, MN 55455

We consider a class of dynamical mean-field models for nematic liquid-crystalline polymers, in which a polymer containing one or more rod-like nematogens, with an otherwise arbitrary architecture, moves in a time-dependent, self-consistently determined Maier-Saupe field, which couples to the nematogen orientations. The Doi model with a Maier-Saupe interaction, in which the polymer consists of a single rod, is the simplest such model. We show how the hydrodynamic coefficients predicted for the nematic by any such model may be related to the response functions
of non-interacting chains in a fixed orienting field. This approach allows one to extract predicted values for linear hydrodynamic parameters, including the tumbling parameter lambda, from simulations of polymers in fixed orienting field, and thereby study the dependence of lambda upon molecular parameters such as backbone rigidity.

Tuesday 10:35 Diplomat/Ambassador ML17

**Capillary instabilities in thin nematic liquid crystalline fibers**

Ae-Gyeong Cheong¹, Alejandro D. Rey¹, and Patrick T. Mather²

¹Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada; ²Institute of Materials Science, Polymer Program, University of Connecticut, Storrs, CT 06269-3136

A complete identification and characterization of three distinct capillary instabilities in nematic liquid crystal fibers is presented. Linear stability analysis of capillary instabilities in thin nematic liquid crystalline cylindrical fibers is performed by formulating and solving the governing nemato-capillary equations. A representative axial nematic orientation texture is studied. The surface disturbance is expressed in normal modes, which include the azimuthal wavenumber m to take into account non-axisymmetric modes of the disturbance. Capillary instabilities in nematic fibers reflect the anisotropic nature of liquid crystals, such as the orientation contribution to the surface elasticity and surface bending stresses. Surface gradients of bending stresses provide additional anisotropic contributions to the capillary pressure that may renormalize the classical displacement and curvature forces that exist in any fluid fiber. The exact nature (stabilizing and destabilizing) and magnitude of the renormalization of the displacement and curvature forces depend on the nematic orientation and the anisotropic contribution to the surface energy, and accordingly capillary instabilities may be axisymmetric or non-axisymmetric, with finite or unbounded wavelengths. Thus, the classical fiber-to-droplet transformation is one of several possible instability pathways while others include surface fibrillation.

Tuesday 11:00 Diplomat/Ambassador ML18

**Dynamics of shear-induced monodomains for finite-aspect-ratio macromolecules**

Greg Forest¹ and Qi Wang²

¹Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250; ²Mathematics, Florida State University, Tallahassee, FL 32306

The bulk response of monodisperse macromolecules to shear is a classical rheological benchmark. Experimentalists have compiled flow-phase diagrams for diverse nematic liquids, which are then classified according to their monodomain fixed-shear response (e.g., flow-aligning, logrolling, tumbling, wagging, etc.), and according to shear-rate-dependent transitions. Theoretical advances are likewise measured against the ability to reproduce shear-induced bulk modes and to predict transition phenomena, with significant progress primarily dealing with infinite aspect ratio models. We focus in this lecture on finite-aspect-ratio phenomena from a dynamical systems perspective. We present results from various mesoscopic flow-nematic models derived from an extended Doi theory of Wang, indicating surprising sensitivity of the flow-phase diagrams to aspect ratio. New transition phenomena emerge that are not captured by standard infinite aspect ratio models for rod-like and discotic nematic polymers. We also visualize the diverse monodomain modes relative to the flow plane and vorticity axis as a means toward distinguishing them in an experiment.

Tuesday 11:25 Diplomat/Ambassador ML19

**Dynamics of flow induced isotropic/nematic transition with the Doi model**

Massimiliano Grosso¹ and Pier Luca Maffettone²

¹Dipartimento di Ingegneria Chimica, Università Federico II di Napoli, Napoli 80125, Italy; ²Dipartimento di Scienze dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino 10129, Italy

The dynamics of the flow induced isotropic/nematic phase transition is studied with the rigid-rod model for nonhomogeneous systems. Spatial dependences are explicitly accounted for also for the rod density, and a Maier-Saupe mean field nematic potential is used. Preliminary results are obtained by resorting to closure approximations. Work is progress to solve the problem without closure approximations.
Tuesday Afternoon

Symposium SS
Simple Fluids To Suspensions
A Symposium in Honor of William R. Schowalter
Organizers: Andrew M. Kraynik and William B. Russel

Tuesday 1:30 Cabinet SS20
Tubular entry flows revisited
David V. Boger
Chemical Engineering Department, The University of Melbourne, Parkville, Victoria 3052, Australia

My first contact with Bill Schowalter was via a publication with Morton Collins on tubular entry flows [“Behavior of non-Newtonian fluids in the entry region of a pipe”, A.I.Ch.E.J., 9(6), 1963] and then later in 1971 at the Princeton Autumn meeting of the Society of Rheology where we presented our first paper on entry flows. The original work by Collins and Schowalter in 1963 will be used as a springboard to examine the current status on tubular entry flows of viscoelastic fluids. Particular emphasis will be placed on this flow field and the impact it has had as a test problem in computational rheology.

Tuesday 1:55 Cabinet SS21
Modeling fiber spinning: From liquid to semi-solid
Anthony J. McHugh
Chemical Engineering, University of Illinois, Urbana, IL 61801

Melt and solution dry spinning of polymeric fibers are industrial processes of great commercial importance. Accurate simulation of these requires constitutive models that explicitly account for the complex viscoelastic response of the material due to the rapidly changing temperature and deformation fields (particularly for high-speed melt spinning) and composition changes (in the case of dry spinning) that take place along the spinline, leading to solidification of the fiber. Accurate prediction of the locking-in of stresses and microstructure at the solidification point is critical, since these are intimately related to the fiber properties. This talk will discuss recent advances in the application of single-phase and two-phase viscoelastic constitutive models to fiber spinning. Simulations of melt spinning of semi-crystalline systems are based on a two-phase constitutive model that combines a modified Giesekus equation for the melt phase and a rigid rod equation for the semi-crystalline phase. Relaxation times for the two phases are coupled to the crystallization kinetics through a modified Avrami formalism. Examples of 1-d and 2-d simulations will be shown to illustrate the ability of the model to predict relevant behaviors under low and high speed spinning conditions. Simulations of dry spinning to be described are based on single phase constitutive models whose relaxation times are strongly coupled to the rapid rise in viscosity resulting from solvent evaporation along the spinline. Predictions of velocity profiles and stresses for typical spinning conditions based on 1-d simulations will be shown and application to 2-d structure prediction will be discussed.
Tuesday Afternoon

Tuesday 2:20 Cabinet SS22

**Kinetic phase diagrams of star polymers**

Dimitris Vlassopoulos¹, Emmanuel Stiakakis¹, and Jacques Roovers²

¹Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete 71110, Greece; ²Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ontario, Canada

Multiarm star polymers are known to represent model soft spheres encompassing both polymeric and colloidal behavior. This dual character, stemming from their complex topology, is responsible for the occurrence of liquid-like order in the interaction regime. When dispersed in good solvent, the star dispersion undergoes a liquid-gel transition as the concentration increases, much like conventional colloids. Here, we explore the effects of the suspending medium; we use molecular solvents of intermediate quality or viscoelastic solvents consisting of linear homopolymer solutions, where the polymer molecular weight can vary at will. With the aid of rheological and scattering measurements we identify the state of the 'crowded' star dispersions and produce kinetic phase diagrams of liquid-gel transition as function of volume fraction and/or linear chain size. Our results suggest ways for molecular manipulation of the properties of soft materials. We discuss them in the context of two mechanisms: swelling of stars and star-linear polymer interactions (penetration of short chains and exclusion of long ones).

Tuesday 2:45 Cabinet SS23

**Identification of genes regulated by shear stress using microarray technology in human endothelial cells**

Larry V. McIntire

Institute of Biosciences and Bioengineering, Rice University, Houston, TX 77005

Gene microarray analysis is a powerful method for analyzing the effect of biological stimuli on gene expression profiles. We used Research Genetics microarray GF211, which contains over 4000 known human genes, to identify those regulated by fluid shear stress exposure. Message levels of genes in primary human umbilical vein endothelial cells exposed to a shear stress of 25 dyn/cm² for 6 or 24 hours were compared with message levels in control cells. For several of the genes, Northern analysis was used to confirm the results. The microarray analysis identified many shear stress regulated genes, including genes that have been previously shown to be regulated by shear stress such as endothelin-1, monocyte chemotactic protein-1 and prostaglandin transporter. Overall the expression of 32 genes increased two fold or greater and the expression of 20 genes decreased 50% or more in response to shear stress.

Shear stress is considered by many to be the most important stimulus for NO production in EC. Several genes identified as being shear stress responsive from our DNA microarray analysis may play a role in the regulation of NO production by shear stress, and suggest exciting new pathways for shear stress regulation of NO production in endothelial cells. The use of microarray technology to study the biological effects of shear stress has the potential to expedite our understanding of the role of shear stress in vascular biology and to allow the development of new hypotheses concerning genetic networks regulated by mechanical forces.

Tuesday 3:35 Cabinet SS24

**Toward a molecular interpretation of turbulent drag reduction**

Eric S. Shaqfeh¹, Joe Hur², Vince Terrapon³, and Parviz Moin³

¹Chemical Eng. and Mechanical Eng., Stanford University, Stanford, CA 94305-5025; ²Chemical Engineering, Stanford University, Stanford, CA; ³Mechanical Engineering, Stanford University, Stanford, CA

In the mid-90's Schowalter, Hanratty and coworkers made the important step of applying Brownian dynamics simulation of a polymer model containing internal modes to turbulent channel flow. The object was to attempt to understand molecular configuration change and stretch with application to turbulent drag reduction. We now know that such an approach can be critical in understanding the physics of solution dynamics in many simpler time-dependent flows because of fast stress response and configurational hysteresis of molecules in rapidly time-dependent flows. We also know now that if careful mechanical models of chains are created, then quantitative agreement with measured molecular dynamics can be achieved. In this talk we will revisit this approach but now employing a number of molecular models designed to model existing drag reducing agents in dilute solution. We shall simulate these models in the "Minimal Channel" discovered by Jimenez and Moin as the smallest unit which
allows the statistics of turbulent channel flow to be recovered. The combination of fast Brownian dynamics algorithms and efficient DNS of the minimal channel flow allows us to simulate a large ensemble of molecules per spatial grid point such that meaningful average quantities can be determined. Thus the molecular mechanism of molecular configuration change and stress in a Newtonian turbulent flow can be unambiguously examined. We shall compare this mechanism for various molecular models to the coupled calculations for the FENE-P model by Beris and co-workers. Moreover we shall compare the stochastic simulations of FENE models with more sophisticated multi-mode models to assess how internal modes affect the molecular stretch and stress production in turbulent channel flow.

Tuesday 4:00 Cabinet SS25

On the role of surface conduction in the electrohydrodynamic deformation of drops and bubbles

C. L. Burcham and D. A. Saville
Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

The Taylor-Melcher leaky dielectric model is often used to explain the behavior of drops, bubbles, and jets in electric fields. In most situations, agreement between theory and experiment is satisfactory. However, recent experiments with liquid bridges delineate situations where the model appears to fail. One possible explanation for the failure is over simplification of ion transport processes across interfaces. Here we address extensions of the model to treat situations where conduction processes near an interface differ from those in the bulk. Using a two-dimensional 'surface conductivity' we compute the deformation of small drops and bubbles in a steady field to delineate the effects of ion transport parallel to an interface.

Tuesday 4:25 Cabinet SS26

Compatibilizer effects on drop coalescence

L. G. Leal1, C. C. Park2, J. W. Ha3, and Y. Yoon3
1Depts of Chemical Eng. and Materials Eng., Univ. of Calif at Santa Barbara, Santa Barbara, CA 93106; 2Mechanical Engineering, Univ. of Calif. at Santa Barbara, Santa Barbara, CA 93103; 3Chemical Eng., Univ. of Calif. at Santa Barbara, Santa Barbara, CA 93106

It is well-known that flow-induced coalescence is strongly inhibited by the presence of a high MW surfactant-like material ("compatibilizer") at the drop-fluid interface. In this work, we explore the details of this effect experimentally by means of variations in the concentration and molecular weights of the surfactant for systems in which the bulk fluids are polymers with Newtonian rheology under conditions of the coalescence process. The mechanism(s) by which the compatibilizer influences coalescence are discussed.

Tuesday 4:50 Cabinet SS27

Cell-level stress in random soap foams

Andrew M. Kraynik1, Douglas A. Reinelt2, and Frank van Swol3
1Engineering Science Center, Sandia National Laboratories, Albuquerque, NM; 2Mathematics Department, Southern Methodist University, Dallas, TX 75275-0156; 3Materials and Process Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185-1349

Dry soap foams are prototypical jammed systems. Under static conditions, the total surface energy is minimized by individual polyhedral cells adjusting to the presence of neighbors to satisfy Plateau's laws. The Surface Evolver is used to calculate the microstructure of random polydisperse foams and evaluate the shape and stress contribution of individual cells. The shear modulus decreases with increasing polydispersity. Under quasi-static simple shearing flow, the structure and stress are piecewise continuous functions of strain. The discontinuities correspond to intermittent rearrangements within isolated clusters of bubbles; these avalanches of topological transitions have been observed during the flow of commercial shaving foam with diffusing-wave spectroscopy and found in 2D simulations. The connection between cell-level statistics and macroscopic rheology is explored.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract #DE-AC04-94AL85000.
Symposium SM
Viscoelasticity In Polymer Solutions and Melts
Organizers: David Venerus and Guy C. Berry

Tuesday 1:30 Old Georgetown SM1
On the origins and consequences of the BKZ theory
Barry Bernstein
Chemical and Environmental Engineering, Illinois Institute of Technology, Chicago, IL 60616

The BKZ theory, originally called the theory of Perfect Elastic Fluids, has had an important influence on the
development of non-linear continuum theories of viscoelasticity. In the 1960's it arose out of work by B. Bernstein,
E.A. Kearsley and L.J. Zapas who were trying to connect what were then new continuum theories with experimental
results and was made possible only because of close collaboration between the mathematician, B. Bernstein, the
physicist, E.A. Kearsley and the experimenter, L.J. Zapas. It also dealt with thermodynamics. It was not only
successful in breaking new ground, but led others to challenge it and seek to improve on it in a continuing effort to
treat large viscoelastic strain successfully. The equations of stress-strain were simultaneously and independently
written by A. Kaye in England, but the latter had neither the experimental results nor the thermodynamics to
distinguish them from other candidates for theoretical importance. The theory is presented, including the essentials
of the thermodynamics and the original experimental evidence. Further developments are discussed.

Tuesday 2:20 Old Georgetown SM2
Some comments on the K-BKZ constitutive equation as applied to biaxial extensional flows
of polymer sheets
Alan S. Wineman
Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109

The K-BKZ single integral constitutive equation for the nonlinear response of polymeric fluids was an important
contribution to the mechanics of polymer fluids. The 25th anniversary of its publication was acknowledged at a
previous meeting of the Society of Rheology. As B. Bernstein, E. Kearsley and L. Zapas were associated with NBS
(now NIST) during its development, it is appropriate to commemorate the constitutive equation at the present
meeting of the Society of Rheology. The K-BKZ constitutive equation has been used to study a variety of flows of
polymer fluids. This talk will review its application to unsteady inhomogeneous biaxial extensional flows of thin
polymer sheets. Some stability phenomena arising in their response will be discussed.

Tuesday 2:45 Old Georgetown SM3
Bernstein, Kearsley and Zapas: Extension of the model using time-strain separability and
the Valanis-Landel function
Gregory B. McKenna
Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121

The BKZ model has proven to be one important cornerstone of much that we do in Rheology primarily because it
has a structure that captures some of the major physics of entangled polymer melts. One important assumption that
makes the BKZ model easier to use has been time-strain separability, which was subsequently found to be a
consequence of the reptation theory. Here, we combine time-strain separability with the Valanis-Landel ideas of
strain separability of the strain energy function. Because the BKZ model uses a strain potential function which looks
like a time-dependent strain energy function, this is a logical extension. We will demonstrate the usefulness of this
approach using experimental results for both polyvinyl chloride above its glass transition and for a crosslinked
polyurethane rubber.
Tuesday 3:35 Old Georgetown SM4

**Evaluation of molecularly-based constitutive equations for branched polymers in single- and double-step strain flows**

Chirag Chodankar, David Venerus, and Jay Schieber

*Department of Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616*

The Pom-Pom model of McLeish and Larson has been shown to be capable of describing many important phenomena observed in both shear and elongation flows of branched polymer melts. For example, the multi-mode, differential version of the Pom-Pom model with a single set of parameters quantitatively describes stress growth in constant strain rate simple shear and uniaxial elongation flows. In this study, we consider single- and double-step strain flow. In particular, we focus on reversing double-step strain flows, which have been shown in the past to provide rather discerning tests of the well-known K-BKZ and Doi-Edwards constitutive equations. To conduct this evaluation we use a low-density polyethylene melt (Lupolen 1810H) that has been extensively characterized in other flows. Semi-analytic predictions from the Pom-Pom model in single- and double-step strain flows are compared with experimental observations. In single-step strain flows, we find, contrary to experimental results, that the multi-mode Pom-Pom model does not exhibit time-strain factorability even at modest strains. Despite this, the model gives a reasonable prediction for the strain-dependent damping function when averaged over a range of times. In double-step strain flows, predictions of the Pom-Pom model are found to be inconsistent with experimental results, particularly for flows with strain reversal. Predictions from the Pom-Pom model are also compared with those from the K-BKZ and Doi-Edwards models and with Oettinger's, thermodynamically inspired, Pom-Pon model.

Tuesday 4:00 Old Georgetown SM5

**Incompressible finite elements for BKZ fluids**

David S. Malkus

*Engineering Physics/Rheology Research Ctr., University of Wisconsin, Madison, WI 53705*

Techniques for the numerical simulation of steady flows of BKZ fluids were proposed by B. Bernstein in the '70s. He envisaged an Eulerian finite element formulation with a background Lagrangian construction of particle paths and finite strain tensors to evaluate the history integrals giving the stress. Such a method would rest on the foundation of an efficient solution of the Stokes problem. This talk discusses the development of finite element Stokes solvers in the light of the difficulties encountered in accurate imposition of the incompressibility constraint. Elements with redundant constraints were developed, and the result was an element formulation for which rigorous error analysis in the Stokes problem was possible and which had several unique advantages that allowed for Bernstein's vision to be completely realized. The unique properties of the formulation inspired Bernstein to invent several elegant generalizations of his original semi-Lagrangian approach, which will be discussed here.

Tuesday 4:25 Old Georgetown SM6

**Some success stories in the numerical simulation of polymer flows with the K-BKZ model**

Evan Mitsoulis and Savvas Hatzikiriakos

*Mining Engineering and Metallurgy, NTUA, Zografou 157 80, Greece; Chemical Engineering, UBC, Vancouver, BC V6T 1Z4, Canada*

In recent years good progress has been achieved in the viscoelastic simulation of polymeric liquids by using integral constitutive equations of the K-BKZ type (1,2). This is particularly true for the modelling of polymer solutions and melts with a spectrum of relaxation times. Considerable success has been achieved with a particular type of the K-BKZ integral equation, the PSM model (3). This equation has been used to predict several well-known viscoelastic phenomena for polymer melts, such as extrude swell from long dies for a low-density polyethylene (LDPE) melt and enhanced swelling from short dies for the same LDPE, difference in behaviour between LDPE and HDPE melts in flows through contractions, stress birefringence patterns for HDPE and LLDPE melts, etc. Further developments have included non-isothermal calculations of polymer melt flows through extrusion dies and coextrusion flows of polymer melts. Also strain-hardening in planar and biaxial extension has been quite recently correctly predicted for branched polymers by introducing a new damping function (4). The present talk will focus on past and up-to-date achievements in viscoleastic simulations of polymer fluid flows and will discuss future developments and challenges in the field of computational non-Newtonian fluid dynamics.
Tuesday Afternoon


Tuesday 4:50 Old Georgetown SM7

A microscopic-based, stochastic model for polymeric fluids and its equivalence to the Rivlin-Sawyers model

Kathleen Feigl

Department of Mathematical Sciences, Michigan Technological University, Houghton, MI 49931

A class of microscopic-based, stochastic models for polymeric fluids is discussed. This class combines aspects of microscopic models with continuum mechanics. The dynamics of the macromolecules is described by two independent Gaussian random variables, or vectors, which can be interpreted within the frameworks of network theory and reptation theory. One random vector represents the configuration of temporary strands in a network structure formed by the macromolecules, while the other serves as a representation of an area element of the strand and corresponds to the concept of anisotropic tube cross section from reptation theory. The expression for the polymeric stress tensor is given as a function of these dynamics.

It is shown that this class of stochastic models is equivalent to the macroscopic class of factorized Rivlin-Sawyers models for viscoelastic fluids. Furthermore, it is seen that the class of factorized K-BKZ models, which is a subclass of the factorized Rivlin-Sawyers models, has a natural equivalent counterpart subclass in the class of stochastic models.

Model predictions of rheometric data of several polymer melts, obtained using stochastic simulations, are also presented, and various model modifications are discussed.

Symposium CF

Quantifying Microstructure In Complex Fluids

Organizers: Norman Wagner and Alan I. Nakatani

Tuesday 1:30 Judiciary CF19

High-shear-rate optical rheometer for polymer solutions and melts

Khaled Mriziq¹, Horng-ji Dai², Mark D. Dadmun², and Hank D. Cochran³

¹Physics Dept, University of Tennessee, Knoxville, TN 37996; ²Chemistry, University of Tennessee, Knoxville, TN 37996; ³Chemical Technology, Oak Ridge National Laboratory, Oak Ridge, TN

Understanding the shear induced structure of long-chain molecules presents fundamental challenges and yet is of immense technological importance in such applications as polymer processing and lubricant performance. The shear-induced structures and rheological property changes in systems of long-chain molecules have attracted a great deal of attention both experimentally and theoretically in recent years. A variety of experimental methods are available for studying the shear-induced behaviors in fluids; the most commonly used instruments are optical rheometers. Transparent light scattering shear cells with cone and plate and Couette geometries have been constructed to examine long-chain systems by many researchers. Both geometries can provide a uniform shear rate throughout the sample; however, optical rheometers of these geometries can only apply moderate shear rate (up to about $10^5 \text{ s}^{-1}$) on the fluid, primarily because of the difficulty of removing viscous heat from the sample at this sample thickness. Lubricants experience shear rates in excess of $10^{10} \text{ s}^{-1}$ in critical applications, a range of shear rates that is not currently accessible experimentally in an optical rheometer.

Thus, we have designed and constructed a new optical rheometer to study the shear-induced structures and rheological properties of polymer melts and solutions at high shear rate. This apparatus utilizes the geometry of a
magnetic disk drive in which a very thin film is sheared between optically transparent disk and slider surfaces at relatively low rotation speed. While the rheological properties of the polymer film can be obtained from the stresses on the slider, small-angle light scattering and other optical techniques can investigate the sample structure. A 5% solution of polystyrene in dioctyl phthalate has been used to test this apparatus.

Tuesday 1:55 Judiciary CF20

Study of uniaxial extensional flow and morphology of elastomeric polypropylenes
Gerald G. Fuller1, Willy Wiyatno1, Holger Schonherr1, John Pople2, Robert M. Waymouth3, Curtiss Frank1, and Alice Gast1
1Chemical Engineering, Stanford University, Stanford, CA 94305-5025; 2Stanford Linear Accelerator Center, Stanford Synchrotron Radiation Laboratory, Stanford, CA 94309; 3Dept. of Chemistry, Stanford University, Stanford, CA 94305

The uniaxial extensional flow of elastomeric polypropylenes (ePP) synthesized with unbridged 2-arylindene metallocene catalysts was investigated by tensile stress, optical birefringence, Wide Angle and Small Angle X-rays Scattering (WAXS and SAXS). Simultaneous tensile stress and birefringence measurements of ePP show the birefringence relax faster than the tensile stress. The residual strain (tensile set) and residual birefringence are shown to correlate with strain deformation, crystallinity, and time held at strain.

Investigation of the fractions comprising the parent ePP from solvent-boiling fractionation shows contrasting behavior to the parent ePP. Relaxation of the ether-soluble (ES) fraction (lowest crystallinity) held at a constant strain causes the birefringence to relax to a negative plateau, indicating perpendicular orientation to the flow direction. The disappearance of negative birefringence with heating to 75°C suggests a crystalline contribution to the negative birefringence. This is confirmed by WAXS which shows strain-induced crystallization. During uniaxial deformation, crystalline arcs appear on the meridional axis parallel to the direction of strain (perpendicular crystallite orientation). In contrast to the ES fraction, heptane soluble fraction develops relatively bright spots of intensity on the equatorial axis of the WAXS during uniaxial deformation. This indicates a molecular-scale alignment parallel to the applied strain direction which is also collaborated by the positive birefringence. SAXS, which probes larger distances than WAXS, also displays anisotropy during deformation.

Morphology studies with polarized light microscopy and tapping mode AFM give clear evidence that the parent ePP as well as all of its fractions can crystallize. Lamellar crystals, hedrites, and imperfect spherulites as well as the typical cross-hatching morphology known for the α-modification of isotactic PP are evident for ePP and its fractions.

Tuesday 2:20 Judiciary CF21

Rheology and morphology of phosphate glass-PS-LDPE ternary blends
Peter C. Guschl and Joshua U. Otaigbe
Material Science & Engineering, Iowa State University, Ames, IA 50014

Various ternary blends of low-density polyethylene (LDPE), polystyrene (PS), and a low Tg tin-based phosphate glass (Pglass) were prepared at certain compositions in which either LDPE or PS is the continuous matrix phase. A special, interesting, time-dependent transient and steady shear rheology was observed. This observed rheology is ascribed to a unique composite morphology of this multi-component system. Two Newtonian plateaus at low and moderate shear rates connected by two distinct shear-thinning regimes are apparent in the viscosity versus shear rate curves of the blends. Rheological data on the binary Pglass-polymer systems suggest that LDPE contributes significantly to this unusual behavior, perhaps due to the formation of a network structure between the phases. SEM and TEM observations were utilized in order to provide a qualitative assessment of the system morphology. Optical shearing data also was employed in order to confirm the evolution of this microstructure under particular shear conditions. Differential scanning calorimetry was used to investigate the phase behavior of the blends.
Real-time SAXS studies of flow alignment processes in a lamellar diblock copolymer

Wesley R. Burghardt and Franklin E. Caputo

Department of Chemical Engineering, Northwestern University, Evanston, IL

We report studies on the development of macroscopic orientation in a lamellar diblock copolymer. Samples of a symmetric polysisoprene-polystyrene BCP were quenched into the ordered phase, resulting in an ordered but random polycrystalline initial condition. We have studied the transient development of orientation using real-time synchrotron small-angle x-ray scattering. Alignment has been studied both in large amplitude oscillatory shear and in unidirectional shear flow. Two shear flow geometries have been employed: a rotating parallel disk shear cell in which the incident beam propagates along the shear gradient (2) direction and hence probes anisotropy in the 1-3 plane, and an annular cone and plate shear cell in which the beam propagates along the gradient (3) direction and hence probes anisotropy in the 1-2 plane. This latter geometry, in particular, is used to study the initial stages of alignment, and to test models of 'grain rotation' in sheared lamellar diblocks.

Robust simulation of rheologically complex multiphase systems using a novel 3D finite element method

Russell W. Hooper, Vittorio Cristini, John Lowengrub, Christopher W. Macosko, and Jeffrey J. Derby

Chemical Engineering, University of Minnesota, Minneapolis, MN 55455; School of Math, University of Minnesota, Minneapolis, MN

Accurate and robust modeling of microstructure development during polymer processing provides a level of understanding greatly aiding the prediction and control of blend properties. The key challenges to such modeling involve the complex fluid rheology of the matrix and dispersed phases and the extremely large topology changes experienced by the microstructure under strong flow conditions. We have developped an adaptive 3D finite element method that addresses these key issues. Specifically, our method provides simulations of 3-dimensional, time-dependent moving boundary problems involving multiple particles and complex fluid rheology including full viscoelasticity. After a brief description of the methodology, results are presented for problems relevant to polymer blending. Single drop deformations in simple shear and combined shearing and extensional flows are presented for both Newtonian and viscoelastic fluids in the creeping flow limit. Multiple drop systems are demonstrated with results for two interacting Newtonian drops in simple shear. Where possible, the validity of the novel 3D FEM is established by comparison to boundary integral and axisymmetric finite element results as well as to some experimental results. Progress toward our ultimate goal of a 'numerical rheometer' will also be summarized. This concept involves simulating realistic emulsions and other microstructures of rheologically complex fluids without recourse to phenomenological models. Numerically determined measureables such as torque, drag and normal forces can then be related to the corresponding microstructures directly. Such a tool holds great potential for uniting experimental data with constitutive modeling as well as for extending fundamental understanding of real processing scenarios.

Exact numerical solutions of particle interactions in nonlinear shear fields

Wenxian Lin, Alan L. Graham, Jeremy W. Leggoe, and Marc Ingber

Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121; Department of Mechanical Engineering, University of New Mexico, Albuquerque, NM 87131

In this study, pairs of particles interacting in linear and nonlinear shear field are performed with three-dimensional boundary element codes. In this work, direct simulations are carried out to examine the particle migration of two neutrally-buoyant rigid spheres moving freely in unbounded shear flows. Here, three-dimensional transient simulations were performed in Couette flow, simple shear, axisymmetric and plane Poiseuille flows. The numerical results are in excellent agreement with the exact analytical solutions for simple shear flow.

The numerical results show that in a homogeneous simple shear flow, there is no migration of the center of mass of the spheres during the particle interactions. However in nonlinear shear fields, the particle interaction defines a
preferred direction in the system along the shear rate gradient. As the spheres initially approach each other, the center of mass of the particles is displaced from higher shear regions to regions of lower shear rate. However, as the particles recede from each other the center of mass returns to its original streamline. The magnitude of the transient displacement increases as the shear rate gradient increases. In all cases, the simulations are reversible in these two particle simulations in unbounded shear fields.

Tuesday  4:25  Judiciary  CF25  
**Calculation of transient stress behavior in dilute immiscible blends via experiments and numerical simulations**
Thomas Jansseune¹, Jan J. Mewis¹, Paula Moldenaers¹, Vittorio Cristini², and Christopher W. Macosko²

¹Dept. of Chemical Eng., K.U. Leuven, Leuven, Belgium; ²Dept. of Chemical Engineering, K.U.Leuven, Leuven 3001, Belgium

Transient stresses are very sensitive to the underlying morphology changes in a sheared blend. In order to predict stresses the microstructural evolution should be well known and accurately modeled. In this study rheological predictions of transient stress and deformation based on adaptive numerical simulations, capable of describing accurately large drop deformations, are compared with experimental data on a dilute blend with Newtonian components, revealing very good agreement. This critical comparison allows one to identify different types of droplet deformation in the experimental system. The validity of existing theories based on small or rather simplified deformations is also tested.

Tuesday  4:50  Judiciary  CF26  
**Numerical simulation of drops and bubbles in three dimensional viscoelastic flows**
Shriram B. Pillapakkam¹ and Pushpendra Singh²

¹Mechanical Engineering, New Jersey Institute Of Technology, Newark, NJ 07029; ²Mechanical Engineering, New Jersey Institute Of Technology, Newark, NJ 07102

Direct Numerical simulation (DNS) is implemented through a three dimensional finite element scheme that uses Level Set Method to track the interface and the Marchuk-Yanenko operator splitting technique to decouple the governing equations into sub problems. Using this numerical capability, the shape of Newtonian drops in a simple shear flow of viscoelastic fluid and vice versa as well as bubbles rising in gravity driven flow are analyzed as a function of Capillary number and Deborah number. The viscoelastic fluid is modeled via the Oldroyd-B model. The role of viscoelastic stresses in deformation of a drop subjected to simple shear flow and its effect on the steady state shape, transient deformation as well as modes of break up are analyzed by comparison with corresponding Newtonian results.

**Symposium GP**
**General Papers**
Organizers: James Harden and Deepak Doraiswamy

Tuesday  1:30  Diplomat/Ambassador  GP1  
**Dynamics of fiber coating with surfactant solution**
Amy Q. Shen¹, Stone Howard¹, and Gareth H. McKinley²

¹Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138; ²Dept. Mechanical Engineering, M.I.T., Cambridge, MA 02139

When a fiber is withdrawn at low speeds from a pure liquid, the thickness of the entrained film is well-predicted by the Landau-Levich-Derjaguin (LLD) equation. However, surfactant additives are known to alter this response, e.g. Quere, de Ryck and Ramdane, (1997). We study the film thickening properties of the anionic surfactant SDS, the nonionic surfactant Triton X-100, and the protein BSA. For each of these additives, the film thickening factor a (the ratio of the measured thickness to the LLD prediction) for a fixed fiber radius varies with the ratio of surfactant concentration c to the critical micelle concentration cmc. Due to Marangoni effects, a reaches a maximum as c
approaches the cmc from below. However, when the surfactant concentration c exceeds the cmc, the behavior of a
varies as a consequence of different sorption kinetics of these additives, as indicated recently by Quere, de Ryck and
Ramdane (1997). For SDS, a begins to decrease when c is sufficiently high for the surface to become partially or
completely remobilized, which is consistent with the theoretical picture elucidated by Stebe and Maldarelli (1994) in
studies of slug flows of bubbles and surfactant solutions in a capillary tube. However, when c is well above cmc, we
observe that a increases once again and, concommitant with this increase, we observe the formation of aggregates
much larger than typical micelles. Results for very high concentrations of surfactants will be discussed and a model
will be proposed.

Tuesday 1:55 Diplomat/Ambassador GP2
Microscale polymer processing
Ashish K. Lele and Malcolm R. Mackley
Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, United Kingdom

We have developed an experimental technique for studying the processing behaviour of 10g quantities polymer
melts. Using the recently built MultiPass Rheometer (MPR) with two purpose built flow cells: a standard slit die and
a new 'product cell', we have measured the processing behaviour of monodisperse polybutadienes of linear and
branched architectures. Matching simulations were established using the Polyflow package for linear polymers and a
Langrangian-Eulerian flowSolve package for branched polymers. We compare the stress fields inferred from flow
birefringence data and the principle stress difference contours predicted by simulations. The experimental results
point out qualitative differences between the processing behaviour of linear and branched polymers.

Tuesday 2:20 Diplomat/Ambassador GP3
Contraction flow behavior of metallocene-catalyzed polyethylenes
Phillip J. Doeringhaus and Donald G. Baird
Center for Composite Materials and Structures, Virginia Polytechnic Institute and State University,
Blacksburg, VA 24060

The presence of flow contractions in polymer extrusion applications often leads to added pressure drops and may
initiate flow instabilities at higher flow rates. The magnitude of the response is generally determined by the
rheological characteristics of the melt. The development of metallocene catalysts now provides the ability tailor
polyethylene resins with specific molecular attributes and rheological properties. In the present study, the
contraction flow behavior of various conventional and metallocene polyethylene resins has been investigated using
abrupt planar and axisymmetric contraction geometries. Pressure measurements combined with full-field flow
birefringence observations have been collected for each resin and compared to corresponding numerical simulations.
In addition, the particular choice of constitutive equation used and its effectiveness on simulation performance has
also been addressed.

Tuesday 2:45 Diplomat/Ambassador GP4
The Smoluchowski equation and the electroviscous effect
Lawrence C. Cerny and Elaine R. Cerny
1Research, CERNYLAND OF UTICA, Huber Hts., OH 45424-3467; 2CERNYLAND OF UTICA, Huber
Hts., OH 45424-3467

In 1916, Smoluchowski corrected the Einstein viscosity equation for rigid spherical particles. The modified
treatment included the effect of electrostatic charges on the particles. He reasoned that the electrokinetic potential of
the suspended charged spheres would cause an increase in the viscosity of the suspension over that due to the
volume fraction of the particles. For this study of the electroviscous effect, a polystyrene latex was selected. This
latex is a suspension of rigid spherical particles in water, stabilized by a soluble soap whose anions are adsorbed by
the polystyrene. This adsorbed monolayer of soap gives the spheres a uniformly charged surface of known charged
density. These features make this latex a suitable system for the proposed study. Theoretical expressions relating the
viscosity of colloidal suspensions and their electrical environment were tested. In the limit of low volume fraction,
and low soap content, the Einstein equation was obeyed. It was found that the zeta potentials calculated from
viscosity behaved in a manner at variance with theory, and did not agree with those determined by electrophoretic
mobility measurements.
Tuesday Afternoon

Tuesday 3:35 Diplomat/Ambassador GP5

Axial flow between eccentric cylinders
Chanyut Kolitawong and A J. Giacomin
Mechanical Engineering, The University of Wisconsin-Madison, Madison, WI 53706-1572

Plastic pipe production must use annular dies with eccentricity to compensate for gravity flow in the cooling chamber. Here an algebraic analytic solution is obtained in bipolar cylindrical coordinates for Newtonian and power-law liquids. Dimensionless average velocity profiles around eccentric dies are provided to help plastic pipe engineers determine the needed eccentricity. In curved hose manufacture, the die centerpiece is made eccentric to cause curvature. Dimensionless radii of curvature are plotted to help curved hose manufacturers select proper die eccentricity.

Tuesday 4:00 Diplomat/Ambassador GP6

Mechanics of two rigid spheres falling co-linearly in a Bingham material
Benjamin T. Liu¹, Susan J. Muller¹, and Morton M. Denn²
¹Chemical Engineering, University of California, Berkeley, Berkeley, CA 94720; ²Benjamin Levich Institute for Physico-Chemical Hydrodynamics, City College of the City University of New York, New York, NY 10031

We examine the interaction between two rigid spheres falling co-linearly in a Bingham material. The effects of varying the Bingham number and the distance between the spheres are investigated using the penalty finite-element method and a regularized constitutive model. The range of interaction between the two spheres is found to be larger that that estimated from prior single-sphere calculations. The present study shows a drag reduction of up to 10% in the regime where the spheres are predicted to have no interaction. Methods for locating the yield surface are discussed.

Tuesday 4:25 Diplomat/Ambassador GP7

Rheological characterization of complex ABS/PC blends
Ruifeng Liang and Rakesh K. Gupta
Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506-6102

Acrylonitrile-Butadiene-Styrene (ABS), Polycarbonate (PC), and their alloys are an important class of engineering plastics widely used in applications such as computer and electronic housings. PC is a homogeneous polymer while ABS is a heterogeneous material where the rubber phase (grafted PB) is dispersed in the plastics phase (SAN). Blends of ABS with a high molecular weight PC were found to exhibit very complicated rheological behavior. In this paper, the rheology of ABS/PC blends at 5 different compositions, namely, 15%, 30%, 50%, 70, 85% by weight of ABS content was investigated. The blends were prepared in a twin screw extruder at an optimized temperature profile for each composition. The responses of these blends in steady shear, oscillatory shear, and step shear rate were measured on a Rheometrics RMS800 rheometer with a parallel geometry at 2250C. Results demonstrated that ABS is more shear-thinning than PC, and the blends behave similarly to ABS rather than to PC. However, a wave-like viscosity vs. composition curve is found as the ABS content in the blend increases, showing two minima (even lower than pure ABS) at (15%, 50%) and two maxima at (30%, 85%). The dynamic viscosity data also show the same characteristics. Another unusual observation is made from dynamic storage modulus data, which reveal that the blends at 70% and 85% ABS content have a higher G’ and smaller loss tangent than pure ABS, indicating an elasticity enhancement effect. Loss tangent is found to be less sensitive than dynamic moduli themselves to the blend preparation conditions. These results are further correlated to the tensile and impact properties of the blends. The effect of temperature, time and strain history and the flow behavior in step rate were also studied, and these are explained.
Temperature monitoring of capillary rheometry

Anthony J. Bur and Hubert Lobo

1Polymers Division, NIST, Gaithersburg, MD 20899-8542; 2Datapoint Labs, Ithaca, NY 14850

The temperature of the extrudate from a capillary rheometer was measured using a method based on fluorescence spectroscopy. This method requires that a fluorescent dye is mixed with the resin, but this is done at dopant concentrations, less than $10^{-6}$ mass fraction of dye in the polymer. At this level of doping, the dye is soluble in the resin at the elevated temperature of the experiment, and its presence has no effect on the rheological properties of the resin. Temperature is obtained from the fluorescence spectrum by correlating changes in the spectrum shape with temperature. Using a confocal fiber optic sensor design, excitation light is focused onto a small region (0.1 mm$^3$) of the extrudate stream of a 1 mm diameter capillary. Using polyethylene, temperature measurements were carried out over shear rates ranging from 10 s$^{-1}$ to 10,000 s$^{-1}$. At the highest shear rates, we found that effects due to shear heating caused the temperature to increase by 25 °C over the set point of the experiment. The results indicate that significant corrections to the viscosity values obtained at high shear rates must be made.
Wednesday Morning

Symposium PL
Plenary Lectures
Sponsored by a generous contribution from NIST Polymers Division

Wednesday 8:30 Crystal Ballroom
PL3

Microrheology of DNA near surfaces
Ronald G. Larson, Lei Li, and Manish Chopra
Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136

Recent advances in single-molecule imaging methods applied to DNA molecules in flow (Smith and Chu 1998), as well as advances in computer speed have allowed detailed comparisons to be made between observed and predicted behavior of polymeric DNA molecules in simple flows, such as shear and uniaxial extension (Larson et al. 1999; Hur et al. 2000). These comparisons have shown that conformations and rheology of DNA molecules in bulk solution can be predicted with high accuracy by Brownian dynamics simulations using bead-spring or bead-rod course-grained models for DNA. A logical next step is to extend these experimental and computational methods to confined flows, where polymers interact with surfaces. Such flows are of increasing interest because of their importance in the development of microfluidic devices for processing of DNA and other large molecules for genomics, bio-assays, combinatorial polymer science, and other applications. Here using single-molecule experiments and Brownian dynamics simulations we will consider the simple case of isolated DNA molecules near adsorbing and non-adsorbing walls in the presence of a simple shearing flow or in an evaporating droplet. Large deviations are observed between predicted and measured DNA configurations, both near non-adsorbing silica surfaces and when bound to treated silica during flow. The steps required to resolve these differences will be discussed.


Symposium CA
Polymers With Complex Architecture
Organizers: Faith Morrison and Patrick T. Mather

Wednesday 9:45 Cabinet
CA1

Rheological properties of dendritically branched polystyrenes
John R. Dorgan, Dimitris Vlassopoulos, and Dan M. Knauss
Chemical Engineering Department, Colorado School of Mines, Golden, CO 80401; Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete 71110, Greece; Chemistry Department, Colorado School of Mines, Golden, CO 80401

The rheological properties of a novel series of dendritically branched polystyrenes are reported. A new chemistry allows control of molecular architecture to produce dendritically branched materials having different molecular weights but possessing the same generational number.[1] That is, the molecular architecture is very similar to the so-called Cayley tree. A series of samples in which the molecular weight varies from 70,000 to 1,070,000 (g/mol) is studied. Entanglements are evident only in the highest molecular weight sample. Remarkably, this implies that polystyrenes having a molecular weight of 740,000 (g/mol) remain unentangled. Melt dynamics are complex;
exhibited behavior encompasses aspects of both classical Rouse-Zimm response and the power-law behavior associated with gelling [2] or fractal [3] systems. Zero shear viscosities and the normalized longest relaxation times correlate better with the hydrodynamic radius than with either total or span molecular weights. A simple model incorporating a polydispersity of longest relaxation times into the Rouse and Zimm models is proposed. Fractal and spectral dimensions, characterizing the internal polymer structure, are determined from the data by applying theoretical considerations.[3] An understanding of the detailed nature of the internal molecular structure is sought. Relative viscosities are measured as a function of concentration. Through a comparison with results for star architectures, it is possible to characterize the polymer-polymer interaction. These combined findings provide some insight into the structure and dynamics of these unique materials.

Rheo-optical investigation of star and hyperbranched polystyrene melts: Role of architecture
Rangaramanujam M. Kannan¹, Semen B. Kharchenko¹, Jeff Cernohous², and Shivshankar Venkataramani²
¹Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202; ²3M Corporate Research Laboratories, St. Paul, MN

With the increase in sophisticated synthesis methods, it appears that polymer architecture may be a tunable property. Therefore, the role of architecture on the rheological and processing properties has received renewed attention, mainly due to dendrimer synthesis and metallocene-catalyst technology. Linear polymers and hyperbranched polymers represent two ends of branching complexity. Some previous studies have suggested that hyperbranched polymers may behave like unentangled polymers, while others have suggested that they may behave like soft-colloids. In an effort to compare the response of linear and hyperbranched polymers, we have synthesized star-like hyperbranched polystyrenes (HBPS) of varying arm length and number of arms. Rheological and rheo-optical properties of the hyper-branched polymers are compared with those of linear and symmetric star polystyrenes. Our results suggest that the flow behavior of HBPS is significantly different from the linear polymers: (a) HBPS shows non-terminal behavior in the low-frequency rheological response; (b) When the stress-optic rule (SOR) holds, the stress-optic coefficient of the HBPS is much lower than those of analogous linear polymers; (c) When the branch density is high, and the branch length is sufficiently low, the SOR fails for these homopolymer melts. The significant increase in the birefringence for a given amount of stress in the low-frequency region suggests that there may be a soft-core in these materials due to preferential orientation of parts of chains near the center. The predominantly elastic response of the soft structures may be responsible for the enhanced birefringence. Our results show that these materials may exhibit both polymeric and soft-colloidal nature. Blends of the hyperbranched and linear PS appear to be partially miscible, with the 'elastic' core contributions to flow properties diminishing with the addition of linear chains.

The molecular rheology of hyperbranched architectures
Anand T. Lee and Anthony J. McHugh
Chemical Engineering, University of Illinois, Urbana, IL 61801

A goal of our experimental and rheological modeling studies of hyperbranched polymers is to isolate the effects of molecular architecture from those of molecular weight and concentration. To achieve this, a series of constant molecular weight systems with varying degrees of branching have been studied. Dilute solution calculations are performed using Nonequilibrium Brownian Dynamics (NEBD) of freely- draining trumbbell-bead-spring models. Model predictions are in close agreement with experiment, most notably in exhibiting a sharp rise in the zero-shear viscosity when the mole fraction of linear units exceeds 0.8. A linear relationship between the viscosity and the average distance between branch points is also observed, in accord with experimental observations. Rheological properties in the entangled melt state are predicted utilizing a variation of the recently proposed Blackwell-Harlen-McLeish model for tree-like polymer melts. A sharp transition in the viscosity of the constant molecular weight systems is observed for mole fractions of linear AB units on the order of 0.8, even in the entangled state. The melt rheology is also modeled using the simpler "multi-mode pom-pom" approach and the effects of molecular architecture on the various modes are investigated. In the semi-dilute regime, experimental studies indicate that the zero-shear viscosity scales with the concentration and intrinsic viscosity, independent of the architecture. An empirical expression is proposed for the viscosity-concentration scaling behavior of these hyperbranched systems in the overlapped state.
Temperature and Hencky strain shifting of convergent flow measured effective elongational viscosity

John R. Collier, Simion Petrovan, and Parag Patil
Chemical Engineering Department, The University of Tennessee, Knoxville, TN 37996-2200

Effective elongational viscosity data on a series of polyolefins as a function of temperature are shifted to a reference temperature using the approach for shifting shearing viscosity data. The temperature shift factors are obtained from complex and capillary shear rheology and are the same factors used for shifting the shear rheology. A Carreau rheological model was used to determine the zero shear rate viscosity at different temperature and an Arrhenius expression was used to determine the temperature shift factors. The same shift factors are shown to produce separate master curves for shear and elongational rheology at reference temperatures. The commercial grades of polyolefins studied include extrusion and melt blowing grades of polypropylene, and metallocene and conventional catalyzed low density, linear low density and high density polyethylene materials.

Effective elongational viscosity data on the same series of polyolefins as a function of Hencky strain are shifted to a reference Hencky strain using an approach similar to that used for temperature shifting shearing viscosity data. The basis of this shifting is the order that develops, i.e. the decrease in entropy that occurs, during forced flow through semi-hyperbolically convergent dies. The entropy decrease is proportional to the "orientational contribution" to the effective elongational viscosity. The Hencky strain shift factors are obtained from the convergent flow effective elongational rheology, and the complex and capillary shear rheology. The combination of the temperature shift factors and the Hencky strain shift factors in this paper enable the creation of master curves for the effective elongational rheology.

The breakup of free jets of dilute polymer solutions

Brian G. Price, David S. Ross, and Christopher J. Kloxin
Eastman Kodak Company, Rochester, NY 14650

The breakup behavior of microscopic free jets of dilute polymer solutions is studied by stroboscopic optical technique and is found to be well-described by a one-dimensional model. The capillary instability is triggered by small amplitude velocity disturbance and breakup behavior is quantified by the minimum radius of the jet as a function of time. The model dilute polymer solutions exhibit the effects of increased extensional viscosity at moderate strain rates, i.e. a renormalized minimum radius trajectory. At higher strain rates (exceeding 10^6 s^-1), the solutions exhibit a dramatic kink in the trajectory, displacing the ultimate breakup time considerably.

Stress and birefringence measurements in non-homogeneous transient uniaxial extensional rheometry

Jonathan P. Rothstein¹, Yong L. Joo², Gareth H. McKinley³, Robert C. Armstrong², and Robert A. Brown²

¹Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003; ²School of Chemical Engineering, Cornell University, Ithaca, NY 14850; ³Dept. Mechanical Engineering, M.I.T., Cambridge, MA 02139

In order to develop physically-consistent constitutive models capable of predicting the behavior of polymeric liquids in complex flows, one must first understand the behavior of these elastic fluids in rapid transient extension. It is believed that the stress-conformation hysteresis recently observed both numerically and experimentally in homogeneous uniaxial elongation flows may explain the enhanced values of pressure drop and viscoelastic that are
measured in prototypical processing flows with mixed kinematics. To investigate this hypothesis, the strain rate profile imposed on a cylindrical fluid sample in a filament stretching rheometer is modified to reproduce the extensional flow along the centerline upstream of a 4:1:4 axisymmetric contraction-expansion. Using the filament stretching device allows us to simultaneously measure the evolution of the tensile stress and the conformation of polymer chains in a nonhomogeneous extensional flow over a wide range of Deborah numbers. For strain rate profiles corresponding to $De<0.5$, little polymer stretch is generated and no hysteresis is observed. At $De=0.5$, an extremely weak hysteresis loop is observed and the associated integral representing the dissipative energy loss per unit volume is minimal. As the Deborah number is increased, the stress, conformation and dissipative energy loss all increase monotonically. The onset of dissipative energy loss for a strain rate profile of $De=0.5$ directly correlates with the development of the enhanced pressure drop observed in axisymmetric contraction-expansions. The adaptive length-scale model of Ghosh [2001], which incorporates a time-evolving finite extensibility parameter into the FENE model, is capable of predicting a stress-conformation hysteresis in rapid stretching flows. This adaptive length-scale model is used to numerically simulate the same strain rate profiles used in our experiments. The resulting hysteresis loops and dissipative energy loss are found to be in good qualitative agreement with the experiments.

Wednesday 11:00 Old Georgetown SM11
Jet break up of viscoelastic solutions using forced disturbances
Yenny Christanti and Lynn M. Walker
Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15232

We are investigating the relationship between viscoelasticity and drop formation from Rayleigh break up of a laminar jet. For Newtonian fluids, the jet break up is influenced by the bulk properties of the fluid, namely viscosity, surface tension, and density. The addition of highly extensible polymer molecules changes the rheology of the bulk fluid influencing interfacial break up. Here we quantify the capillary break up of well-characterized dilute polymer solutions due to forced disturbance.

Previous studies show that the formation of a beads-on-string structure at the last stage of break up is a characteristic of extensional-hardening fluids. We found the draining rate of fluid from the filaments into the beads to be constant for a given fluid. The relaxation times of the fluids were estimated from the measured extensional rates. We probe the effect of the fluid relaxation time as well as the applied disturbance frequency and amplitude on the drop formation. The results show that viscoelasticity suppresses the formation satellite drops at small wavelength to jet diameter ratios. Increasing the fluid relaxation time results in the broadening of the satellite-free region. We also found that decreasing the initial jet diameter enhances the effects of viscoelasticity on break up.

Wednesday 11:25 Old Georgetown SM12
The effects of fluid elasticity on drop formation
Justin J. Cooper-White, Jill E. Fagan, and David V. Boger
Chemical Engineering, The University of Melbourne, Melbourne, Victoria 3010, Australia

The effect of fluid elasticity on drop dynamics during drop formation at a nozzle has been investigated using a set of constant low viscosity Boger fluids, and compared directly with an equivalent Newtonian glycerol/water solution. All solutions had the same shear viscosity ($\sim 6$ mPa.s), equilibrium surface tension, and density, but differed greatly in elasticity. Inertial, viscous and capillary forces are balanced in the early stages of drop formation, with inertia in cohorts with capillarity finally perpetuating rapid necking of the drop. It was found that the early stages of drop formation were the same for all solutions, regardless of differences in elasticity, up to the establishment of two ‘pinch’ regions within the neck. The radius of the neck was found to scale linearly with time prior to the onset of these ‘pinch’ regions, as predicted by Brenner et al. (1996) for an inertial flow of a Newtonian fluid during drop formation. This behaviour suggests that, contrary to observations made with high viscosity elastic fluids, in these low viscosity elastic fluids, there is no contribution of elastic stresses prior to the approach of break-up or the critical ‘pinch’ region. Once the two distinct ‘pinch’ regions had formed at either end of this neck of fluid, rapid rupture occurred at the ‘pinch’ nearest the drop for the Newtonian low viscosity solution. However, in the case of the elastic solutions, these two ‘pinch’ regions were sustained and the neck of fluid in-between the ‘pinch’ points thereafter formed near axisymmetric cylindrical filaments in these high molecular weight solutions. The Rouse/Zimm relaxation time for these fluids was found to be proportional to the lag time, $t_l$, prior to break-off of the elastic solution behind a reference Newtonian fluid, or the limiting drop elongation length, $L_d$. We discuss the possibility of
elucidating unknown fluid properties of complex low viscosity fluids, such as the transient and steady state extensional viscosity, from these simple drop formation experiments.

**Symposium TS**

**Two Phase Systems: Emulsions, Blends and Suspensions**

Organizers: Kalman B. Migler and Jan Vermant

**Wednesday 9:45** Judiciary TS1

**Polymer bicontinuous microemulsions under shear**

Timothy P. Lodge¹, Kasiraman Krishnan², Frank S. Bates³, and Wesley R. Burghardt⁴

¹Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431; ²Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN; ³Department of Chemical Engineering, Northwestern University, Evanston, IL

Appropriate mixtures of homopolymer A, homopolymer B, and an AB diblock copolymer form equilibrium bicontinuous microemulsions, with the structural lengthscale in the range 50 - 200 nm. Although formally analogous to oil/water/surfactant microemulsions, the polymeric versions differ in important respects. For example, the symmetry of the A/AB and B/AB interactions renders the microemulsion stable over much wider temperature intervals. Furthermore, the relatively high viscosities of the components brings the structural relaxation times well into the experimentally convenient range. We have investigated the effect of shear flow on a polymeric bicontinuous microemulsion in detail, using rheology, neutron scattering, x-ray scattering, light scattering, and optical microscopy. The microemulsion consists of a ternary blend of poly(ethyl ethylene) (PEE), poly(dimethyl siloxane) (PDMS) and the diblock copolymer PEE-PDMS. Four distinct regimes of behavior emerge as a function of shear rate. At low shear rates (regime I) the system is Newtonian, whereas at intermediate shear rates (regime II) the microemulsion structure develops anisotropy, which leads to shear thinning. When the shear rate is further increased, there is an abrupt breakdown of the bicontinuous structure, resulting in a flow-induced phase separation (regime III). In this interval the shear stress is almost independent of shear rate, and light scattering and microscopy indicate the formation of a streak-like pattern. We speculate that this corresponds to three-phase coexistence, which would also occur at equilibrium if a small amount of block copolymer were removed. Upon further increase of shear rate (regime IV), the system behaves like an immiscible binary blend with the block copolymer playing no significant role; the stress increases strongly with shear rate. Comparisons between this behavior and the response of other complex fluids, including polymer solutions, polymer blends, and wormlike micelles, will be drawn.

**Wednesday 10:35** Judiciary TS2

**Drop dynamics under large-amplitude oscillatory shear flow**

Riccardo Cavallo¹, Stefano Guido¹, Danilo Bogetti², and Pier Luca Maffettone²

¹Dipartimento di Ingegneria Chimica, Università Federico II, NAPOLI 80125, Italy; ²Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino 10129, Italy

The dynamics of a single Newtonian drop in an immiscible Newtonian liquid under large-amplitude oscillatory shear flow is studied. The drop is buoyancy free, and the viscosity ratio is above criticality. Experiments are carried out in a parallel plane apparatus equipped with video optical microscopy. The drop orientation and the two principal axes within the shearing plane are measured by image analysis technique. Experimental observations are compared with the Maffettone-Minale model. Depending on the imposed frequency, different responses are found. At high frequencies, the principal axes response is quasi-sinusoidal in the range of amplitudes investigated. On the other hand, at low frequencies, the response deviates progressively from a sinusoidal wave as the amplitude increases. Namely, multi-peaked evolutions are observed. The model predictions well compare with experimental results.
Wednesday  11:00  Judiciary

**Droplet deformation and breakup in mixed flow fields**

*Kathleen Feigl*¹, *Peter Fischer*², *Stefan F. Kaufmann*², *Michael Loewenberg*³, and *Erich Windhab*²

¹Department of Mathematical Sciences, Michigan Technological University, Houghton, MI 49931; ²Lab of Food Process Engineering, Swiss Federal Institute of Technology, Zurich CH-8092, Switzerland; ³Department of Chemical Engineering, Yale University, New Haven, CT 06520

We investigate numerically and experimentally the deformation and breakup behavior of liquid droplets in a fluid-fluid multiphase system when the system experiences a mixed flow field. Under the assumptions of Newtonian fluid phases, negligible inertial effects and constant interfacial tension, the deformation and breakup behavior of a droplet in steady linear shear flow and extensional flow have been investigated extensively. In industrial dispersing processes, however, the flow field is a mixture of shear and elongational flow. Moreover, a droplet in such a flow experiences transient rates of strain as it moves through the flow field. In order to understand better the relative efficiency of dispersing processes, we investigate the deformation behavior of a single droplet as it moves along a particle path in a mixed flow field. We consider a rotor-stator apparatus used for the processing of highly viscous systems and take the annular gap flow between two eccentric cylinders as one idealization of such a process flow that produces transient shear rates and relatively small elongation rates. In the numerical investigation, a boundary integral method is used to calculate the droplet deformation where the particle paths and velocity gradients are determined from a calculated flow field. Complementary experiments are performed in flow cells that allow for the imposition of desired flow fields. The droplet is visually recorded by a CCD-camera as it moves in the flow field and its deformation is determined via image analysis. Comparisons are made between experiments and simulations. We discuss the effect of processing parameters, such as geometry and deformation rates, and the effect of fluid parameters, such as the viscosity ratio, on drop breakup. We find, for example, that a small change in geometry alone improves the dispersing ability of the eccentric cylinders due to the transient shear rates felt by the drop.

Wednesday  11:25  Judiciary

**Complex flows of concentrated emulsions**

*Nina C. Shapley*¹, *Marcos A. D'avila*¹, *Jeffrey H. Walton*², *Stephanie R. Dungan*¹, *Ronald J. Phillips*¹, and *Robert L. Powell*¹

¹Chemical Engineering and Materials Science, University of California, Davis, CA 95616; ²NMR Facility, University of California, Davis, CA 95616

We use nuclear magnetic resonance imaging (NMRI) to investigate velocity profiles in both homogeneous and nonhomogeneous, concentrated, oil-in-water emulsions. The emulsions undergo shear flow generated in a horizontal, wide-gap concentric cylinders geometry. The NMRI technique allows us to probe droplet concentration and velocity profiles noninvasively and in situ within a flowing, concentrated emulsion of isooctane and water stabilized with nonionic surfactant. We measure velocity profiles by using two NMRI methods while varying emulsion and flow parameters. The time-of-flight method provides direct visualization of steady-state or transient flows, and the phase encoding method yields maps of multiple velocity components at steady state.

We have observed recirculating flow in the oil-rich layer of density-separated emulsions, which may lead to the observed "diffusive" rather than convective mixing behavior in slow shear flows of these nonhomogeneous emulsions. In addition, we have observed partially counter-rotating flows in homogeneous, concentrated emulsions when the velocity of the outer cylinder is sufficiently low. Above a critical velocity, the emulsion co-rotates with the outer cylinder. At slower rotation speeds, however, the flow profile qualitatively changes to exhibit a partially counter-rotating pattern. At the outer wall of the device, the emulsion moves in the direction of the rotating cylinder, while near the inner, stationary cylinder, the flow moves in the opposite direction. Our aim is to determine key dimensionless groups that govern transitions between co-rotating and counter-rotating velocity profiles. To our knowledge, such transitions have not been reported previously. We believe that this phenomenon is driven by buoyancy effects, and are currently performing additional experiments and modeling to elucidate the underlying physics.
Field-induced gelation, yield stress, and fragility of an electrorheological suspension
Byung D. Chin and H. Henning Winter
*University of Massachusetts, Amherst, MA*

We studied model electro-rheological suspensions (ERS) at low field strength near the threshold for the liquid-to-solid transition. Upon application of the electric field, dynamic moduli $G'$, $G''$ grow by orders of magnitude and evolve in a rheological pattern which is otherwise typical for gelation of network polymers (random chemical or physical gelation). At the gel point, which is reached already at very low field strength ($30\sim60V/mm$), the slow dynamics is governed by power-law relaxation. The percolating particle structure is still very fragile and can be broken by the imposition of low stress. For inducing a finite yield stress, the field strength needs to be increased further until the long-range electrostatic interaction generates string-like particle alignments (and then columns) which become clearly visible under the optical microscope. The ERS was probed dynamically at low frequencies where the transition is most pronounced, and also in steady shear where the rate of structure formation equals the rate of internal breaking.

Field-aided manufacturing of polymer composites with anisotropic structure
Geunhyung Kim, Torrey R. Filanc-Bowen, Tim A. Osswald, Lih-Sheng Turng, and Yuri M. Shkel
*Mechanical Engineering and Polymer Engineering Center, University of Wisconsin-Madison, Madison, WI 53706*

Solid composites with uniaxial anisotropy are prepared by arranging suspended particles with an electrical field during the processing stage of the polymer. Such composites possess unique mechanical, thermal and electrical properties. Because of they electric field--controllable mechanical response such materials are often called *smart* or *controllable* materials. These polymer composites are made under various electrical field magnitudes, suspending particle sizes, particle compositions and the curing procedures. Resulting anisotropic materials were characterized by a number of mechanical, electrical and optical methods. Obtained data were compared with same measurements conducted on isotropic systems of similar compositions.

In this presentation we will discuss a dramatic effect of the structure anisotropy on mechanical, electrical and thermal properties of polymer composites. One of our primary interests includes developing new *controllable* materials. We will present data showing strong electroactive response of anisotropic composites, which makes them feasible for various sensing and transducer applications.

A constitutive theory for acicular ferromagnetic dispersions
Anand S. Bhandar and John M. Wiest
*Chemical Engineering, University of Alabama, Tuscaloosa, AL 35487-0203*

A constitutive theory for dispersions of acicular ferromagnetic particles has been developed. The theory models the magnetic particles as rigid dumbbells dispersed in a solvent, and the effects of Brownian motion, anisotropic hydrodynamic drag, steric forces (in the form of a Maier-Saupe potential), and - most importantly -magnetic interactions (via a mean-field potential) are included. The states of order in the dispersion are described in terms of an orientational order parameter $S$ and an average alignment parameter $J$; the latter is introduced because the magnetic particles have distinguishable polarity as a result of their magnetic moments. A transition from isotropic to nematic phases at equilibrium is predicted. In addition, multiple nematic phases: both prolate and oblate - are predicted in the presence of steady shear flow and an external magnetic field parallel to the flow direction. The effects of increasing magnetic interparticle interactions and particle aspect ratio are also presented. Material
functions for shear flow have been determined, and comparisons with viscosity data for metal particle dispersions show very good agreement.

Wednesday 11:00 Diplomat/Ambassador GP12

Influence of the chainlength distribution on the magnetorheological properties of inverse ferro-fluids

Dirk Van den Ende and Jorrit Mellema
Dept of Applied Physics, University of Twente, Enschede 7500 AE, The Netherlands

We present a colloidal model system comprising monodisperse silica spheres suspended in a magnetic fluid or ferrofluid. The application of a magnetic field induces a dipolar interaction between the silica particles, resulting in the formation of chainlike aggregates. At the same time the mechanical behavior changes from liquid- to solid like. Due to the monodispersity of the silica particles our ‘inverse’ ferrofluid can serve as a model system to study the magnetorheological effects. We measured linear viscoelasticity, yield stress and viscosity in the presence of a magnetic field as a function of particle radius, volume fraction and magnetic field strength, with a magnetic field along the gradient direction of the shear flow. The results show a strong size dependence. We explain our measurements using the concept of particle chains whose length varies with the (radius dependent) interaction strength and particle concentration [M.A. Osipov, Phys. Rev. E 54, 2597 (1996)]. The transition from liquid- to solid like behavior is observed when the average chain length exceeds the gap size in our measuring geometry. As soon as gap spanning chains are formed the size dependence vanishes, which can also be deduced from simple scaling arguments. The measured rheological behaviour is compared with model calculations. Qualitatively good agreement between theory and experiment is found. Quantitatively both the yield stress and the linear viscoelastic measurements are well described by the model calculations. Also the low shear plateau of the flow curves, typically for low field strengths, small particles and/or low concentrations, is well described. However, the calculated plastic behavior, typically for high field strengths and/or high concentrations, is only in agreement with the measurements if one shifts the calculated curve over one order of magnitude towards lower rates of shear. This indicates that the structure of the dispersion under flow is not yet well understood.

Wednesday 11:25 Diplomat/Ambassador GP13

Magneto-sweep: A method to characterize magneto rheological fluids

Joerg Laeuger, Klaus Wollny, and Siegfried Huck
Physica Messtechnik GmbH, Stuttgart D-70567, Germany

Magneto-rheological Fluids (MRF) are complex suspensions containing particles which can be magnetized. The rheological behavior of MRF is changing dramatically from a liquid to a solid state by increasing the applied external magnetic field. Up until recent years, however, industrial application was unsatisfactory due to the poor quality of the available magnetic fluids. The introduction of Nano MRF containing rather small particles has solved sedimentation problems making MRF more attractive for commercial applications again and drawing more research interest onto the properties of MRF. A new magneto-rheology chamber was constructed which is available for any commercial rheometer of the Physica MCR line. It allows a simultaneous software controlled setting of the magnetic field strength and the use of all possible rheological test modes of the rheometer. In the past mostly flow curves based on purely rotational measurements have been used to investigate the rheological behavior of MRFs thus giving only limited information. A measuring method is introduced which is based on oscillatory measurements and allows an exact determination of a substance's visco-elastic properties as a function of the magnetic field strength. An oscillation measurement with constant amplitude and constant frequency was performed while changing the magnetic field strength in a logarithmic ramp (magneto-sweep). On a typical MRF two significant transition points are observed which distinguish three regions: 1. a slight viscosity decrease with increasing field strength at small magnetic flux densities; 2. a strong increase in the storage modulus with increasing field strength at medium magnetic flux densities; 3. a maximum in the loss modulus is reached at high magnetic flux densities. These transitions can be directly correlated to corresponding changes in the material structure resulting from the increase in the magnetic flux density.
Wednesday Afternoon

Symposium CA
Polymers With Complex Architecture
Organizers: Faith Morrison and Patrick T. Mather

Wednesday 1:30 Cabinet CA6
Effect of solvent quality on the behavior of model HASE polymer solutions: A tracer microrheology study
Ahmed A. Abdala¹, Samiul Amin², Saad A. Khan², and John H. van Zanten²
¹Fiber and Polymer Sciences, North Carolina State University, Raleigh, NC 27606; ²Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7905

The effect of solvent quality on the viscoelastic properties of model hydrophobically modified alkali-soluble emulsion (HASE) polymer solutions has been investigated using diffusing wave spectroscopy (DWS) tracer microrheology. DWS is a multiple light scattering technique with which the viscoelastic properties of a suspending medium can be determined by tracking the mean squared displacement of spherical probe particles dispersed within the medium in question. The technique offers unique advantages over mechanical rheometry in that a much wider frequency range can be probed utilizing very small strains. The structure and dynamic response of the HASE polymer solutions is affected by the solvent (water/propylene glycol) composition. The effect of the structural modifications brought about by changes in the solvent composition on both long and short time dynamics will be discussed. Comparison with mechanical rheometry measurements will be presented and discussed in view of tracer microrheology and rheological measurements carried out on polyethylene oxide (PEO) solutions.

Wednesday 1:55 Cabinet CA7
Aspects of deformation in dynamically vulcanized EPDM/iPP thermoplastic elastomers
Alan J. Lesser
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003

Over the recent decades, a new class of thermoplastic elastomers consisting of ethylene propylene diene monomer (EPDM) and isotactic polypropylene (iPP) has been commercially introduced. The resulting product consists of polydispersed dynamically vulcanized EPDM particles embedded within a continuous phase of iPP. Recently modeling studies have focused on trying to explain the origins of elasticity in such complex systems. The majority of these studies have utilized numerical methods such as Finite Element etc. In this paper we phenomenologically characterize the deformation of this class of materials over a range of compositions involving changes in crosslink density and relative concentrations of EPDM to iPP. Additionally we introduce a simple analytical model estimate the deformational response of this class of materials. The model is described and evaluated in contrast to other studies and the experimental results. The limitations of the model together with other insights are also discussed.

Wednesday 2:20 Cabinet CA8
Rheology and morphology of rod/coil molecular composites
Jian Wu¹, Gyeong-Man Kim², and Patrick T. Mather²
¹Chemical Engineering, University of Connecticut, Storrs, CT 06269; ²Institute of Materials Science, Polymer Program, University of Connecticut, Storrs, CT 06269-3136

For more than twenty years, attempts have been pursued to create molecular composites wherein discrete reinforcement is achieved with molecular rods; however, progress has been hampered (until recently) by inevitable
phase separation in blends with insufficiently strong interchain interactions. We have investigated the rheological behavior and microstructure of new molecular composites, in which a reinforcing rigid-rod polymer of a sulfonic acid-pendant poly(p-phenylenebenzobisimidazole) (SPBI) is molecularly dispersed in a flexible coil polymer matrix of poly(2-vinylpyridine) (P2VP). Not surprisingly, the rheological behavior of the molecular composites differs dramatically from that of the neat P2VP matrix. While the master curves of P2VP show an expected terminal-rubber-transition sequence on increasing frequency, the molecular composites show a tendency to inhibit the terminal zone, featuring instead a low frequency rubbery response. Furthermore, increases in SPBI rigid-rod concentration yield higher values of the loss modulus; i.e., mechanical energy is more readily dissipated under dynamic loading. From our results, it is postulated that the interactions between the basic P2VP matrix and the acidic SPBI serve as physical crosslinks that cause an increase in the effective chain entanglement density. This postulation is tested by examining the response of our composites to creep of increasing stress. Transmission electron microscopy (TEM) of a molecular composite with 5 wt.% SPBI rigid-rod reveals a network structure wherein the rigid-rod "phase" is well dispersed in flexible coil matrix. Based on these experimental results, we propose a semi-quantitative relationship between rheological properties and molecular composite morphology.

Wednesday 2:45 Cabinet  
Low shear rate rheology of thermotropic liquid crystalline polymers  
Eric C. Scribben, Priya Rangarajan, and Donald G. Baird  
Center for Composite Materials and Structures, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060

Over twenty years ago Onogi and Asada proposed that a general three-region flow curve describes the viscosity behavior in many lyotropic liquid crystalline polymer (LCP) systems. At low rates a shear-thinning region indicates the presence of yield stress. Moderate rates bring on a Newtonian plateau that, at high rates, eventually leads to another shear thinning region. Creep, creep recovery, and dynamic oscillatory tests were performed with two commercial TLCPs: Vectra B950, a polyesteramide (60 Hydroxy Naphthoic Acid/ 20 Terephthalic Acid/ 20 Aminophenol), and Vectra A950 (Hydroxy Benzoic Acid/ 2,6 Hydroxy Napthoic Acid). The resulting flow curve is highly dependent on deformation and thermal history, especially at low shear rates. A yield stress was not observed for Vectra B950 but was for Vectra A950.

Symposium SR  
Solid Rheology From Glasses To Gels  
Organizers: Alan S. Wineman and Andre Lee

Wednesday 3:35 Cabinet  
Solid rheology of polymers: From networks to glasses  
Gregory B. McKenna  
Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121

The influence of NBS/NIST in the field of Rheology has a long and important history. My own experiences and the roots that they are built upon in studying the rheological response of solid polymers and nonlinear viscoelasticity make this clear. I was fortunate to benefit from a legacy that began with L.A. Wood and A. McPherson in the 1920's when I took over the rubber program in 1977. But, my work was also strongly influenced by Bernstein, Kearsley and Zapas-NBS legends of renown in the Rheology Society. But the links go further. In my work with Andre Kovacs in Strasbourg in the early 1980's, the tentacles of NBS were present, not only with my (then) youthful presence, but also because Kovacs had followed on the development of volume dilatometry pioneered by N. Bekkedahl (also of WWII rubber program fame) from NBS. Finally, in my latest works studying the physics of glasses, it is the fundamental data of J.E. McKinney on PVAc that contribute significantly to our understanding of the fragility response of glassy materials. In my presentation, I hope to show that our work on rheology of solids, from the strain energy density function of crosslinked rubber and swelling to the rejuvenation and nonlinear mechanics of polymeric glasses is supported by the shoulders we stand on-and many of those have the brand of NBS/NIST upon them.
Hierarchical aspects of yield and nonlinear deformation in rubber modified glassy polymers

Alan J. Lesser

Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003

Recent models that predict the macroscopic yield behavior of rubber modified glassy polymers presume a specific sequence of irreversible mechanisms during the deformation process. The most popular theories suggest that rubber particle cavitation or particle-matrix de-bonding initiates the yield process on the local scale, and this process is believed to occur at a critical hydrostatic stress. This is followed by local matrix yielding around the micro-cavity in the form of inelastic void growth until macroscopic yielding of the matrix is realized. This paper reports results of an experimental investigation whose aim is evaluate these processes on model systems over a range of controlled axi-symmetric loading conditions ranging between uni-axial compression and bi-axial tension. The process of irreversible deformation in the form of micro-damage that occurs on the micron scale is monitored in-situ during the test. This damage and its affect on the pseudo-yield behavior at the macroscopic scale is characterized over a range of stress states for three polymer systems. The micro-mechanisms of this damage are investigated and are discussed relative to the popular models that predict toughening in this class of polymer systems. The results suggest that new models are required to accurately predict the macroscopic yield behavior of this class of systems.

Stress optical behavior across the dynamic glass transition and prediction of residual birefringence in injection molded parts

Hee Hyun Lee¹, Young Bok Lee², Julia A. Kornfield¹, Tai Hun Kwon², and Kyunghwan Yoon³

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Rheo-optical properties of polystyrene, hydrogenated polystyrene and polycarbonate are investigated from the terminal and plateau regions, where the familiar stress-optic-rule holds, up to the high frequency, glassy regime. A shear geometry is used throughout this dynamic range to avoid complications associated with the Poisson ratio which varies in an unknown manner from 0.5 for the melt to 0.33 for the glass. The different molecular structures and chain dynamics of three polymers showed specific rheo-optical properties, respectively. A significant general feature is that the transition from the stress optic behavior characteristic of the melt to that characteristic of the glass occurs over a very wide dynamic range (6-8 decades). Reliable rheo-optical data encompassing this whole dynamic region are needed for prediction of residual stresses and birefringence in injection molded articles of precise optical products such as CDs, DVDs and various lenses. In such products, birefringence and residual stresses are of great importance because of optical performance and dimensional accuracy, respectively. We used the experimentally measured stress-optic properties in numerical simulations to predict residual stress and birefringence in injection molded articles.

Rheology of glass formation

Brian M. Erwin and Ralph H. Colby

Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802

The fragility of a glass is proportional to the apparent activation energy for viscosity at the glass transition temperature, \( T_g \). The apparent activation energy at \( T_g \) varies over a factor of ten range for different glass-forming liquids. Small apparent activation energies at \( T_g \) lead to the less fragile glass formers, such as GeO\(_2\). Many flexible polymers are at the other extreme with large apparent activation energies, leading to very fragile glass formers. The temperature dependence of viscosity near \( T_g \) will be reviewed in this talk. With polymers, there are general trends towards a reduction in fragility with decreasing chain length or the addition of bulky side groups. We shall rationalize these observations by considering the fact that these two chain modifications both increase the mobility of the polymer. The utility of a new equation for the temperature dependence of viscosity that directly incorporates fragility effects will be discussed in detail.
Dynamic fragility in polymers: A comparison in isobaric and isochoric conditions
Gregory B. McKenna and Dinghai Huang
Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121
The dynamic fragilities of six polymeric materials have been compared for isobaric (constant pressure) and isochoric (constant volume) conditions. Data were taken from the published literature for dynamic experiments performed at elevated pressures. Published Pressure-Volume-Temperature (PVT) data were then used to determine the dynamic response as a function of temperature for both the isochoric and isobaric conditions. It is found that the pressure and volume dependences of the dynamic fragility vary greatly among the polymers for which data were available. For poly(vinyl acetate) (PVAc) and poly(ethyl acrylate) (PEA), the dynamic fragility is independent of the pressure and specific volume and the isochoric and isobaric fragilities are almost the same. On the other hand for poly(vinyl chloride) (PVC), polystyrene (PS) and poly(methyl acrylate) (PMA), the dynamic fragility is sensitive to changes of pressure and volume and the isobaric behavior is more fragile than the isochoric behavior when referenced to the same glass formation points \( (P_g, V_g, T_g) \). It is also remarked that the signature Vogel-Fulcher temperature dependence of the dynamics is lost for the isochoric behavior of both PEA and PVC.

Viscoelastic properties of some inorganic glass-formers
Donald J. Plazek\(^1\), Sindee L. Simon\(^2\), and Kevin M. Bernatz\(^3\)
\(^1\)Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261; \(^2\)Chemical Engineering, Texas Tech University, Lubbock, TX 79409; \(^3\)Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261
The viscoelastic behavior of inorganic polymers and glass-formers has not been elucidated to the same extent as that of organic polymers. We therefore have investigated several inorganic glass formers above and below their glass temperatures, including boron trioxide and several compositions of As\(x\)Se\(1-x\) alloys. The behaviors of the inorganic glasses have been compared with a low molecular weight polystyrene in the hopes of answering several questions regarding the inorganic glasses. Of paramount interest is the question regarding the existence of molecular networks in both boron trioxide and selenium. Based on the viscoelastic behavior observed in these materials, it has been concluded that boron trioxide does not appear to have any long range coordinated molecular network while the arsenic selenides appear to contain structures with long range coordinated motion.

Development of an apparatus for the measurement of dynamic viscoelastic properties of rheologically complex materials at ultrasonic-frequency
Ilan Zeroni and Moshe Gottlieb
Chemical Engineering Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
Rheologically complex materials are often exposed to frequencies that are above the capabilities of mechanical rheometers. Time-temperature superposition is not always an option as a result of structural changes, phase transitions or other thermodynamic limitations. Yet, current technological applications create the need to determine the mechanical properties of these fluids at elevated frequencies.

The purpose of this work is to develop a reliable, accurate and relatively simple apparatus, capable of measuring the dynamic, viscoelastic properties of fluids at ultrasonic frequencies, i.e. 1-10 MHz, utilizing the inclined-incidence pulse wave-reflection technique. The material sample is placed on a fused quartz prism, creating an acoustic impedance discontinuity. Plane shear ultrasonic bursts are impinged upon this impedance discontinuity at an oblique angle, and are reflected. The pressure amplitude and the phase of the reflected waves are set by the acoustic impedance of the sample, which is directly related to its viscoelastic properties at that frequency. The signal is
filtered, digitized, and analyzed using a LabVIEW(r) algorithm developed in our lab. This development has made available the use of another method: ultrasonic spectroscopy. The measurements are taken under rigorous temperature control (±0.01 degree).

Results have been obtained for ink simulants and PDMS of varying molecular weight. These show that inks maintain a nearly constant viscosity with frequency. As for low molecular weight PDMS, it exhibits typical viscoelastic behavior at frequencies well beyond those accessible by mechanical rheometers. The values of the both shear modulus components, $G'$ and $G''$, of PDMS were found to be about 1 MPa at 10 MHz for all molecular weights, and rising slightly with molecular weight. An unusual relaxation behavior of the reflection-phase has been detected.

Wednesday 2:45 Old Georgetown SM16

**Direct numerical simulations of turbulent channel flow with polymers close to maximum drag reduction**

Piotr K. Ptasinski, Martien A. Hulsen, Bendiks J. Boersma, Frans T. Nieuwstadt, and Ben H. Van den Brule

*J.M. Burgerscentre for Fluid Dynamics, Delft University of Technology, Delft 2628 CB, The Netherlands*

We consider direct numerical simulations of drag reduction of a polymer solution in a turbulent channel flow. Contrary to most studies in the past, our simulations are performed under conditions close to the maximum drag reduction or Virk asymptote that corresponds with relatively high polymer concentrations. We have used the FENE-P model with a large extensional parameter, a large Weissenberg number and a shear thinning viscosity. The increase of the flow rate with respect to Newtonian flow at an equal wall shear stress is approximately 80%.

The simulations show an increase of the slope of the mean velocity profile close to the Virk asymptote. The turbulent (Reynolds) shear stress is strongly reduced compared to the Newtonian case. This is compensated by the introduction of a large polymer stress that is about 30% of the total shear stress. Furthermore, the polymer stress is a linear function of the distance from the wall. The polymers are primarily oriented in the direction of the flow and strongly stretched in the region near the wall, which corresponds with a large extensional viscosity.

Next the turbulent kinetic energy budgets will be presented, which show that the energy redistribution over the three coordinate directions is much smaller than for Newtonian flow. This corresponds with a decrease of the energy transfer from the streamwise direction to the other directions.

Finally the transfer from kinetic energy of the mean flow and of the turbulence to the elastic energy of the polymers and to viscous dissipation will be discussed.

Wednesday 3:35 Old Georgetown SM17

**Shear-enhanced crystallization of isotactic polypropylene: The role of long chains in crystallization kinetics and morphology development**

Motohiro Seki1, James P. Oberhauser2, Derek W. Thurman3, Julia A. Kornfield3, and Katsuhiko Takagi4

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The role of polymer chain length in shear-enhanced crystallization was studied by *in situ* rheo-optical measurements and *ex situ* microscopic observations. In order to elucidate the effect of long chains in the crystallization dynamics, we prepared model systems in which fractionated, high molecular weight isotactic polypropylene was blended with metallocene-based iPP of lower molecular weight. The long chain concentration was varied from zero to twice its overlap concentration ($c^*$). All blends showed accelerated crystallization kinetics with increasing wall shear stress $\sigma_w$. When the wall shear stress exceeded a critical value $\sigma_w^*$, the birefringence exhibited a non-linear dependence upon the long chain concentration from zero to twice its overlap concentration ($c^*$). All blends showed accelerated crystallization kinetics with increasing wall shear stress $\sigma_w$. When the wall shear stress exceeded a critical value $\sigma_w^*$, the birefringence exhibited a non-linear dependence upon the long chain concentration from zero to twice its overlap concentration ($c^*$). Also, quenched samples showed a typical skin-core morphology for wall shear stress above $\sigma_w^*$. The oriented skin possessed a typical "shish-kebab" structure, but the number density and thickness of the "shish" threads depended strongly on the concentration of the long chains, suggesting a link between long chains and the formation of point-like nuclei and their elaboration into threads.
Effect of pressure on the viscosity of polymer melts swollen with dissolved carbon dioxide
Joseph M. Smolinski, Charles W. Manke, and Esin Gulari
Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Dissolved carbon dioxide and other supercritical gases can greatly reduce the viscosity of molten polymers, leading to many promising applications of supercritical fluids in polymer processing. However, considerable pressure (~10 MPa) is required to achieve significant solubility of carbon dioxide in polymer melts at typical processing temperatures. Thus the effect of pressure on the viscosity of polymer-carbon dioxide mixtures plays an important role in the rheological behavior of these systems. Here, the viscosities of polystyrene and PMMA melts containing up to 5 wt% dissolved carbon dioxide are measured as functions of pressure in a sealed, high-pressure capillary rheometer. Like pure polymer melts, the viscosity of these polymer-gas mixtures are found to vary with the exponential of a pressure multiplied by an empirical constant b. In polymer-gas mixtures, however, the compressibility of the material varies with gas content, and systems with high gas contents are significantly more compressible than the pure polymer melt. These variations in compressibility with dissolved gas content lead to a corresponding variation in b, the coefficient of pressure dependence of viscosity. Values of b are reported as functions of composition for polystyrene and PMMA melts containing 0-5 wt% carbon dioxide at temperatures ranging from 150-180°C.

Plasticization with carbon dioxide to facilitate melt spinning of high acrylonitrile content copolymers
Michael J. Bortner and Donald G. Baird
Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24060

Carbon dioxide can be used as an environmentally benign plasticizer to facilitate melt spinning of traditionally solution spun polymers. An exemplary system of an acrylonitrile/methyl acrylate copolymer to produce carbon fiber precursors via melt spinning techniques comprises the thrust of the current study. Carbon fiber precursors are currently solution spun with the toxic solvent dimethyl formamide (DMF) to hinder a crosslinking reaction that renders the extrudate intractable. Plasticization with carbon dioxide facilitates melt spinning of the same materials below the crosslinking temperatures. Saturation (with CO₂) of various acrylonitrile content copolymers at multiple temperatures has been studied. DSC analysis indicates Tₐ reductions up to 40°C in plasticized feedstocks. Pressurized capillary rheometry verifies a substantial viscosity reduction, on the order of 50%. The WLF equation with universal constants gives a similar prediction for the viscosity reduction, and back calculation yields a 20°C processing temperature reduction. This would slow the kinetics of degradation sufficiently to allow melt spinning of such materials.

Shear enhanced concentration fluctuations in a polymer solution
Grant T. Templin and David J. Pine
Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106

Semi-dilute polymer solutions exhibit concentration fluctuations which are enhanced by shear flow, most strongly for theta solvents but also for good solvents. Light scattering was used to study the effect of shear flow on the structure of the concentration fluctuations. The structure factor was obtained for several shear rates while varying both concentration and temperature. A quantitative comparison has been made between experimental results and dynamical theories of shear enhanced concentration fluctuations. In order to make this comparison, important parameters to the theory were measured using standard rheological and light scattering techniques. Among the parameters measured were: the concentration dependence of the viscosity, normal stress, characteristic relaxation rates, and osmotic compressibility. Concentration fluctuation enhancement occurred only for a preferred range of length scales, which decreased with decreasing concentration. In addition, as the solvent quality increased with increasing temperature, the enhancement of fluctuations by shear was observed to diminish. Dynamic light scattering shows evidence of two distinct relaxation ranges with the slower of the two corresponding to the same time scale of rheological relaxation.
Local chain motion and macroscopic behaviour of poly(dimethyl siloxane)

R Ocone, V Arrighi, and S Gagliardi
Heriot-Watt University, Edinburgh, United Kingdom

Polymer motion is an area of intensive research, both experimentally and theoretically. Compared to low molecular weight liquids, polymer melts display unique viscoelastic properties. This behaviour is a direct consequence of the dynamic properties of long polymer chains. It is of great importance to establish links between microscopic dynamics and bulk properties in order to fully understand the flow behaviour of polymeric materials. Scattering studies may be particularly informative as they provide a detailed description of microscopic motion at the molecular level. The neutron wavelengths used in quasi-elastic neutron scattering experiments (~ 5 Å) are of similar magnitude to that of the polymer repeat unit. It follows that dynamic studies of polymer melts (at temperatures above the glass transition, Tg) using the technique of quasi-elastic neutron scattering probe the local motion of the polymer chains. The dynamic properties of long polymer chains are discussed in terms of the reptation model. This is based on the assumption that the motion of a polymer chain is confined within a tube of diameter dr and this restriction is a consequence of intermolecular entanglements with neighbouring molecules. For shorter chains (below the entanglement molecular weight) the bead-spring model proposed by Rouse well describes chain dynamics. At even shorter length scales, the chain structure and more local relaxation processes may come into play; deviations from the Rouse model are expected. We have investigated the dynamic incoherent structure factor, S(Q, w) as probed by quasi-elastic neutron scattering (QENS) of various poly(dimethyl siloxane) melts, as a function of molecular weight. The temperature dependence of the microscopic dynamics probed by QENS is compared to the rheological bulk properties.

Symposium TS
Two Phase Systems: Emulsions, Blends and Suspensions
Organizers: Kalman B. Migler and Jan Vermant

Shear-induced coalescence in compatibilized polymer blends
Paula Moldenaers, Sachin Velankar, and Peter Van Puyvelde
Department of Chemical Engineering, K.U. Leuven, Leuven 3001, Belgium

Compatibilizers are often added to a polymer blend to achieve a finer dispersion of droplets. The compatibilizer may either be added prior to mixing (physical compatibilization) or may be generated at the interface by a chemical reaction (reactive compatibilization). In many cases, the compatibilizer is believed to reduce the interfacial tension. The view that effects of compatibilization are entirely attributable to a decrease in interfacial tension has been challenged by several studies, pointing towards for instance coalescence suppression. In an attempt to clarify the dynamical effects of adding a compatibilizer to a blend, we will present rheological studies on an immiscible PIB/PDMS blend compatibilized with an unentangled PIB/PDMS diblock copolymer. Uncompatibilized PIB/PDMS blends have been studied extensively in the past. They are considered as experimentally convenient representatives for commercial polymer blends and are used here as a reference for the uncompatibilized blends. The effect of viscosity ratio on the coalescence behaviour of compatibilized blends is presented. In addition the amount of block copolymer has been varied from 0% to 10%. The linear dynamic moduli will be used to probe the coalescence as it occurs when the shear rate is reduced. The analysis focusses on dimensionless properties such as capillary number, relative viscosity and relative excess normal stress. This emphasis on dimensionless quantities, rather than on details of the droplet-matrix morphology, highlights effects not attributable to a simple decrease in interfacial tension and allows generalization beyond the specific system studied.
Droplet coalescence in polymer blends: The effects of droplet deformation and interface immobilization

Steven D. Hudson, Alex M. Jamieson, Brian E. Burkhart, Prasad V. Gopalkrishnan, Michael A. Rother, and Robert H. Davis

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The evolution of the droplet size distribution in immiscible fluid mixtures following well-specified shear histories is investigated by in situ videomicroscopy, allowing determination of the shear-induced coalescence efficiency $e$. At small capillary number $Ca$, $e$ is constant, whereas at larger values of $Ca$, $e$ decreases, in agreement with theory accounting for slight deformation of the droplets in close approach. Coalescence causes the drop size distribution to broaden, in general, but greater deformation of the larger droplets at high shear rates causes the droplet size distribution to remain narrow. The addition of block copolymer influences the coalescence behavior. When the droplets are small the effect of copolymer is also small. However, at larger sizes, the coalescence efficiency decreases abruptly. Strikingly, we find that this sudden decrease occurs much before droplet deformation becomes significant, indicating that although the amount of copolymer is insufficient to reduce the interfacial tension significantly, it effectively immobilizes the droplet interface. These experiments suggest that copolymer adsorption kinetics play an important role in the morphology control of polymer blends. In our experiments, the degree of adsorption of copolymer to the interface is determined from interfacial tension measurements. We are exploring the effect of interfacial thermodynamics and kinetics. The financial support of NSF grant CTS-9731502 and NASA Grant NAG3-2116 is gratefully acknowledged.

The effect of surfactants on drop deformation, collisions and breakup

Hua Zhou, Vittorio Cristini, John Lowengrub, and Christopher W. Macosko

Dept. of Chemical Eng. and Materials Sci., University of Minnesota, Minneapolis, MN; School of Math, University of Minnesota, Minneapolis, MN

The dynamics of deformable drops in viscous flows are investigated via numerical simulations. A novel adaptive finite-element/sharp-interface algorithm (Hooper et al. 2001) for three-dimensional simulations is used. Drop deformation is studied in the presence of a surfactant coating of the drop interface. Under these conditions, flow-driven surfactant redistribution induces Marangoni stresses at the interface that modify the hydrodynamics and thus affect the rheology of emulsions and polymer blends. The effects of the equation of state that relates the concentration of surfactant on the interface to the surface tension, and of diffusion and solubility of surfactant molecules are included in our model.

Results of simulations are presented that describe the effect of surfactants on the development of lamellar structures in emulsions, that form under strong-flow conditions (Wetzel & Tucker 2001; Cristini et al. 2001). More stable drop lamellae with larger interfacial area are predicted by our model, with respect to the clean-interface case, in agreement with recent experimental observations (Jeon & Macosko 2000). In addition, the feasibility of accurate simulations of drop collisions and breakup is demonstrated using our model, and preliminary results on the effects of surfactants on these phenomena are presented.

Melt rheology of polyphosphate glasses

Peter C. Guschl, Sunil B. Adalja, and Joshua Otaigbe

Material Science & Engineering, Iowa State University, Ames, IA 50014

The melt rheology of a low $T_g$ tin phosphate glass (Pglass) has been studied with oscillatory shear flow experiments to accelerate efforts to melt process the glass with different organic polymers. The frequency dependence of the complex viscosity of the Pglass is easily predicted by a modified Rouse model with two relaxation times. The complex viscosity of the glass at different temperatures and frequencies can be superimposed and described by the Arrhenius equation. At higher temperatures, the melt viscosity of the Pglass increased monotonically with time. This viscosity rise is thought to be due to sample crystallization. The Pglass was melt-mixed with two different
thermoplastic polymers (low density polyethylene and polystyrene) to produce unique hybrid materials with interesting microstructures.

Wednesday 3:35 Judiciary TS9
String formation in immiscible polymer blends
Jai A. Pathak and Kalman B. Migler
Polymers Division, NIST, Gaithersburg, MD 20899-8544

Our group has recently reported the occurrence of a droplet-string transition in immiscible polymer blends* when they are sheared under conditions where the gap width between the confining parallel plates approaches the characteristic dimensions of the dispersed droplets. In that study only one composition, 28% poly(dimethylsiloxane) (PDMS), was investigated in model immiscible blends of PDMS and polyisobutylene (PIB). Here we investigate the effect of blend composition on the droplet-string transition and we find a significant impact on the morphology. We observe that blends containing less than app. 20% PDMS do not form strings, but do spontaneously organize into coherent trains of droplets aligned in the flow direction. Currents efforts are focusing on elucidating the effect of composition (including blends rich in PDMS) on the kinetics of string formation and the dimensions of the morphologies obtained in these systems.


Wednesday 4:00 Judiciary TS10
The effect of a confinement on the kinetics of polymer threads and droplets in an immiscible matrix
Younggon Son and Kalman B. Migler
Polymers Division, NIST, Gaithersburg, MD 20899-8544

We investigate the stability of a polymer thread imbedded in a matrix in the regime where the diameter of the thread (d) is comparable to the height (H) of the matrix. We find three regimes as a function of H/d. For H/d > 2, the thread breaks up into droplets via a finite wavelength capillary instability as described by Rayleigh and Tomotika. As H/d decreases below approximately 2, the effects of the confinement are felt; the growth rate decreases dramatically, concomitant with an increase in the wavelength of the instability. In this regime, it was also observed that the growth is no longer symmetric, the growth rate parallel to the confining plates is greater than that perpendicular. The wavelength diverges at a critical value of H/d ~ 1.3. Below this value, the thread is stable with respect to the capillary instability. We explain the wavelength divergence through our observations that the hydrodynamic interaction of the thread with the wall suppresses growth in the direction of the wall, leading to an asymmetric thread. We consider the surface area of these asymmetric threads and show that as the asymmetry increases, the wavelength at which a sinusoidal fluctuation minimizes total surface area increases, until the critical wavelength diverges.

Wednesday 4:25 Judiciary TS11
Motion of a cylindrical viscoelastic drop immersed in planar flow of a Newtonian fluid
Krishnamurthy Jayaraman1, Douglas J. Backes2, and Bhaskar Patham1
1Department of Chemical Engineering, Michigan State University, East Lansing, MI 48824; 2Thiokol Corporation, Brigham City, UT

The motion of viscoelastic drops immersed in a Newtonian fluid and subjected to flow within a square array of cylinders (of 60% porosity) has been investigated experimentally. The Newtonian suspending fluid was chloroparaffin oil with a specific gravity of 1.19 and a viscosity of 0.109 Pa-s at 23°C while the viscoelastic drop fluid was a 0.3 wt % solution of polyacrylamide in a mixture of glycerol and water. The polymer solution has a closely matching specific gravity and a zero shear viscosity of 1.43 Pa-s at 23°C. This fluid was also evaluated by fiber spinning for extensional flow behavior and the transient extensional viscosity curves were used to estimate the extensibility parameter. A Newtonian mixture of glycerol and water was also used as a reference drop fluid. The drop is cylindrical with an aspect ratio (l/d) ranging from 2 to 12.5. The capillary number for mobilization of the viscoelastic drop is clearly higher than for the Newtonian drop because of the greater resistance to deformation in the viscoelastic drop. This is consistent with the calculations of Leal and coworkers. The velocity of the drop relative to the suspending fluid increases with aspect ratio at lower capillary numbers following the trend for
Newtonian drops. This trend is reversed at higher capillary numbers or correspondingly higher planar stretch rates. The drop relative velocity is also much more sensitive to aspect ratio at higher planar stretch rates. This trend is discussed in light of observed drop shapes in the mobilization process.

Wednesday 4:50 Judiciary

Two-fluid demixing theory predictions of stress-induced turbidity of polystyrene solutions in dioctylphthalate

Mario Minale and Kurt F. Wissbrun

1 Aerospace Engineering Department, Seconda Università di Napoli, Aversa, CE 81031, Italy;
2 Consultant, Summit, NJ 07901

Stress induced demixing of a polymer solution is predicted in the frame of a two fluid theory. Recently it has been shown that, even in rectilinear uniform shear flows, migration in an initially homogeneous polymer solution can generate a stratified morphology. Two layers can be identified, one with low polymer concentration and high shear rate, the other with high concentration and low shear rate. The two fluid theory was reformulated to be able to impose all the interface boundary conditions required. In the new formulation of the two fluid theory the individual stress of the single "fluids" can be isolated; this marks the main difference between the new formulation and the previous ones where the individual stresses were not recognisable.

This theory has now been applied to published data on solutions of polystyrene in dioctyl phthalate of Rangel-Nafaile et al. at one molecular weight at various temperatures, and to additional unpublished data at various molecular weights. The dependence of elastic compliance on concentration was approximated adequately by an appropriate equation that permitted the analytic differentiations and integrations required for the equations of the theory. The prediction of visual cloud point stresses at various temperatures were excellent within the concentration range over which the compliances had been fitted. The calculated demixing stresses were somewhat higher than those measured by extrapolation of photometric data to onset of turbidity, possibly because the onset correlates more closely to the occurrence of concentration fluctuations preceding demixing. It should be noted that the earlier kinetic theories that predict fluctuations but not demixing assumed a monotonic dependence of elasticity on concentration, contrary to theoretical and experimental results, and do not account for the light scattering observation of phase separation in shear flow.

Wednesday 5:15 Judiciary

Shear-induced coalescence of aqueous biopolymer mixtures by optical sectioning

Sergio Caserta, Marino Simeone, and Stefano Guido

Dipartimento di Ingegneria Chimica, Università di Napoli "Federico II", NAPOLI 80125, Italy

The flow behavior of food emulsions is the subject of many investigations, aimed at a rationale design of the processing routes to obtain the desired product microstructure. In this work, we focus on shear-induced coalescence of aqueous biopolymer mixtures by following the time evolution of the drop size distribution. The biopolymers investigated include Na-alginate, Na-caseinate, dextran and gelatin. The mixtures are sheared in a parallel plate apparatus and observations are carried out by video optical microscopy. The drop size distribution is measured as a function of time by optically sectioning the sample via 3D motorized scanning and digital image acquisition. Automated processing of a large number of images is performed by image analysis algorithms and the results are tested by statistical methods. The morphological results are compared to rheological measurements on the same mixtures in a controlled-stress rheometer. The case of a gelling phase has been also investigated.
Symposium LS  
Probes of Local Rheology and Structure  
Organizers: Thomas G. Mason and Alex J. Levine

**Wednesday 1:30 Diplomat/Ambassador LS1**  
**Dynamics and microrheology of biopolymers and membranes**  
Frederick C. MacKintosh  
*Division of Physics and Astronomy, Vrije Universiteit, Amsterdam NL-1081HV, The Netherlands*

New techniques have recently been developed to probe the rheological properties of such soft materials including polymer solutions and gels at the micrometer scale. This has permitted both rheological studies of very small samples and high frequencies. We describe some of the theoretical principles behind these techniques, as well as the origins of some of the unique dynamics of biopolymer systems in particular. We also discuss in detail the dynamics and response of biopolymer-membrane composites.

**Wednesday 1:55 Diplomat/Ambassador LS2**  
**Factors determining the microrheology of cytoskeletal networks**  
Scot C. Kuo, James L. McGrath, and Fay Peng  
*1Biomedical Engineering, Johns Hopkins University, Baltimore, MD 21205; 2Biomedical Engineering, University of Rochester, Rochester, NY 14642*

Microrheometric techniques, such as laser-tracking microrheology (LTM) hold great promise to measure the mechanical properties of biological materials and living cells under physiological conditions (Yamada et al., 2000 *Biophys. J.*, 78:1736-47). In phagocytosis, for example, cells use cytoskeleton to quickly engulf and ingest individual particles and bacteria. However, Schmidt et al. (2000 *Phys. Rev. E* 61:5646-53) claim that microrheometry significantly underestimates the macroscopic moduli of F-actin networks. Discovering an unrecognized variable, our recent work (McGrath et al., 2000 *Biophys. J.* 79:3258-66) found that the ability of a particle to bind F-actin affects the viscoelastic moduli it senses. Actin binding by probe particles is essential for microenvironments to reflect macroscopic properties induced by cross-linking. In contrast, non-binding particles ignore cross-linking of the network that increase macroscopic moduli ~400-fold. Electron microscopy shows no obvious heterogeneity to explain the aberrant behavior of non-binding particles. We suspect that a local depletion of cross-linking around non-binding particles explains their behavior.

To further understand the factors that affect microrheometry, we have used LTM and systematically varied the length scales, cross-linking density, and concentration of F-actin gels. Like Schmidt et al., we find that non-binding particles are insensitive to macroscopic properties; in contrast, actin-binding particles are faithful and surface chemistry dominates the mechanics of all microenvironments. Differences from surface chemistry disappear in the softest gels made of filaments severed with gelsolin. Overall, although one must be cautious, microrheometry can be accurate in measuring moduli of a biological material.

**Wednesday 2:20 Diplomat/Ambassador LS3**  
**Combining two-point and one-point microrheology**  
Alex J. Levine and Tom C. Lubensky  
*1Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106; 2Department of Physics, University of Pennsylvania, Philadelphia, PA 19104*

Recent experiments and theory have shown that the correlated motion of well-separated tracer particles provide an accurate determination of the rheological spectra of soft, complex materials in cases where the single-particle autocorrelations do not. The difference between the one and two particle measurements is due to the local perturbations of the material by the introduction of the probes.

In this talk we will show how the combination of one and two particle measurements can be used to extract rheological information about both the bulk, unperturbed medium and the perturbation zone surrounding the tracer.
particles. Such an analysis can be used to study polymer depletion around colloidal particles. Extensions of these concepts are applied to membrane microrheology as well.

Wednesday 2:45 Diplomat/Ambassador

Viscoelasticity of synovial fluid

Katherine M. N. Oates, Wendy E. Krause, and Ralph H. Colby
1Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802; 2Lynntech, Inc., College Station, TX 77840

The mechanism responsible for the excellent lubricating properties of synovial fluid (found in mammalian joints) is not well understood, but may be dictated by interactions between synovial fluid component macromolecules. Rheology is a useful tool to probe the interactions between hyaluronic acid, the high molecular weight anionic biopolysaccharide in synovial fluid, and the protein components of synovial fluid. The rheological properties of a synovial fluid model, consisting of the proteins albumin 11mg/mL, γ-globulins 7mg/mL, and hyaluronic acid 3mg/mL, in phosphate buffered saline, pH 7.4, have been studied. PBS solutions of 3 mg/mL hyaluronic acid (M_w = 1500K) have a rheological profile typical of a polyelectrolyte in the high salt limit, with a viscosity of 65 cp and exhibit shear thinning above 10 s⁻¹. The viscosity of hyaluronic acid plus the albumin (M_w = 66K) and γ-globulins (M_w = 150K), showed pronounced viscoelasticity at low shear rates, with a drastic increase in viscosity. Our synovial fluid model is a weak reversible gel. The time and shear history dependencies of its viscoelastic character will be discussed in detail.

Wednesday 3:35 Diplomat/Ambassador

Two-particle microrheology of actin solutions with a high-speed microscope

John C. Crocker, Ronak Beigi, Andreas Bausch, and Margaret L. Gardel
1Applied Physics, California Institute of Technology, Pasadena, CA 91125; 2Physics Department, Harvard University, Cambridge, MA 02138

Recent studies have suggested that the macroscopic rheology of the semi-flexible polymer F-actin differs from that determined by conventional microrheological measurements. Specifically, the high-frequency ω³/₄ dependence of the shear modulus has not been reproduced by any macroscopic experiment. To elucidate this discrepancy, we have performed measurements on F-actin using a new formalism called two-particle microrheology. This technique overcomes many of the limitations of earlier microscopic techniques related to tracer boundary conditions and polymer network drainage. We employ a new stroboscopic imaging system to perform the measurements at high frequency. We find that the bulk rheology scales as ω¹/₃ at low frequencies, and attribute the discrepancy to the local caging of the actin polymers.

Wednesday 4:00 Diplomat/Ambassador

One- and two-particle microrheology in biological and synthetic polymer solutions

Christoph F. Schmidt, Fred Gittes, Frederick C. MacKintosh, Peter Olmsted, K. Addas, Jay X. Tang, and Alex J. Levine
1Department of Biophysics and Physics of Complex Systems, Vrije Universiteit Amsterdam, Amsterdam 1081, The Netherlands; 2Dept. of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235; 3Department of Physics, Leeds University, Leeds LS2 9JT, United Kingdom; 4Molecular Biology Institute, Indiana University Bloomington, Bloomington, IN; 5Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106

We have developed and used one and two-particle microrheology techniques, employing micron-sized beads embedded in polymer solutions and gels. Thermal fluctuations of the embedded probes are measured and the viscoelastic parameters of the embedding medium are derived. We have studied entangled solutions of the semi-flexible biopolymer F-actin, and solutions of filamentous fd-virus particles. The methods as well as results will be presented and the advantages and disadvantages of microrheology will be discussed.
Wednesday Afternoon

Wednesday 4:25 Diplomat/Ambassador LS7

Mechanical properties and microstructure of living cells
Megan T. Valentine, Andreas Bausch, Hallam Stevens, and David A. Weitz
Department of Physics and DEAS, Harvard University, Cambridge, MA

We present a multiple particle tracking technique for making precise, localized measurements of the mechanical microenvironments of inhomogeneous materials. Using video microscopy, we simultaneously measure the thermally activated dynamics of fluorescent tracer particles embedded in a complex medium, and interpret their motions in terms of local viscoelasticity and microstructure. This technique is particularly well suited to studying biological materials where small sample volumes and complex, heterogeneous structures necessitate localized measurements. We will present our work on the local mechanical response of living fibroblasts and endothelial cells.

Wednesday 4:50 Diplomat/Ambassador LS8

One- and two-point microrheology of F-actin networks
Margaret L. Gardel1, Megan T. Valentine1, John C. Crocker2, Andreas Bausch1, and David A. Weitz1
1Physics Department, Harvard University, Cambridge, MA 02138; 2Applied Physics, California Institute of Technology, Pasadena, CA 91125

The technique of microrheology is now widely applied to study the microscopic viscoelastic properties of complex fluids, including polymer networks. The thermal motion of single micron-sized beads embedded in the polymer is used to extract viscoelastic moduli. However, in networks of the semi-flexible polymer F-actin, comparison of bulk and micro-rheological results exhibit discrepancies, which are thought to be either due to the heterogeneous nature of the network or the coupling of the probe particles to the medium. We are able to eliminate the differences between the micro- and macro-rheology by extracting moduli from the pairwise correlated movements of the probes instead of single probe motion. We use a multiparticle tracking approach to observe the motion of several hundred probes embedded in the actin network. Here we present results of experiments in which we vary both probe size and surface chemistry to explore the interpretation of both single and correlated probe motion in actin networks.

Wednesday 5:15 Diplomat/Ambassador LS9

Dynamics of actin-coated membranes
Emmanuelle Helfer1, L. Bourdieu2, S. Harlepp2, J. Robert2, Frederick C. MacKintosh3, and D. Chatenay2
1van der Waals-Zeeman Institute, Universiteit van Amsterdam, Amsterdam 1018 XE, The Netherlands; 2Laboratoire de Dynamique des Fluides Complexes, Strasbourg, France; 3Division of Physics and Astronomy, Vrije Universiteit, Amsterdam NL-1081HV, The Netherlands

In living cells, cytoskeletal filaments interact strongly with the plasma membrane and other associated proteins to form stable or dynamic structures involved in cell shape, mechanical properties and locomotion [1]. To study the properties of these complex structures, we designed an in vitro system by self-assembling a network of actin filaments on the surface of giant vesicles. Using optical tweezers and single-particle tracking we studied the rich dynamics of these actin-coated membranes (ACM) [2]. Probe beads were biochemically attached to the membranes and their thermally excited position fluctuations were measured. We proposed a model that relates the power spectrum of these thermal fluctuations to the viscoelastic properties of the membrane. We showed that microrheology experiments could be carried out on individual micrometer-sized objects such as vesicles. The presence of the actin shell increases significantly the bending modulus and induces the existence of a 2D shear modulus. Both bending and shear moduli exhibit a viscoelastic behavior, scaling with frequency with respective power laws of exponents $0.55 \pm 0.21$ and $0.85 \pm 0.07$. These results are consistent with a common exponent of 0.75, expected from our model and prior rheology measurements on bulk actin solution [3].

Thursday Morning

Symposium SR
Solid Rheology From Glasses To Gels
Organizers: Alan S. Wineman and Andre Lee

Thursday 8:05 Cabinet SR5
On the inhomogeneous shearing deformation of a non-homogeneous Gent slab: Self-homogenizing effect of finite chain extensibility
Barry Bernstein, Ecevit Bilgili, and Hamid Arastoopour
Chemical and Environmental Engineering, Illinois Institute of Technology, Chicago, IL 60616

Rubber-like materials are inherently non-homogeneous due to either imperfect vulcanization during their production or their interaction with severe thermo-oxidative environments. The purpose of this paper is to theoretically examine the effect of a material non-homogeneity on the shearing response of an infinite rubber-like slab. We generalize the Gent material model by considering the spatial variation of the small-strain shear modulus and the finite chain-extensibility parameter across the thickness of the slab. A semi-inverse method is used to determine the shear strain and the inhomogeneity in the shear strain: first an inhomogeneous deformation field is postulated; then the static equilibrium equations are reduced to an ordinary differential equation. A finite difference method with Newton-Raphson algorithm is used to solve the non-linear boundary-value problem. We have found that the non-homogeneous Gent (NHG) slab exhibits a markedly different shearing response than its homogeneous counterpart. The degree and the spatial pattern of the non-homogeneity have a profound effect on the strain field. We also compare the behavior of the NHG slab with a non-homogeneous Neo-Hookean slab having the same spatial non-homogeneity pattern. Our simulations have indicated that the NHG slab has a more homogeneous strain field than the non-homogeneous Neo-Hookean slab, thus suggesting the self-homogenizing effect of the strain-induced stiffening (finite chain extensibility). The implications of our results in terms of the rheological characterization and the performance of rubber-like materials are also discussed.

Thursday 8:30 Cabinet SR6
Predicting in-service performance for sealant
Christopher C. White, Mark R. VanLandingham, Carl Buch, and Joannie W. Chin
Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

Current widely adopted test methods for establishing the viability of a sealant formulation rely on either multi-year static outdoor exposure or accelerated “torture” test protocols such as ASTM C719. These methods include serial exposure of sealant joints to extreme conditions followed by visual examination to assess performance. There is little faith in the correlation between outdoor testing, accelerated testing or in-service performance. The current standards rely primarily on multi-year outdoor testing. Because of this reliance on outdoor testing, the average time for introduction of new products or formulations can be decades. The alternative is to introduce products to market with little or no knowledge of the service life. Quite often these products have guaranteed performance for 35-50 years in all service environments; this liability exposure can threaten the very survival of the company.

We believe that a shift in philosophy to that of a reliability based testing methodology will allow for accurate prediction of in-service performance in compressed time. This method relies on quantifying the change in the rheological properties in response to controlled environmental stress exposure, verifying this with known outdoor exposures, and modeling the response of the material to the environmental stress.
The details of this approach, the initial development of the apparatus, and preliminary results will be presented.

Thursday 8:55 Cabinet

**Anisotropic thermal conduction in cross-linked elastomers subjected to uniaxial elongation**

David Venerus, Rajeev Dilipkumar, Jay Schieber, and Andrew Broeran

*Department of Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616*

Despite its technological significance, our understanding of energy transport in deforming polymeric materials is insufficient from both experimental and theoretical standpoints. Simple arguments suggest that thermal conductivity is anisotropic in deformed polymers. In this study we use a sensitive and non-invasive optical technique known as Forced Rayleigh Scattering to measure anisotropic thermal diffusivity in cross-linked elastomers subjected to uniaxial elongation deformations. Data are collected for two cross-linked systems: polysiloxane and polybutadiene. As expected, the measured thermal diffusivity in the stretch direction is greater than the equilibrium value by an amount that increases with increasing strain. The thermal diffusivity in the direction perpendicular to the stretch direction is less than the equilibrium value. The thermal diffusivity data used in conjunction with stress and birefringence data are used to evaluate the stress-optic and stress-thermal rules.

Thursday 9:20 Cabinet

**Segmental dynamics of low molecular weight cyclic polystyrene**

Patrick G. Santangelo¹, C M. Roland¹, Taihyun Chang², and Jacques Roovers³

¹Chemistry, US Naval Research Laboratory, Washington, D.C. 20375; ²Department of Chemistry and Center for Integrated Molecular, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea; ³Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ontario, Canada

Local segmental motion of low molecular weight, cyclic polystyrene (PS) has been examined by dynamical mechanical spectroscopy, and compared to measurements on a series of linear PS of varying molecular weight. The Tg-normalized Arrhenius plots of segmental relaxation times were quite similar for the low molecular weight cyclic PS and linear PS of high molecular weight. In contrast, significant reduction in the steepness of the scaled temperature dependence of the segmental relaxation time for low molecular weight linear PS was observed. These results are interpreted by considering the contribution of chain ends to the configurational entropy. Since the shape of the relaxation function is invariant to both molecular weight and chain topology, these results are deviations from the usual correlation between time and temperature dependencies. Although the dependence of relaxation times on Tg-normalized temperature is weaker, lower molecular weight, linear PS has a larger heat capacity change at Tg. This result is at odds with an interpretation of temperature dependencies in terms of the degrees of freedom available to the glass upon transition to the viscous liquid.

Thursday 10:10 Cabinet

**Effect of solvent quality on the elastic and osmotic moduli of polymer gels**

Ferenc Horkay

*Section on Tissue Biophysics and Biomimetics, LIMB, NICHD, National Institutes of Health, Bethesda, MD 20892*

The shear modulus G of lightly cross-linked polymer gels is usually insensitive to the thermodynamic quality of the solvent. This result is consistent with the prediction of the classical theory of rubber elasticity. In contrast, the longitudinal osmotic modulus Mos, which controls the osmotic concentration fluctuations in the gel, is expected to depend on the solvent quality. The value of Mos can be independently determined from scattering measurements (e.g., from SANS) and from measurements of the osmotic swelling pressure and the shear modulus.

Since cross-links are not uniformly distributed in the network local variations of polymer concentration develop as the network swells. On the microscopic scale, concentration fluctuations frozen-in by the cross-links give rise to excess scattering at lower values of the scattering vector q. Consequently, the scattering intensity of a swollen gel contains at least two contributions: an osmotic term that is governed by Mos and a cross-linking term. The latter depends on the detailed structure of the network and the mechanism of the cross-linking process.
The effect of solvent quality on the elastic and osmotic moduli of poly(vinyl acetate) gels is investigated in good (toluene and acetone) and theta (isopropyl alcohol) solvents. It is found that G is practically independent of the nature of the solvent while the value of Μos drops with decreasing solvent quality. In isotropically swollen gels the frozen-in component of the scattering intensity does not change with the solvent quality. Under anisotropic deformation, however, the solvent quality significantly alters the scattering pattern. It is likely that in anisotropically deformed gels the extent of disinterpenetration of the cross-linked clusters depends on both the swelling degree and the excluded volume interactions.

Thursday 10:35 Cabinet

**Predicting the yield stress of particulate suspensions via computer simulation**

Stacy Pyett and Robert A. Lionberger  
*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136*

At either high volume fractions or in the presence of attractive interparticle forces, colloidal suspensions can form a solid-like phase exhibiting a measurable yield stress. However, the connection between gel microstructure and the rheological properties is still not well understood. Nonequilibrium simulations can observe both the microscopic structure of a colloidal gel and a stress-strain response analogous to experimental rheological data. To observe stress-strain behavior, the most straightforward simulations apply a strain to the system and observe the stress response. To check the validity of this method, we first compare constant strain-rate simulations to data for a well-characterized system, then conduct simulations on the same system under constant stress. After verifying the validity of our simulation technique, we proceed to link the gelled-state micro-structure with macroscopic observations. Specifically, we investigate the dynamic versus static signatures common to systems displaying a yield stress. We present simulation data from gelled and glassy states and gather information on the role of inter-particle potential, volume fraction, and temperature on determining the measurable yield stress values.

Thursday 11:00 Cabinet

**Change of hydrogel elastic modulus at a pH-induced swelling transition**

In S. Bang¹, Robab Emami¹, Jules J. Magda¹, Man H. Han², In S. Han², and Ferenc Horkay³  
¹Chemical & Fuels Engineering, University of Utah, Salt Lake City, UT 84112; ²M-Biotech, Inc., Salt Lake City, UT 84119; ³Section on Tissue Biophysics and Biomimetics, LIMB, NICHD, National Institutes of Health, Bethesda, MD 20892

The elastic shear modulus is reported for pH-responsive polyelectrolyte hydrogels. These hydrogels are designed for biomedical use and exhibit swelling transitions in the physiological pH range. When the environmental pH value decreases below 7.4, hydrogel swelling ratio abruptly rises due to an increase in gel degree of ionization, and the gel elastic modulus also increases sharply. This trend is in disagreement with predictions of theory for hydrogels in the weak stretching regime. Possible reasons for the disagreement will be discussed.

Thursday 11:25 Cabinet

**Validation of a unified thermodynamic theory of polymer nonlinear viscoelasticity**

Douglas B. Adolf¹, Robert S. Chambers², and James M. Caruthers³  
¹Materials Sciences, Sandia National Laboratories, Albuquerque, NM 87185; ²Engineering Sciences, Sandia National Laboratories, Albuquerque, NM 87185; ³Chemical Engineering, Purdue University, West Lafayette, IN 47907

Starting from the free energy of a glassy polymer, we have developed and validated a thermodynamically consistent material model for predicting a wide variety of physical phenomena including such effects as enthalpy relaxation, volume recovery, physical aging, and yield in tension and compression. The constitutive formalism acknowledges that polymers are intrinsically viscoelastic materials that undergo a glass transition and employs the concept of a material clock to regulate relaxations due to loading or temperature/volume conditions. The material clock is constructed from the potential internal energy that is attainable readily from thermodynamic functions. The requisite model development has been undertaken in a tightly coupled environment constrained by the framework of Rational Mechanics, guided by fully three-dimensional finite element analyses, and validated through the quantitative data from a comprehensive suite of tests. Predictions and measurements on an unfilled epoxy show quantitative
agreement for a broad range of experiments leading one to believe the underlying physical picture is nearly correct. In this presentation, we will show additional results obtained for other materials and filled systems.

Thursday 11:50 Cabinet

A thermodynamically consistent theory of nonlinear viscoelasticity in curing thermosets
Robert S. Chambers¹, Douglas B. Adolf², and James M. Caruthers³
¹Engineering Sciences, Sandia National Laboratories, Albuquerque, NM 87185; ²Materials Sciences, Sandia National Laboratories, Albuquerque, NM 87185; ³Chemical Engineering, Purdue University, West Lafayette, IN 47907

In an earlier presentation, we discussed the validation of a thermodynamically consistent nonlinear viscoelastic material model for polymers. Although the theory is useful for analyzing a wide variety of physical phenomena, it is not capable of predicting the nonlinear viscoelastic stresses and strains generated as a thermoset cures. To accommodate chemical coupling, we have incorporated an additional variable in the Frechet expansion of the Helmholtz free energy. This extent of reaction variable represents the sum of perhaps many individual reactions and gives rise to three important new terms involving cure-shrinkage, heat-of-reaction and entropy-of-reaction. The stress and entropy equations are derived naturally from the thermodynamic relationship involving the time derivative of the Helmholtz free energy. One noteworthy result is the formalism provides an explicit definition of the reaction dependence of the glass transition temperature. Experiments have been conducted to provide data characterizing the nonlinear viscoelasticity of curing thermosets, and the formalism has been implemented in a three-dimensional finite element code. We will discuss the data and testing, present the formalism and review the status of our model validation efforts.

Symposium SM

Viscoelasticity In Polymer Solutions and Melts
Organizers: David Venerus and Guy C. Berry

Thursday 8:05 Old Georgetown

Rheology and orientation behavior of metallocene-catalyzed semi-syndiotactic polypropylenes: Role of tacticity
Rangaramanujam M. Kannan¹, Gautam Parthasarathy¹, Vivek Maheshwari¹, Michael Sevegney¹, and Allen Siedle²
¹Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202; ²3M Corporate Research Laboratories, St. Paul, MN

With metallocene-catalyst technology, it has become possible to synthesize polymers with well-defined tacticity, thereby providing materials with a wide range of properties, with the same monomer. However, understanding the role of tacticity on the structure, mechanical, and flow behavior has been a challenge since tacticity appears to have a wide influence. We are studying syndiotactic polypropylenes (s-PP) with varying degrees of 'syndiotacticity', ranging from nearly atactic to nearly syndiotactic. These materials have been custom-synthesized using asymmetric, bridged cyclopentafluorenyl catalysts, and characterized using NMR, modulated DSC, mechanical testing, rheology, and rheo-optical FTIR spectroscopy. In contrast to what is seen in traditional isotactic polypropylenes, our DSC and rheological results indicate that these materials may possess a unique crystal morphology that melts at around 70°C. Rheology, flow birefringence and FTIR spectroscopy are especially sensitive to the onset and evolution of the slow crystallization process. This unique 'mesophase' plays a critical role in the mechanical and the orientation behavior. Using rheo-optical FTIR spectroscopy, we are currently studying the distinct contributions of the 'mesophase' and the amorphous regions in these elastomeric materials. In the melt state, the entanglement behavior and the flow birefringence depend significantly on the tacticity of the materials. The stress-optical coefficient of s-PP appears to be higher than that of atactic or isotactic PP. In the semi-syndiotactic s-PP, the highly elastic nature of the materials is manifested in the normal stress component of the flow birefringence signals. Blends of s-PP with other polymers are also being investigated.
Structure, relaxations and gel formation in enzymatically modified guar gum solutions
Michael H. Duits, Roland H. Wientjes, and Jorrit Mellema
Applied Physics, Rheology group, University of Twente, Enschede 7500 AE, The Netherlands

We studied the effect of molecular modifications (with α-D-Galactosidase) and solvent modifications on the linear visco-elastic properties of aqueous Guar Gum solutions. All modifications were done on a 1% w/w solution of a Guar with an M of 1 Mg. In its native state this system shows two storage modulus plateaus that are well separated in the frequency domain. Our experiments were aimed at gaining more insight into the mechanisms of stress relaxation in the different frequency regions. Also we wanted to explore the possibilities for making weak gels. In the molecular modifications, Galactose sidegroups were removed in different fractions f of the available amount, up to f = 0.57. Storage and Loss moduli were measured as a function of frequency (0.003-20 Hz) and temperature (283-353 K). On increasing f, a sharp transition from a liquid to a gel was found at f = fc. Below fc the changes in the relaxation behavior were surprisingly modest. In the high frequency range (above 0.1 Hz), the characteristic relaxation time and strength, and the TTS remained much alike that of unmodified Guar. Also changing the solvent had little effect. Therefore interchain bonding could be ruled out as the origin for relaxation behavior in the Hz range. Instead diffusion processes involving multichain structures are proposed. Above fc gels were formed. The storage moduli at low frequencies (below 0.03 Hz) strongly increased whereas the high frequency moduli remained constant. This corroborated that interchain bonds must be involved in the stress relaxations in the mHz range. Further mechanistic information is hard to obtain. Yet we propose a microscopic picture that can explain our observations. It would merit a further study with other techniques. The possibility to make weak gels of modified Guar was demonstrated. A remarkable finding was that different values for fc were found for samples stored at 277 K or at 248 K (and thawed). The melting temperature of the modified guar gels could make them interesting for applications.
tumbling parameter for different molecular weigh side-group LCs, dissolved in small molecule nematic LCs. We want to determine what conditions lead to low values for the tumbling parameter for solutions of side-group liquid crystalline polymers (SGLCPs) dissolved in small molecule nematic liquid crystals. Previous studies on this type of solution have found a flow aligning condition to occur with greater than 7.5% polymer where the tumbling parameter is less than negative one and the steady state angle is close to the velocity gradient direction. The current work uses polymers with a molecular weight range between 70,000 g/mol to 800,000 g/mol. The methods used in this study include conoscopic and rheological techniques. The results will be compared with a 2-D version of the Leslie Erickson theory and with theories by Brochard.

**Non-linear viscoelasticity and modeling of entangled polymer solutions: From shear to uniaxial extension**

Pradipto K. Bhattacharjee\(^1\), James P. Oberhauser\(^2\), L. G. Leal\(^3\), Tam Sridhar\(^4\), and Gareth H. McKinley\(^5\)

\(^1\)Department of Chemical Engineering, Monash University, Clayton Campus, Victoria 3800, Australia; \(^2\)Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904; \(^3\)Depts. of Chemical Eng. and Materials Eng., Univ. of Calif at Santa Barbara, Santa Barbara, CA 93106; \(^4\)Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia; \(^5\)Dept. Mechanical Engineering, M.I.T., Cambridge, MA 02139

The reptation theory of Doi and Edwards provides an appealing and reasonably successful theoretical framework for describing the dynamics of entangled polymer solutions and melts. Recently, other mechanisms (i.e., convective constraint release, contour length fluctuations, etc.) have been offered to rectify some pathologies of the original model, such as excessive shear thinning. These additions to the theory qualitatively improve model predictions; however, more rigorous comparison with experimental data spanning a variety of flow types is necessary in order to accurately assess their efficacy.

We will present rheo-optical experimental data for nearly monodisperse entangled polymer solutions in shear flow along with mechanical measurements obtained from a filament stretching device. We will compare these results with reptation model predictions incorporating convective constraint release and contour length fluctuations. Steady state results suggest that the model proposed by Mead, Larson, and Doi coupled with the contour length fluctuation model of Doi and Kuzuu offers improved quantitative predictions. Comparisons between theory and experiment for transient flows will also be discussed.

**A critical examination of reptation models for binary polymer mixtures**

Shanfeng Wang and Shi-Qing Wang

Department of Polymer Science, The University of Akron, Akron, OH 44325

We have carried out a systematic investigation of polymer dynamics in the terminal region of binary polymer mixtures of high and low molecular weights (N_L and N_S). Specifically, Oscillatory shear measurements have been carried out to determine the overall relaxation times for binary blends of nearly monodisperse 1,4-polybutadiene, polyisoprene, and 1,2-polybutadiene respectively. Our experimental results point to a severe limitation of the current theories for chain reptation dynamics, all of which consider for simplicity the effect of constraint release (CR) (i.e., tube reorganization) due to short chains and the chain reptation in the tube separately. This CR model of Klein and Graessley apparently is only correct in the dilute limit of long chains in an entangled matrix of short chains where long chains diffuse by Rouse type motion of the tube, as verified by the tracer diffusion experiments of Green and Kramer. We found that the relaxation time of the long chains \(\tau(\phi)=\tau(1.0)\phi^\theta\) as long as \(N_S<N_L\), where \(\phi\) is the concentration of the high molecular component. For a fixed \(N_L\), \(\theta\) decreases with increasing \(N_S\). For a given matrix of short chain \(N_S\), \(\theta\) is larger for a lower \(N_L\). Concepts of contour length fluctuation and varied contour length (or tube dilation) are applied to explain our results.
Distinct and interesting differences between steady shear flow dynamics of marginally entangled and well entangled polymer liquids are studied in several flow configurations. Cone-and-plate and parallel-plate mechanical rheometry experiments and planar Couette shear flow birefringence polarimetry measurements, for example, reveal early power-law deviations from Newtonian fluid response at shear rates well below the reciprocal terminal relaxation time of well entangled materials. The width of the power-law regime and the strength of the deviations are found to increase in a well defined manner with degree of molecular entanglement. Very similar power-law deviations in the velocity dependence of drag coefficients for rigid discs and spheres submerged in entangled polymer liquids are also reported. A detailed study of the gap and flow rate dependence of the flow curve in the power-law regime rules out a critical role for wall slip, and points to new constraint release-like relaxation process in well entangled polymers as a possible source of the observations. These results bear important qualitative similarities to previous reports of damping function transitions (from type A damping in marginally entangled polymers to type C in well entangled ones) in entangled polymer liquids. We will discuss possible molecular origins of both phenomena in this presentation.

In the recent past several new reptation models for polymer melts have been proposed which are based on the original Doi and Edwards reptation theory. The most sophisticated versions of this class of models are capable of predicting the rheology of entangled polymers with good accuracy. However with the new and better models comes the difficulty of simulating them efficiently in complex flows. In the last decade tremendous progress in development of efficient computation techniques for simulation of entangled polymeric systems in complex flow geometries has been made. Examples of such techniques are the Brownian Configuration Fields Method and the recently proposed Deformation Fields Method. However, these methods are restrictive to a certain class of reptation models and cannot be used to simulate complex flow of the most advanced reptation based models. To overcome this shortcoming we have developed a new technique called the "Adaptive Configuration Fields Method" that combines the essential features of the Brownian Configuration Fields Method and the Deformation Fields Method to allow simulation of advanced reptation models in complex flows. To illustrate the accuracy and computational efficiency of our computational technique, we have performed simulations with the recently proposed Thermodynamically Admissible Reptation model of Ottinger in simple kinematics flows (plane shear and uniaxial extension) and have compared the results with pure Brownian dynamics simulations. We see an excellent agreement between the two. Complex flow calculations of various benchmark problems using this technique have also been performed and the results of these simulations will be presented.

A phase separated polymer melt under shear is the simplest example of slip at a polymer-polymer interface. Recent experiments by Zhao and Macosko on laminate systems provide quantitative data for this phenomenon. Interfacial slip is manifested as a lower apparent viscosity, and is shear-rate (or stress) dependent. We examine whether scaling theories by de Gennes, Brochard and Ajdari can be used to qualitatively interpret the data.
Symposium TS
Two Phase Systems: Emulsions, Blends and Suspensions
Organizers: Kalman B. Migler and Jan Vermant

Thursday 8:05 Judiciary TS14
Yield stress measurements in suspensions: A round robin project
Daniel C. De Kee1 and Dzuy Q. Nguyen2
1Department of Chemical Engineering, Tulane University, New Orleans, LA 70118; 2Department of Chemical Engineering, University of Adelaide, Adelaide, SA 5005, Australia

Yield stress measurements are notoriously difficult to interpret. Most multiphase systems such as suspensions, creams, food products, paints, etc. exhibit a yield stress and a correct determination of this property could be used in quality control. A variety of methods have been proposed and practiced, resulting in rather large deviations in obtained results. In the past, these difficulties were due mainly to the fact that researchers relied on extrapolated values, frequently obtained from rheometric measurements. More recently, a number of so called static techniques have been proposed to improve on the situation. Here we report the results of a round robin exercise involving suspensions of TiO2 and Silica. The cooperating laboratories are those of Boger, Carreau, Coussot, De Kee, Franks, Nguyen, Tiu and Usui. Different laboratories used different measurement techniques (stress as well as strain controlled rheometers, vane and plate techniques, stress ramp, strain ramp, creep, ...) and the, so far obtained results, will be compared and discussed.

Thursday 8:30 Judiciary TS15
Rheological properties of silica suspensions
Saeid Savarmand1, Pierre J. Carreau1, Francois Bertrand1, and David J. Vidal2
1Department of Chemical Engineering, Ecole Polytechnique, Montreal, QC H3C 3A7, Canada; 2Pulp and Paper Research Institute, Paprican, Pointe-Claire, QC H9R 3J9, Canada

The rheological properties of silica suspensions having an average particle diameter of 330 nm and a density of 1.948 kg/m³ at different concentrations have been studied. More attention has been paid to the yield stress of these suspensions at different pH values ranging from 2 to 9 and for different ionic strengths adding KCl to the initial suspension. Rheological measurements have been made using two rheometers (a stress controlled Bohlin CVO120 and a rate controlled ARES). In order to measure the yield value, successive step stress (creep) tests have been carried out. The transition from solid-like behavior to liquid-like one has been taken as the criterion for determining the yield value [Citerne et al., Rheol. Acta 40, 86-96 (2001)]. It has been found that for a 40-vol% suspension in deionized water, decreasing pH from its natural value of 6.3 to 4.5 drops the value of the yield stress from 6 to 0.02 Pa while further reduction of pH to 2 increases the yield stress to 1.3 Pa. On the contrary, increasing pH above the natural value decreases the yield value. These results will be discussed in light of particle-particle interactions.

Thursday 8:55 Judiciary TS16
Rheology and microstructure of mixed colloidal gels
Jeffrey A. Yerian, Courtney L. Griffin, Saad A. Khan, and Peter S. Fedkiw
Chemical Engineering, North Carolina State University, Raleigh, NC 27695

We are investigating colloidal systems containing more than one colloidal particle to develop relationships between the microstructure and interaction forces between the colloidal particles. In general, we are interested in determining whether the addition of a second colloidal particle hinders or assists the network formation. We will study systems containing different types of surface-modified fumed silicas in a range of polar organic. Initial work will focus on hydrophilic fumed silica (native silanol surface, Degussa A200) and hydrophobic fumed silica (~50% silanol + 50% octyl, Degussa R805) since the proposed mechanism of gel formation in the A200 and R805 systems are very different: hydrogen bonding versus chain stickiness caused by contact dissimilarity with solvent. Steady and dynamic rheology will be used to measure the elastic moduli and yield stress of the dual component fumed silica systems. Static light scattering studies will be conducted in conjunction with the rheology experiments to probe material microstructure directly to measure the fractal dimension of these systems. Comparisons of the dual
component data with the single fumed silica systems will show if the individual types of fumed silica interact independently, synergistically or adversely.

Thursday 9:20 Judiciary

Rheology and flow X-ray scattering of soft sterically stabilized latices
Jan Vermant\textsuperscript{1}, Hans Hoekstra\textsuperscript{1}, Jan J. Mewis\textsuperscript{1}, and T. Narayan\textsuperscript{2}
\textsuperscript{1}Department of Chemical Engineering, K.U. Leuven, Leuven B-3001, Belgium; \textsuperscript{2}ESRF, Grenoble F-38403, France

In these experiments the time evolution of the flow-induced structure has been investigated using synchrotron X-ray radiation. A Couette flow cell at the European Synchrotron Radiation Facility was used for this purpose and installed on beamline ID02. By translating the Couette geometry with respect to the beam, both the flow-vorticity and the vorticity-gradient plane could be accessed, hence providing an insight into the 3D structure of the dispersions under flow.

The structure of polybutylacrylate latex suspensions, sterically stabilized by adsorbed polymer layers, has been investigated as a function of volume fraction, shear rate and particle size. In these systems large-scale bundle structures have been recently observed by means of 2D-SALS experiments under flow [1]. It has been suggested that these bundles are due to either a shear-banding instability [2], or by a coexistence of an ordered and disordered structure during flow as suggested from Stokesian dynamics simulations [3]. The SAXS data compare favorably with the latter interpretation.

From the SAXS experiments the following conclusions could be obtained: 1. The detail structure of the recently observed flow-induced bundles reveals a coexistence crystalline and amorphous material. 2. A flow-induced order-disorder (OD) transition takes place without the occurrence of shear-thickening of the viscosity. This demonstrates that an OD transition is not a necessary condition for shear thickening.


Thursday 10:10 Judiciary

Computational study of colloidal suspensions using dissipative particle dynamics
Nicos S. Martys\textsuperscript{1} and James S. Sims\textsuperscript{2}
\textsuperscript{1}Building Materials, NIST, Gaithersburg, MD 20899; \textsuperscript{2}Mathematical and Computational Sciences, NIST, Gaithersburg, MD 20899

Results are presented of a numerical study concerning the role of particle shape and size distribution in the rheology of suspensions. In studies of the relative viscosity of dense sphere suspensions we found reasonably good agreement with recent experiments. At low solid fraction of ellipsoids under shear our simulations recover the well known Jeffreys orbits. However, at intermediate solid fraction we find evidence of orientational order. The flow of suspensions under a variety of boundary conditions (applied stress or strain) and for the case of a coaxial geometry will be discussed.

Thursday 10:35 Judiciary

Simulation of flexible fiber suspensions
Leonard H. Switzer and Daniel J. Klingenberg
Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706

Fiber suspensions are found in a variety of applications including, papermaking and fiber filled composites. Fiber suspensions subjected to flow will often develop spatial heterogeneities, or flocs, that are undesirable in processing. We have developed a particle level method for simulating the flow of flexible fiber suspensions in order to investigate the effect of various fiber features and fiber interactions on the suspension structure, and to probe mechanisms of flocculation. Fibers are modeled as linked rigid spherio-cylinders connected by ball and socket joints. The model incorporates features such as fiber flexibility, irregular fiber equilibrium shapes, and fiber-fiber...
interactions such as colloidal-like forces and interfiber friction. Simulations show that fibers in flowing suspensions will flocculate if the fibers are sufficiently stiff, have irregular equilibrium shapes, and possess a sufficiently large coefficient of static friction. Under such conditions, fiber flocs form in the absence of an attractive force. This presentation will focus on the relationships between fiber properties and suspension structure. Fiber properties investigated include those mentioned above, as well as anisotropic fiber bending, kinetic friction interactions, and attractive forces. We will also illustrate how this simulation method can be used to simulate the formation and testing of paper handsheets, in order to examine the effect of fiber properties on paper strength.

Thursday 11:00  Judiciary  TS20

**Sedimentation of a sphere in a fiber suspension**
Mohend Chaouche and David Antonio  
*LMT, ENS-cachan, CNRS, Cachan 94235, France*

The sedimentation of a dense sphere in a suspension of neutrally buoyant non-Brownian fibers is investigated experimentally. We consider in particular the effect of the ratio of the sphere diameter $D$ to the fiber length $L$ on the extra drag force experienced by the sphere in a broader range than the previous studies reported in the literature. For a given fiber concentration, the drag coefficient is found to be a strong function of the sphere diameter to the fiber length ratio. It rises, passes through a maximum for $D = O(L)$, and then decreases to a steady state value for large spheres. Our results are consistent with those of Milliken et al (J. Fluid Mech., 202, 212 (1989)) for $D/L \ll 1$, and those of Ralambotiana et al (Physics of Fluids, 9(12), 3588, (1997)) for $D/L \gg 1$. When the sphere diameter is much smaller than the fiber length, the sphere undergoes large velocity fluctuations which are analyzed in terms of the sphere's diffusivity tensor. Our experimental results are in good agreement with the numerical simulations reported by Harlen et al (J. Fluid Mech. 388, 355, (1999)).

Thursday 11:25  Judiciary  TS21

**Sedimentation of solid particles in viscoelastic fluids**
Howard H. Hu and Mingyu Zhu  
Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104

The sedimentation of rigid spherical particles in a cylindrical tube filled with viscoelastic fluids is studied using 3D direct numerical simulations. In the simulation, a Galerkin finite element formulation is used to solve the fully coupled motion of the solid particles and the fluid that is governed by an Oldroyd-B model. The movement of the particles is handled with an arbitrary Lagrangian-Eulerian technique in conjunction with a mesh update strategy. Effects of the parameters controlling the particle motion, which are the flow/particle Reynolds number, the Deborah number, and the solid-liquid density ratio are investigated. A particle released from rest falls with the overshoot of the settling velocity due to the elastic behavior of the fluid. It is found that the more the elastic the fluid, the larger the velocity overshoot. A smaller tube enhances the overshoot and the oscillation of the settling velocity. It is observed that the effect of fluid elasticity reduces the drag acting on the particle. The wall of the cylindrical tube further enhances the effect of the fluid elasticity. It is also found that in big tubes particles tend to migration toward the tube center; while in small tubes particles tend to migrate towards eccentric positions. The fluid elasticity enhances the inward particle migration near the tube center and the outward migration near the wall. The interaction among multiple settling particles is also investigated.

Thursday 11:50  Judiciary  TS22

**Modeling migration in a suspension of spheres in a shear-thinning liquid**
Ryan M. Miller and Jeffrey E. Morris  
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100

The flow of concentrated particulate suspensions presents a major challenge in many rheology related disciplines. In many of these cases, the suspending fluid itself exhibits complex non-Newtonian rheological behavior adding to the overall complexity of the system. Extension of a continuum modeling approach for particulate suspension flows proposed by Morris & Boulay (J. Rheol. 43, 1213; 1999) to non-Newtonian suspending fluids is described here.

The model couples the mass and momentum balances through the particle concentration dependence of the bulk rheological properties of the suspension. Particular emphasis is given to the role of normal stresses in the migration of the particle phase. The model is modified by substituting in a non-Newtonian viscosity law for the Newtonian
viscosity. Other than this all other model parameters are kept the same as in the Newtonian suspending fluid case. It was concluded that only by including non-Newtonian effects in all the relevant model parameters: normal stresses, shear stresses, and particle phase mobility/sedimentation could the model produce stable results consistent with experiment. The particular case studied is a shear-thinning suspending fluid in a wide-gap circular-Couette geometry, for which experimental data exist (Rao et al., 2000; submitted to Chem. Eng. Comm.). In this work, the suspending fluid is found to obey a Carreau viscosity model. The modeling results were found to match the trends in the experimental data predicting increased particle migration rate with increased rotation rate and increase particle diameter. Quantitative agreement between modeling and experimental data was found for small shear rates and the largest particle size (675 microns). The approach to steady-state was also studied, and predictions from the model indicate a much longer time scale for the suspension with a shear-thinning suspending fluid to achieve steady state than for the suspension with a Newtonian suspending fluid.

Symposium LS
Probes of Local Rheology and Structure
Organizers: Thomas G. Mason and Alex J. Levine

Thursday 8:05 Diplomat/Ambassador LS10
Combinatorial rheology: Microrheology as a tool for rapid materials screening
Victor Breedveld and David J. Pine
Department of Chemical Engineering, University of California, Santa Barbara, CA 93106

Developments in combinatorial chemistry have made it possible to produce large numbers of novel materials by systematically varying their chemistry. One of the challenges is to characterize the properties of these materials at a speed that is competitive to the synthesis rate. Rheology is a sensitive tool for measuring mechanical properties and thereby phase behavior. However, conventional mechanical rheometry is a slow, labor intensive method that generally requires at least 1 ml of sample volume per measurement. Microrheology, on the other hand, needs only very small sample volumes (ca. 10 µl), offers a wide range of accessible frequencies and can easily be automated to process large arrays of sample without intervention. This makes the technique particularly suitable for high throughput screening purposes.

We have implemented combinatorial rheology on the basis of particle tracking video-microscopy. The primary systems under investigation are novel aqueous block copolymer solutions. The phase behavior is a strong function of molecular weight, block length and block architecture. Because of the numerous degrees of freedom, combinatorial rheology is a useful tool in the design process.

Thursday 8:30 Diplomat/Ambassador LS11
Observations of particle dynamics in concentrated polymer solutions
Eric R. Weeks\textsuperscript{1}, Ritu Verma\textsuperscript{2}, John C. Crocker\textsuperscript{3}, and Arjun G. Yodh\textsuperscript{4}
\textsuperscript{1}Physics, Emory University, Atlanta, GA 30322; \textsuperscript{2}Unilever, Edgewater, NJ; \textsuperscript{3}Applied Physics, California Institute of Technology, Pasadena, CA 91125; \textsuperscript{4}Physics, University of Pennsylvania, Philadelphia, PA

Recent interest in using colloidal particles to study the microrheology of cellular environments calls for a detailed study of particle dynamics in complex fluids. We present observations of colloidal dynamics in concentrated polymer suspensions. In particular, we use lambda-DNA as our polymer, and use video microscopy and particle tracking techniques to follow suspended colloidal particles. We find that in semi-dilute polymer solutions, the measured viscosity varies with the colloidal particle size. This is an indication that the presence of the sphere, modifies the effective viscosity by affecting local polymer concentration. Our measurements at a fixed DNA concentration indicate that particles with sizes comparable to the characteristic correlation length diffuse faster than ones that are much larger. We also investigate the hydrodynamic coupling between two colloidal particles in the presence of DNA and observe highly screened interactions. We will discuss these effects in light of the depletion cavities known to form around these spheres [Ritu Verma, J. C. Crocker, T. C. Lubensky and A. G. Yodh, Phys. Rev. Lett., 81, 4004 (1998)].
Thursday Morning

Supported by the National Science Foundation grants DMR 96-23441 and the Materials Research Laboratory Grant DMR 96-32598.

Thursday 8:55 Diplomat/Ambassador LS12

**Microrheology of cross-linked polymers**

Bivash R. Dasgupta and David A. Weitz  
*Department of Physics, Harvard University, Cambridge, MA 02138*

We are studying the elastic and viscous properties of polyacrylamide, a chemically cross-linked polymer using various microrheology techniques. We have experimentally observed that the localized probe of these mechanical properties using light scattering compares very well with macro measurements for polyethylene oxide, a simple flexible polymeric system. The addition of an extra length scale due to the cross-linking of the polymers is the next level of complexity that needs to be investigated using these techniques. We are probing the regime where the polymer undergoes a change of phase between the sol and gel state. The two different phases are obtained by changing the concentration of methylenebisacrylamide, the cross-linking agent, in our samples. We use single scattering, diffusing wave spectroscopy and particle tracking to measure the dynamics of the probe particles that are embedded in the polymer. Using light scattering measurements we can probe the ensemble-averaged response of the beads while particle tracking allows us a more localized measurement of the viscoelasticity of the polymer. These experiments are then compared with bulk measurements that are done on a rheometer.

Thursday 9:20 Diplomat/Ambassador LS13

**Rotational diffusion microrheology of complex fluids**

Thomas G. Mason and Zhengdong Cheng  
*ExxonMobil Research and Engineering Co., Annandale, NJ 08801*

By measuring the time-dependent rotational diffusion of micron-sized tracer particles embedded in a complex fluid using optical methods, we calculate the frequency-dependent viscoelastic spectrum of the complex fluid using a rotational form of the generalized Stokes-Einstein relation. One implementation of this approach is to focus laser light through a microscope objective on a wax disk in a polymer solution and observe the thermally-driven rotational fluctuations both using real space digital video imaging. We compare the results of this method with mechanical rheology and the viscoelastic spectrum deduced from the particle's translational diffusion.

Thursday 10:10 Diplomat/Ambassador LS14

**Measuring the viscosity of nanoliter droplets**

Y. Thomas Hu and Alex Lips  
*Unilever Research, Edgewater, NJ 07020*

A novel technique for measuring the viscosity of small (nano-liters) fluid drops is presented. A drop is immersed in an immiscible suspending liquid and deformed under flow. The time evolution of the drop deformation is obtained as the drop image is captured. The drop viscosity is derived from small deformation theory as \( \eta = \left(-\frac{5\gamma}{2D\alpha-1.5}\right)\eta_s \) for hyperbolic flow, and \( \eta = \left(-\frac{5\gamma}{4D\alpha-1.5}\right)\eta_s \) for shear flow. Here \( \gamma \) is the flow rate, \( D \) is the steady state deformation, \( \alpha \) is the exponent obtained from the deformation growth or relaxation, \( \eta_s \) is the suspending fluid viscosity. Results from model systems are presented and the limit of the technique is assessed.

Thursday 10:35 Diplomat/Ambassador LS15

**Rheological measurements using nanoindentation techniques**

Mark R. VanLandingham¹, Christopher C. White¹, Xiaohong Gu², and Tinh Nguyen²  
¹Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899; ²Building Materials Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8621

For many industry-relevant polymer systems, early times-to-failure can be linked to local chemical and physical degradation, including local changes in rheological behavior. Further, the weak links in multi-component polymer systems are typically the interphase regions that form at the component interfaces. Thus, development of techniques to characterize rheological behavior of material regions with microscale and even nanoscale dimensions is important
for understanding degradation mechanisms and improving the durability of these materials. In this presentation, nanoindentation measurements of several polymer systems, including PMMA, various epoxy systems, PP, and several sealant materials, are discussed. Viscoelastic behaviors of these materials are characterized in some cases as a function of exposure to various weathering conditions, and in other cases as a function of distance from an interface.

Thursday 11:00 Diplomat/Ambassador LS16
Rheo-optical investigation of the thermoreversible gelation of gelatin
Liang Guo and Ralph H. Colby
Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802

Gelatin is an important biopolymer, made by denaturing collagen. At 45°C, gelatin chains in water exist in nearly random-walk conformations. When cooled below ~35°C, the gelatin chains partially renature to form the triple helix of collagen. These helices can involve multiple gelatin chains, and effectively act as crosslinks. Using optical rotation (to measure the helix fraction) and rheometry (to measure viscosity and modulus) we study gelation of gelatin solutions, quenched from 45°C to temperatures between 0 and 30°C. After gelation, its structure can be probed in a remelting experiment. We show how the temperature dependent optical rotation during remelting at 0.1°C/min can be used to estimate the distribution of helix lengths in the gel.

Thursday 11:25 Diplomat/Ambassador LS17
Effect of probe size on the microrheological response of associative polymers with Maxwell linear viscoelasticity
Qiang Lu and Michael J. Solomon
Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136

Recent approaches to extract the linear viscoelastic response of materials by measuring the mean squared displacement of a dispersed probe commonly assume that the probe is sufficiently large that the material response may be described by continuum viscoelasticity. Yet, as the ratio of the probe diameter to a characteristic dimension of the material is decreased, the continuum assumption becomes more tenuous. For example, when the ratio is approximately unity anomalous probe diffusion has been observed in semi-dilute polymer solutions (Won et al. Macromolecules 27 7389 (1994)). We investigated the effect of particle diameter on the probe mean-squared displacement of associative polymers with Maxwell linear viscoelasticity. Particle diameter was varied from 0.3 - 3.2 microns. Probe mean-squared displacement was monitored by diffusing wave spectroscopy and optical microscopy. The linear viscoelastic response of the solutions was extracted by means of recent microrheological theories. By manipulating the molecular weight, endcap chemistry and polymer concentration of the associative polymers, we observed a remarkable sensitivity of the probe displacement to probe diameter at short times. This sensitivity is not consistent with the continuum viscoelasticity assumption for these materials, even though the characteristic dimension of the associative polymer network is nearly two orders of magnitude smaller than the probe diameters studied. The results are discussed in light of analogous experiments performed for model semi-dilute polyethylene oxide solutions and a recent report of the long-range structure of associative polymer solutions (Klucker and Schosseler, Macromolecules 30 4927 (1997)). The results suggest that microrheology can be a sensitive indicator of structural and dynamical features that are otherwise poorly characterized by macroscopic mechanical rheology.

Thursday 11:50 Diplomat/Ambassador LS18
Tracer microrheology of surfactant solutions
Samiul Amin1, Christopher J. Kloxin1, Ryan M. van Zanten2, and John H. van Zanten1
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2Department of Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106-5080

There is growing interest in using the Brownian or thermal motion of spherical colloidal particles to probe the dynamics of soft materials that exhibit viscoelasticity. In principle, the motion of these colloidal spheres is related to the structure and dynamics of the suspending media. Most current investigations have focused solely on establishing the relationship between the measured Brownian motion and viscoelastic moduli-the so-called tracer microrheology.
Thursday Morning

The approach described here is enhanced in that it utilizes not only measurements of the particle mean square displacement and viscoelastic moduli, but also light scattering characterization of the viscoelastic media whereby the concentration fluctuation relaxation spectrum and the osmotic compressibility are determined. This multiple experimental probe approach potentially allows one to account for both transverse and longitudinal contributions to the suspending medium's response. The approach is illustrated with a whole host of surfactant solutions including CTAB/KBr & CTAB/NaSal wormlike micelle solutions, CTAT solutions and aqueous Pluronic solutions. Surfactant solution tracer microrheology results are compared and contrasted with those found for conventional polymer solutions.
Poster Session

Symposium PO
Organizer: Patrick Doyle

Wednesday 6:00 Crystal Ballroom

Modifying the rheological properties of collagen-rich tissues by crosslinking
Julia A. Kornfield1, Giyoong Tae1, Mary Dickinson1, Angelique Louie1, Robert Lambert2, Hampar Karageozian2, John Park3, Kathryn A. Rich4, and Vincent Monnier5

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Non-enzymatic crosslinking causes a variety of collagen-rich tissues to lose their elasticity with age (e.g., hardening of arteries and wrinkling of skin). We examine the effects of crosslinking on the viscoelastic properties of tissue using glyceraldehyde as a model crosslinking agent and the cornea as a model tissue. The nanostructure of the material is reminiscent of a hexagonal-ordered phase in block copolymers, with the cylinders largely composed of collagen fibrils and the continuous phase consisting of proteoglycan hydrogel. Rabbit and human corneas are treated under culture conditions that maintain normal morphology and hydration of the cornea. Glyceraldehyde is applied topically (drops of 3% wt. glyceraldehyde in saline are applied 3 times a day for six days) and the shear modulus is characterized subsequently using a parallel plate geometry. Substantial increases in the shear modulus are observed: 3 fold in rabbit and 5 fold in human corneas. Studies of model collagen systems---collagen fibrils from rat-tail tendon and reconstituted collagen gels---indicate that interfibrillar cross-linking is responsible for the change in the mechanical properties of corneas. Analytical biochemistry is used to identify the molecular structure of chemical crosslinks, which form predominantly between the primary amines of lysine residues.

Wednesday 6:00 Crystal Ballroom

A potential biodegradable rubber – viscoelastic properties of a soybean oil based composite
Jingyuan Xu1, Zengshe Liu2, Sevim Z. Erhan2, and Craig J. Carriere1

1Biomaterials Processing Research, USDA, Peoria, IL 61604; 2Oil Chemical Research, USDA, Peoria, IL 61604

The linear viscoelastic properties of a new biomaterial made by Epoxidized Soybean Oil (ESO) were investigated at 150°C. ESO cross-linked by Triethylene Glycol Diamine exhibited strong viscoelastic solid properties. The storage moduli (G') was 20000 Pa over four frequency decades. The phase shifts were 14 - 18 degrees. Stress relaxation measurements showed that there was no relaxation up to 500 seconds. From plateau modulus we estimated that the molecular weight of cross-linked soybean oil was in the order of 105. The composites of cross-linked ESO with three different fibers had 15 - 50 times higher elasticity (G') than that of without fiber. Phase shifts were the same as cross-linked oil without fibers. But the linear range of rheological properties was much narrower than that of the material without fibers. The rheological properties and molecular weight of this biomaterial are very similar to those of synthetic rubbers such as polyisoprene, polyvinyl ethylene and polybutadiene etc. These results implied that this biomaterial has high potential to replace some of the synthetic rubbers and/or plastics.
Influence of the retardation effects on rheological behaviour of liquid crystalline polymer

Shifang Han and Yubin Wang

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The hydroxypropylcellulose (HPC) is a lyotropic liquid crystalline polymer. Experimental investigation on the rheological and rheo-optical behaviour of the HPC is reported. In the present investigation the polariscope is used to take microstructural photos of the HPC for the different concentrations in water and different temperature. A group of the photos show the process that with change of the concentration the HPC changes from the isotropic behaviour to the anisotropic one, i.e. liquid crystalline. The experiments show with change of the temperature the HPC may be thermostropic. Using the rotating viscosimeter and cone and plate viscosimeter the apparent viscosity is measured with change of the shear rate for different temperature. The results of the rheological measurements are shown by figures. The experimental results are compared with the theoretical results calculated by the constitutive equation of rate type for LC polymer. It is shown that the retardation effects have remarkable influence of the rheological behaviour of the LC polymer fluid.

Aqueous solutions of block copolypeptides: Controlling rheology and phase behavior through block architecture

Victor Breedveld1, Andrew Nowak2, Timothy J. Deming2, and David J. Pine1

1Department of Chemical Engineering, University of California, Santa Barbara, CA 93106; 2Department of Materials, University of California, Santa Barbara, CA 93106

Recently, a novel synthesis method was developed for block copolypeptides of well-controlled size and block composition. The polymerization technique gives access to a large number of amino acid monomeric building blocks with a variety of chemical characteristics. In addition, peptides can exhibit secondary structure (α-helix or β-sheet) as opposed to conventional block copolymers with random coil configuration. This gives rise to additional mechanisms of self-assembly, well-known in proteins, thus controlling the properties of block copolypeptide solutions by block architecture.

We present results for aqueous solutions of diblocks with a water soluble polyelectrolyte block (L-lysine) and a hydrophobic block of varying composition. Both oscillatory and steady shear rheology reveal interesting features. In dilute systems, the block polymers assemble due to their amphiphilic nature, raising the viscosity of the solution. At higher but still low concentrations (as low as 0.25% by weight) the polymer solutions form strong gels even if their molecular weight is low (ca. 25000). When the gels are broken down under steady shear, they show rapid recovery after cessation of flow, generally within a few seconds. The gelation concentration is a strong function of molecular weight, relative block length and secondary block structure. Diblock copolypeptides combine the rapid recovery of short amphiphilic surfactants with the low gelation concentration found in high molecular weight associating polymers. The structure of the gels has been investigated with various techniques. Confocal microscopy and micro rheological tools have revealed that the block copolypeptide gels are macroporous with pore sizes of a few micron.

Micro-rheology of “pom-pom” 1,4-polybutadiene solutions and melts

Juliani Juliani1 and Lynden A. Archer2

1Cornell University, Ithaca, NY; 2School of Chemical Engineering, Cornell University, Ithaca, NY

Linear and nonlinear rheology of various entangled multi-arm 1,4-polybutadienes (H-shaped A2-A-A2; six-arm (A3-A-A3); and eight-arm (A3-A2-A-A3)) are investigated using mechanical rheometry and optical polarimetry measurements. Several features of the rheology of multiarm polymers appear unique and underscore the crucial role played by branch entanglements in dynamics. From small-amplitude oscillatory shear measurements, we find that the zero shear viscosity of entangled multi-arm polymers follow the same dependence on cross-bar (A) molecular weight as observed in linear 1,4-polybutadienes. The terminal time, on the other hand, increases more slowly with cross-bar molecular weight (by as much as a factor of the square root of molecular weight slower than zero shear
viscosity). Side branches are also found to have a more profound effect on rheological response. Specifically, if the degree of polymerization $N_{cb}$ of the central section (cross-bar) of a LCB molecule is held fixed, and the arm degree of polymerization $N_a$ varied in the vicinity of the entanglement threshold ($N_a \sim N_e$), the terminal time and viscosity are enhanced much more than expected from current theories. In non-linear step and steady shear flows we discuss the effect of arm withdrawal mechanism on long-time damping properties and orientation angle dynamics.

Wednesday 6:00 Crystal Ballroom

**Unusual features in the linear viscoelasticity of telechelic fluoroalkyl PEGs**

**Rowan-Louise Hough** and Robert J. English

*Centre for Water Soluble Polymers, North East Wales Institute, Wrexham LL11 2AW, United Kingdom*

We report on the aqueous solution rheology of a series of hydrophobically associating polymers, based on poly(ethylene glycol) end-capped with partially-fluorinated alkyl groups containing 6-9 carbon atoms. These polymers are derived from a poly(ethylene glycol) of molecular weight 35,000 Da, via sequential reaction with a large excess of isophorone disocyanate and a fluorinated alcohol. This yields polymers with complete end substitution and a minimum of chain extension. In contrast with similar polymers based on hydrocarbon hydrophobes, these materials form homogeneous aqueous solutions up to a concentration of 20 gdl$^{-1}$, no region of phase separation being observed. The linear viscoelasticity is characterised by a number of unusual features, not previously observed with hydrocarbon based telechelic polymers. Firstly, the concentration dependence of the zero shear viscosity is characterised by several regimes, described by different scaling exponents. Secondly, the frequency dependence of the small deformation moduli deviates strongly from the simple Maxwellian response often exhibited by associative polymers of this type. Specifically, several plateau regions in $G'$ may be observed. Interestingly, these trends are in good agreement with recent theoretical treatments of comb associative polymers [Rubinstein and Semenov, Macromolecules, 34(2001), 1058-1068; Jongschaap et al., Macromolecules, 34(2001), 1031-1038]. A microstructural interpretation is proposed, specifically that stress relaxation in these materials is governed by self-assembly into large-scale structures.

Wednesday 6:00 Crystal Ballroom

**Model rheological behavior of mixed systems of nonionic polymer and living polyelectrolyte**

**My Hang T. Truong** and Lynn M. Walker

*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15232*

Semidilute systems of wormlike micelles are often characterized by single, dominant relaxation times of the order of tens of seconds. According to Cates and Candau (J. Phys.: Cond. Matter, 2 (1990) 6869), this single timescale corresponds to the reptation of the micelles averaged by the breaking time. In this work, the effects of various polymeric additives on semidilute systems of cetyltrimethylammonium p-toluenesulfonate (CTAT) are quantified using dynamic mechanical testing. The effects of additives on the low frequency dynamic viscosity and dominant relaxation time of these semidilute systems are analogous to the effects on the zero-shear viscosity and critical shear rate in dilute micellar systems. Recovering relaxation spectra with current modeling techniques shows distinct deviations from simple Maxwell or single-relaxation time fluid behavior even at low polymer concentration.

Wednesday 6:00 Crystal Ballroom

**Hydrophobic effects on rheological properties of polyelectrolytes in aqueous solutions without added salt**

**Nopparat Plucktaveesak**, Julia S. Tan, and Ralph H. Colby

*1Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802; 2Imaging Materials and Media, Research and Development, Eastman Kodak Company, Rochester, NY 14650*

A variety of alternating copolymers of maleic acid with comonomers of different hydrophobicity have been used to systematically alter the rheology of polyelectrolyte solutions in pure water. At low polyelectrolyte concentrations, the viscosity is proportional to the square root of concentration, as expected for semidilute unentangled polyelectrolytes. Above an entanglement concentration, a stronger concentration dependence of viscosity is observed, consistent with the prediction of scaling theory for entangled polyelectrolyte solutions. The changes in
entanglement concentration and overlap concentration with the structure of hydrophobic comonomer will be discussed in terms of the Dobrynin/de Gennes scaling theory.

Wednesday 6:00 Crystal Ballroom PO9

Rheological and processing properties of blends of hyperbranched and linear polymers

Ibrahim Sendijarevic and Anthony J. McHugh
Chemical Engineering, University of Illinois, Urbana, IL 61801

The role of molecular architecture and end-group functionality on the rheology and processing behavior of blends of polyetherimide (PEI) hyperbranched polymers (HBP) has been studied. Architecture has been varied from linear to fully hyperbranched by using copolymers synthesized from various AB/AB2 starting compositions. End-group functionality and size has been investigated for systems containing TBS (tert-butyldimethylsilyl) and polyolefin end groups. The linear and non-linear viscoelastic properties of solutions and blends of the various PEI HBPs with polybutadiene and polyethylene indicate that pronounced decreases in solution viscosity occur as the concentration of polyolefin end groups is increased. Confocal and electron microscopy of fluorescent tagged end groups have also been used to provide in-situ data on phase behavior dynamics of blends of these systems. Extrusion of thin films was also used to correlate mechanical properties with the rheological and phase behavior.

Wednesday 6:00 Crystal Ballroom PO10

Encapsulated microbubbles in blood flow: New method for drug/gene delivery

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Encapsulated gas microbubbles are well known as contrast agents for medical ultrasound imaging. Such bubbles, with an average size less than that of a red blood cell, are capable to penetrate even into the smallest capillaries and release drugs and genes, incorporated either inside them or on their surface, under the action of ultrasound. Moreover, the microbubbles will transport a specific drug to a specific site within the body if their surface contains ligands. Commercial development of these ideas is in its initial phase, but methods for preparing such microbubbles have already been patented. From a practical point of view, the targeted drug/gene delivery agents should: 1) be able to reach the target site and flow through it; 2) remain stable long enough to circulate and accumulate at the binding site; 3) not detach from the target in the flowing blood (their binding to the target should be firm); 4) rupture under exposition to ultrasound to achieve targeted drug release; 5) not lead to deleterious bioeffects.

The goals of this project are to model the dynamics of drug- or gene-containing microbubbles in blood flow and, based on the conditions above, to identify the mechanical properties of the microbubble and its coating by which drug/gene delivery will be effective and safe. For this, we plan to study the mechanisms of bubble instability in blood flow, investigate the effects of hydrodynamic and acoustic radiation forces on bubble dynamics during the flow of the microbubble through the target site, consider radial oscillations of a single microbubble and a group of microbubbles (a bubble cloud) near blood vessel walls, and analyze the bioeffects that can arise due to the interaction between ultrasound and the oscillating microbubble.

Wednesday 6:00 Crystal Ballroom PO11

Transient shear and extensional rheological properties of intercalated clay/polymer nanocomposites

Hojun Lee and Gareth H. McKinley
Dept. Mechanical Engineering, M.I.T., Cambridge, MA 02139

The steady and transient rheological properties of nanofilled viscoelastic polymeric fluids were investigated using a commercial nylon melt and a polystyrene-based Boger fluid as matrix materials. The composites were prepared by melt-mixing and stirring the montmorillonite clay particles and polymer. Studies covering a range of clay concentrations and various mixing conditions were performed to determine the effects of the clay and the degree of intercalated structure on the linear and non-linear rheology of the resulting clay/polymer nanocomposites. Both the filled nylon melt and Boger fluid were observed to have an intercalated morphological structure (as determined by X-ray diffraction), with the gallery-spacing of the clay layers increased by about 58% over that of the pure clay. The storage and loss moduli are strongly dependent on the clay content and at moderate volume fractions (ca. 5%) a
yield stress develops as a result of the percolated filler structure. The nonlinear response of the materials also was investigated by following the evolution in both the shear stress and the first normal stress difference. The steady-state values of these viscometric functions both increase moderately as the clay content is increased; however the transient response is dramatically altered. Below the percolation threshold, the transient material functions of the nanoclay/PS solution exhibit nonlinear characteristics such as stress overshoots which are similar to those of unfilled Boger fluids. However, beyond the percolation threshold, the nonlinear properties are dominated by the secondary clay microstructure resulting in dampening of the nonlinear characteristics of the viscoelastic matrix and the development of purely strain-dependent transient responses more reminiscent of paste-like materials. Measurements in a capillary breakup rheometer also show considerable modifications in the transient extensional rheology of the filled nanocomposite Boger fluids due to the presence of the secondary nanofiller structure.

Wednesday 6:00 Crystal Ballroom PO12

Time evolution microstructures in polymer/layered silicate nanocomposites
Jun uk Park¹, Do hoon Kim¹, Kyung H Ahn², and Seung J Lee²

¹School of Chemical Engineering, Seoul National University, Seoul, Republic of Korea; ²Seoul National University, Seoul, Republic of Korea

In this study, we prepared several polymer/layered silicate nanocomposites, and investigated the time evolution of microstructures for both intercalated and exfoliated systems. We could separate the contribution of exfoliation and the dispersion of tactoids. As for kinetics, exfoliation proceeds very quickly, however the dispersion of tactoids may proceed slowly depending on the system. As mixing time goes on, the degree of dispersion increases with mixing time, which influences on the increase of rheological properties of the exfoliated systems. No increase was observed for intercalated systems. In the exfoliated system, the stress transfer is enhanced and the storage modulus increases because it is easy to interact between the matrix polymer and the modified organic silicate layer. In addition, we propose Fast Fourier Transform (FFT) method as a way of probing the nanostructures. As FFT parameters show distinct difference between the systems, FFT provides us valuable information on the microstructure in nonlinear regime.

Wednesday 6:00 Crystal Ballroom PO13

Dynamic properties of shear thickening colloidal suspensions
Young S. Lee, Kyle Miller, and Norman J. Wagner
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The transient shear rheology (i.e. frequency and strain dependence) is compared to the steady rheology for a model colloidal dispersion through the shear thickening transition. Reversible shear thickening is observed and the transition is compared to theoretical predictions. Steady and transient shear thickening are observed to occur at the same value of the average stress. The critical strain for shear thickening was found to depend inversely on the frequency at fixed applied stress. Lissajous plots illustrate the transition in material properties through the shear thickening transition. These results can be used to design devices based on the shear thickening response.

Wednesday 6:00 Crystal Ballroom PO14

Melt rheology, drop deformation and morphology development during crystallization of phase-separated blends
Derek W. Thurman, Lucia Fernandez-Ballester, and Julia A. Kornfield
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Using a homologous series of polyolefins that are based on the same isotactic polypropylene (iPP) graft ethylene-propylene (EP), we examine the role of addition of heterogeneous nucleant and phase-separated EP on morphology development during shear-enhanced crystallization. Complex morphologies develop in the blend as a function of the applied shear stress, suggesting that there is a competition between the timescale for crystallization and the timescale for droplet relaxation. Real-time rheo-optical probes of structure are used to gain insight into the transient events that lead to the solid state morphology observed ex situ. Shear at sufficiently high stress induces a transition to oriented growth and relatively rapid impingment; this transition to oriented growth is enhanced in nucleated samples relative to the base resin. In turn, the flow-enhanced crystallization traps transient droplet morphologies, provided that the local crystallization time is rapid relative to the droplet shape-relaxation time.
Temperature and concentration dependence of bubble dynamics in wormlike micellar fluids

Nestor Z. Handzy and Andrew Belmonte
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Bubbles rising through micellar solutions exhibit interesting behavior. As in polymeric fluids, a bubble of sufficient size has an apparent cusp, though in wormlike micellar fluids bubbles can also undergo oscillations in shape and velocity. We experimentally study the dependence of these properties on temperature and concentration for equimolar solutions of cetylpyridinium chloride and sodium salicylate. For each concentration we find a temperature range in which bubbles lose their oscillations while retaining a cusp. We also find that the oscillations at low concentrations are qualitatively distinct from the oscillations at higher concentrations.

Drop pinch-off and filament dynamics of wormlike micellar fluids

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Observations are presented of several novel phenomena involved in the dynamics of a falling drop of viscoelastic micellar fluid. At low concentration, the cylindrical filament necks down and pinches off rapidly (~ 10 ms) at one location along the filament. After pinch-off the free filament ends retract and no satellite drops are formed. At higher concentrations, the pinch-off also occurs along the filament, but in a more gradual process (~ 1 s). Furthermore, the free filament ends do not fully retract, instead retaining some of their deformation. The falling drop is also observed to slow or even stop (stall) before pinch-off, indicating that sufficient elastic stress has built up to balance its weight. A detailed study of a simple model for the filament using the FENE-CR constitutive equation indicates that this stall occurs in the range of low solvent viscosity, high elasticity, and high molecular weight. At the highest concentrations a surface “blistering” instability is seen along the filament long before pinch-off occurs.

Elastification of concentrated emulsions

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We have experimentally studied how shear-induced droplet rupturing affects the rheology of concentrated silicone oil-in-water/surfactant emulsions. We first make a crude premixed emulsion of polydisperse large (100 µm) droplets at a fixed volume fraction, φ, by gently stirring the water+surfactant solution and slowly adding the oil. Using a controlled strain rheometer, we rupture the droplets by repeatedly applying a small number of large amplitude strain oscillations and then probing the frequency-dependent linear complex shear modulus using small amplitude oscillatory strains. We call this general method of successively altering and probing a complex fluid "Sinusoidal Amplitude Modulation" (SAM) rheometry. For large enough φ where the droplets are packed and eventually ruptured to the micron size scale, we observe that the storage modulus of concentrated emulsions increases dramatically and then saturates, whereas the loss modulus does not change much during the rupturing. The increase in the emulsion's elasticity is consistent with the increase in the average Laplace pressure of the droplets as they are ruptured to smaller sizes.

Elasticity-driven shape oscillations of a non-Newtonian drop

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Small-amplitude axisymmetric shape deformations of a non-Newtonian liquid drop in microgravity are theoretically analyzed. Using the Jeffreys constitutive equation for linear viscoelasticity, the characteristic equation for the frequency and decay factor of the shape oscillations is derived. Asymptotic analysis of this equation is performed in
the low- and high-viscosity limits and for the cases of small, moderate, and large elasticities. Elastic effects are shown to give rise to a new type of shape oscillation which does not depend on the surface tension. The existence of such oscillations is confirmed by numerical solution of the characteristic equation in various regimes. A method for determining the viscoelastic properties of highly viscous liquids based upon experimental measurements of the frequency and damping rate of such shape oscillations is suggested.

Wednesday 6:00 Crystal Ballroom

**Visualizing slip at polymer-polymer melt interfaces**

Rui Zhao and Christopher W. Macosko

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A number of researchers have reported an anomalous lowering of viscosity in immiscible polymer blends. Slip at the interfaces between the polymer melts has been proposed to explain these observations. In our previous study, the rheological measurements on coextruded Polypropylene (PP) and polystyrene (PS) multilayers show strong evidence of interfacial slip. The calculated interfacial viscosity is a function of shear stress and about 30 times lower than that of the bulk materials at a stress of 5000 Pa. Since interfacial slip is basically spatial discontinuity of rate of deformation (velocity gradient) across interfaces, a measure of this discontinuity is a direct evidence of the slip. For this purpose, carbon black particles were imbedded in PP/PS bilayer samples, and the bilayer samples were sheared in a parallel plates rheometer. After steady shear, the carbon black particles were carried with the deformation of the polymer chains. A spatial displacement of those particles in the velocity gradient direction was measured across the interfaces due to slip. This displacement, which was correlated to the interfacial viscosity, is also a function of shear stress.

Wednesday 6:00 Crystal Ballroom

**Critical properties and phase separation in lattice Boltzmann fluid mixtures**

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Basic equilibrium properties of Lattice Boltzmann (LB) fluid mixtures (coexistence curve, surface tension, interfacial profile, correlation length) are calculated to characterize the critical phenomena occurring in these model liquids and to establish a reduced variable description allowing a comparison with real fluid mixtures. We observe mean-field critical exponents and amplitudes so that the LB model may be useful for modeling high molecular weight polymer blends and other fluid mixtures approximated over a wide temperature range by mean-field theory. We also briefly consider phase separation under quiescent and shearing conditions and point out the strong influence of interacting boundaries on the qualitative form of the late stage phase separation morphology.

Wednesday 6:00 Crystal Ballroom

**Rheological characterization of fuel oils and effect of paraffins and asphaltenes constituents**

Ismail M. El-gamal¹, Galal M. Abdel-Aleim², Fatma K. Gad², and Abdel-naby A. Bahran²

¹Petroleum Applications, Egyptian Petroleum Research Institute, Cairo, Cairo, Egypt; ²Faculty of Petroleum and Mining Engineering, Suez Canal Uni., Suez, Egypt

The shear stress-shear rate relationship for three fuel oils with variant paraffins and asphaltenes content was measured. The experimental data were fitted to eight different non-Newtonian flow models. The thixotropic behavior of the fuels was studied above, at and below their pour point. The influence of paraffins and asphaltenes constituents on the rheological parameters; yield stress and viscosity has been investigated. The rheological character of the paraffinic and mixed base types showed pseudoplastic behavior with yield stress at and below their pour point while loose this stress 10° above the pour point. The asphaltic type displayed pseudoplastic fashion without yield stress except that below the pour point. Thus, the higher the paraffin content of the fuel, the more likely to hold a yield stress. On the other hand, the higher the asphaltene content the higher the viscosity above, at and below the pour point. However the rheology of the three types approaches the Newtonian character by increasing temperature above the pour point in the order paraffinic prior to mixed base and asphaltic one. The flow models which fit well the experimental data was only applicable at a limited range of shear rates and temperatures. The flow models of Bingham, Casson, Herschel-Bulkley and Ostwald proved to be superior to the other four
proposed mathematical equations for fitting the test data. The three fuel types showed pronounced thixotropic behavior, which increases with the increase of paraffin content in the fuel and with the decrease of temperature particularly below the pour point. *Author to whom correspondence should be addressed.*

Wednesday 6:00 Crystal Ballroom

**Dynamic self-consistent field study of rheology and morphology of block copolymer under shear flow**

**Maja Mihajlovic and Yitzhak Shnidman**  
*Department of Chemical Engineering and Chemistry, Polytechnic University, Brooklyn, NY 11201*

A dynamic self-consistent field (DSCF) theory is developed to study polymeric fluids under shear. The model combines a self-consistent field (SCF) theory of Scheutjens and Fleer (Scheutjens, J.M.H.M.; Fleer, G.J. J. Phys. Chem., 83, 1619, 1979) with a convective-diffusive lattice-gas (CDLG) model (Khan, A. A.; Shnidman, Y. Prog. Coll. Polym. Sci., 103, 251, 1997). Here, a cubic lattice adjoining two parallel planar surfaces represents a polymeric fluid and chain conformation statistics is generated by the SCF matrix formalism that relates segmental volume fractions to segmental site probabilities. To follow the temporal evolutions of local chain segments and momenta, we are coupling it with convective-diffusive transport equations.

We apply the model to block copolymer fluids under a simple shear, imposed by moving parallel plates into opposite direction with the same velocity. The polymer chains are below entanglement molecular weight and their entropic stretching is accounted by dumbbell model. Here we present a systematic study of the rheology and morphology of such systems; time evolution of segmental volume fractions, free segment probabilities, velocity, chain stretching, shear stress, first normal stress coefficient and viscosity, as well as their dependence on time, shear rate, chain length, the distance between parallel plates and segmental and surface interaction parameters.

Wednesday 6:00 Crystal Ballroom

**Analysis of hydrodynamic interactions for DPD polymer chains in solution**

**Guoai Pan and Charles W. Manke**  
*Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202*

The velocity autocorrelation analysis of Malevanets and Yeomans [1] is employed to evaluate hydrodynamic interactions among the beads of a polymer chain in dilute solution, as modeled by Dissipative Particle Dynamics [2] (DPD). The polymer solution model consists of a 10-bead chain with FENE spring connectors surrounded by a solvent of free DPD particles. Simulation parameters are varied to study the influence of Schmidt number and box size on hydrodynamic interactions. For each case, the contributions of hydrodynamic interactions to the velocity autocorrelation function decay are compared to the predictions of the Malevanets-Yeomans theory.


Wednesday 6:00 Crystal Ballroom

**Viscoelastic free surface instabilities during exponential stretching**

**Ryan D. Welsh, José Bico, and Gareth H. McKinley**  
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A viscous Newtonian fluid and two model polystyrene Boger fluids are used to investigate the evolution of free-surface instabilities during the debonding of two cylindrical parallel rigid surfaces. A filament stretching rheometer is used to separate the surfaces at an exponential rate and simultaneously measure the evolution in the axial force. The experimental configuration also allows for simultaneous imaging of the fluid sample from beneath the endplate during the test. The test method is similar to both the probe-tack test used in adhesive testing and filament stretching rheometry experiments. Several geometric aspect ratios (defined as the ratio of initial sample height to radius) are used to vary the degree of sample confinement. These geometries bridge the gap between conventional adhesive testing and extensional rheometry. Three types of instabilities are seen in the experiments. The first is similar to the classical Saffman-Taylor instability, in which fingers of a less viscous fluid penetrate into a more viscous one during pressure driven flow. In the present three-dimensional analog, the instability occurs at a critical rate of plate separation for a given geometry and fluid. Larger pressure gradients result from higher fluid viscosity, a more
confined geometry and greater rate of plate separation. A second instability is caused by the extensional stress growth in the elastic fluids and occurs at a critical Hencky strain for a given Deborah number. This instability is characterized by the growth of fingers radially outward from the base of a stable, cylindrical fluid column. As this instability progresses, the fingers can repeatedly bifurcate resulting in complex surface morphologies. Finally, cavitation in the test fluids occurs below a critical negative gage pressure within the fluid. Modal interactions of the three instabilities are also observed and lead to complex evolution of the elastic instability. A video is available at: http://web.mit.edu/nnf/fingering.html

Wednesday 6:00 Crystal Ballroom PO25

Cavitation, rupture and extensional deformation in extrusion instabilities
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We present a first observation that polymeric materials cavitate during capillary extrusion. The cavitation is observed at the wall just upstream of the exit at large flow rates that correspond to the "gross melt fracture" instability. The cavities nucleate, grow to a size of (~100x100x10 microns) and then (sometimes) collapse in a time scale of of order 10 ms. Cavitation was numerically predicted in 1991 by Tremblay as a possible cause of the sharkskin instability. Our results demonstrate that cavitation does indeed occur, but not until one reaches the higher flow rates characteristic of gross melt fracture. We attempt to integrate our observations with the established literature result that gross melt fracture is initiated in the entrance region of the capillary. Our findings are also discussed in relation to our recently presented data on the sharkskin instability (which occurs at lower flow rates). There, we measured the flow kinetics and velocity profiles in the exit region of a capillary tube to determine that a surface tearing at the exit causes sharkskin.

Wednesday 6:00 Crystal Ballroom PO26

Creep and recovery of novel organic-inorganic polymer hybrids
Joshua U. Otaigbe and Sunil B. Adalja
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A novel class of organic-inorganic polymer hybrids were developed by melt-blending up to 50 (v/v)% [~83 (w/w)%] tin-based polyphosphate glass (Pglass) and low-density polyethylene (LDPE) in conventional plastics processing equipment. The creep and recovery behavior of these polymer hybrids at 30C were studied to understand the effect of the Pglass on the creep resistance of the LDPE. The results suggest that the Pglass acts as a reinforcement, and an increase in the Pglass loading leads to significantly lower creep strains. This creep resistance is further enhanced by pre-treating the Pglass with coupling agents prior to incorporating them into the Pglass-LDPE hybrids. The experimental creep compliance of these materials conformed excellently with an empirical power-law equation and a modified Burgers' model, suggesting that the materials are linearly viscoelastic under the test conditions.

Wednesday 6:00 Crystal Ballroom PO27

Wall slip and rupture of elastomers
Stephane F. Costeux and John M. Dealy
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Experiments on polybutadiene and polyisoprene were carried out in a Sliding Plate rheometer using steel and glass plates. A method to determine slip velocity on both surfaces from stress measurement was compared with direct observation. Solutions were found to prevent secondary flow of the polymer and a new normal force transducer is presented.

Recorded videos through a glass plate showed that slip and rupture are two coupled mechanisms that prevent proper shearing of the polymer. Videos also revealed unexpected behavior of the polymer to escape slip.

Finally, an attempt was made to prevent slip using a adhesive in order to study the rupture of a long chain branched polyethylene.
Qualitative estimation of blend morphology from normal stress data
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A method to obtain blend morphological information from normal stress measurements is proposed. Blends with Newtonian and immiscible constituents are considered. For dilute blends, at steady state a master curve can be readily obtained. The curve is parametric in the viscosity ratio, and relates the actual capillary number to the dimensionless interfacial stress. As a consequence, stress data determine a capillary number through which a characteristic dimension of the morphology can be extracted. The master curve is here estimated by predicting the drop deformation with a phenomenological model. Morphology predictions are compared with experimental data found in the literature; the comparison gives satisfactory results even at intermediate concentration.

Shear thinning in polyelectrolyte solutions
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Owing to their strong contraction as concentration is increased, polyelectrolyte solutions have a wide range of concentration where they are semidilute (meaning that chains overlap each other) but are not entangled. The longest relaxation time and zero-shear-rate viscosity of semidilute unentangled polyelectrolytes are described by the Rouse model, but the Rouse model does not predict shear thinning. Experimental data demonstrate that the solutions exhibit shear thinning for shear rates larger than the reciprocal of their longest viscoelastic relaxation time. We present a simple model for chain stretching in shear flow that accounts for the observations, and predicts that the apparent viscosity scales as the reciprocal square root of shear rate.

Standard reference materials: Non-Newtonian fluids for rheological measurements
Carl R. Schultheisz¹ and Gregory B. McKenna²
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NIST produces Standard Reference Materials for calibration, for quality assurance and for research into improved measurement methods. NIST is developing two non-Newtonian fluids as standards for comparing measurements of the rheological behaviors of complex fluids. For these fluids, NIST certifies the linear viscoelastic behavior and the shear-rate dependence of the viscosity and the first normal stress difference between 0 °C and 50 °C. Certification has recently been completed for a polymer solution designated SRM 2490, consisting of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane. Work is currently underway certifying SRM 2491, a poly(dimethylsiloxane) melt. A round robin interlaboratory comparison with the fluids is planned to investigate variability in rheological measurements.

Quantitative first and third normal stress measurements in polymer melts: Role of tacticity and architecture
Vivek Maheshwari, Semen B. Kharchenko, and Rangaramanujam M. Kannan
Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Understanding structure-property relationship in polymers is vital to their processing. This has gained further significance with the emergence of novel synthesis methods to produce materials with varying architecture (anionic synthesis) and tacticity (metallocene-catalyst technologies). Normal stresses have profound impact on the processing behavior and product properties, and are very sensitive to molecular details. Measuring the complete stress tensor of complex polymers would not only help characterize the flow behavior, but also enable development of appropriate
constitutive equations for this class of emerging polymeric materials. This has been a challenging task, especially in the linear viscoelastic regime. Quantitative measurements have been very scarce for polymer melts, especially for polymers with varying architectures and tacticity.

We have developed a rheo-optical apparatus, and a signal analysis scheme capable of measuring the shear stress, and either first normal stress difference (N1) or the third normal stress difference (N3) simultaneously and quantitatively, under oscillatory shear. The stress-optical rule (SoR) is used to calculate the normal stress differences from flow birefringence. For homopolymer melts of PDMS and polystyrene, frequency dependence of the measured N1 and N3 agree well with the predictions of traditional constitutive equations. To our knowledge, these are the first quantitative flow birefringence N1 measurements of polymer melts under oscillatory shear.

For a semi-syndiotactic polypropylene, we observe a unique normal stress response characterized by a total failure of the stress-optic rule. This is manifested in the significantly higher optically measured N1 response below 70°C, even though no thermal transition is apparent in the DSC curve. We suggest that this reflects the elastic nature of the mesoscopic crystalline structures that may be forming in these materials. Results will also be presented for star and hyperbranched PS melts.

**Wednesday 6:00 Crystal Ballroom PO32**

**Rheological profile of Okenia hypogaea starch dispersions in aqueous solution of DMSO**

Javier Solorza-Feria, Arturo L. Bello-Perez, Antonio R. Jimenez-Aparicio, and Martha L. Arenas-Ocampo

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Okenia hypogaea (Schlech. & Cham.) belongs to the family of the Nyctaginaceae, with a probable origin in Mexico. It is a perennial herbaceous plant that produces a seed with a high content of starch. The aim of this work was to study the rheological behaviour of Okenia starch dispersions in aqueous solution (90/10, v/v) of dimethyl sulfoxide (DMSO). Okenia starch dispersions with 3 and 7% Total Solids (w/v) were prepared at 20°C and rheological tests (flow curves) were undertaken at 20, 40 and 60°C, using a shear rate controlled rotational viscometer. The data fitted well both the power law equation: \( \sigma = K \gamma^n \) and the Casson model for non-Newtonian fluids: \( \left( \sigma^0.5 \right) = (\sigma_{oc})^{0.5} + (\eta\alpha \gamma^{0.5}) \) with values of \( R^2 \) (coefficient of determination) bigger than 0.9. Flow curves and flow behaviour index indicated shear-thinning behaviour, with a yield stress value for Okenia starch dispersions. All rheological parameters (n, K) were affected by the total solids concentration and the measurement temperature. Overall, Okenia starch dispersions behaved similarly to potato starch dispersions and cornstarch dispersions used as controls.

**Wednesday 6:00 Crystal Ballroom PO33**

**Havriliak-Negami analyses of viscosity data for some model polymer systems**

Jay Janzen

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Results are summarized from Havriliak-Negami (HN) analyses of viscosities of some mathematical model systems and of some very narrowly distributed linear flexible polymers of theoretical interest. The objective is to clarify the physical interpretation of HN fit parameters in these limiting model cases. "Characteristic viscous relaxation times" obtained by HN fitting coincide precisely with number-average relaxation times in log-Gaussian relaxation spectra of modest breadth. A general "rheological breadth index" is constructed as an inverse function of the breadth-controlling exponent in the HN model in such a way that it bears direct comparison with molecular mass distribution breadth determined chromatographically. Some potentially fruitful connections between HN parameters and nonlinear viscoelastic properties are pointed out.

**Wednesday 6:00 Crystal Ballroom PO34**

**Spurt and other shear flow dynamics for a thixotropic Johnson-Segalman model**

Bob W. Kolkka

*Math Sciences, Michigan Technological University, Houghton, MI 49931*

A thixotropic generalization, proposed by Fredrickson AICHE J, 16 (1970), is applied to the Johnson-Segalman model. A nonmonotonic steady shear response can be realized as a result of both non-affine motion and a shear rate dependent destruction function in the fluidity evolution equation. Spurt dynamics are examined in the case where an
added Newtonian viscosity is present. The time evolution is found to exhibit the same basic dynamical features as in the non-thixotropic case examined by Malkus et al. J. Comp. Phys. 87 (1990), even in the upper-convected limit. Also, for applied shear rates in the unstable region, the shear stress does not approach a unique value in contrast to the case without added Newtonian viscosity addressed by Bautista et al. JNNFM, 94 (2000). In addition, results for step strain and startup of steady shear flows for a variety of parameter regimes will be presented.

Wednesday 6:00 Crystal Ballroom PO35

**Numerical analysis and experimental studies on the role of rheological properties in effecting die swell of low-density polyethylene, polypropylene and polystyrene**

Joshua U. Otaigbe and Kamal K. Kar

*Material Science & Engineering, Iowa State University, Ames, IA 50010*

In order to predict die-swell observed in real polymer processing equipment, we develop a model for non-Newtonian fluids using strain energy density function, maximum recoverable deformation, Gaussian network theory and first normal stress difference. The proposed model is tested with experimental data of LDPE, PP and PS and compared with predictions from existing models such as Tanner's model, White and Roman's model, and Kumar et. al. model. A wide deviation is observed between predictions from existing models and experimental data. Further, a special linear relationship between die swell and maximum recoverable deformation and a nonlinear relationship between die swell, storage and loss moduli were found for the polymers tested.

Wednesday 6:00 Crystal Ballroom PO36

**Large amplitude oscillatory shear flow of a network model**

Hoon Goo Sim, Seung hwa Kim, Kyung H Ahn, and Seung J Lee

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As a way to probe its microstructure of a complex fluid, linear viscoelasticity has predominantly been used for many years due to its well-defined mathematical simplicity and ease to use. However, wider realm of nonlinear viscoelasticity is open as a new frontier in the field of rheology. Typical strain sweep test is mathematically imprecise and sometimes misleading in nonlinear region; however, it gives plenty of information provided that enough attention is paid. Fourier transformation concept should be taken. The response to a sinusoidal shear flow shows strong nonlinearity with higher harmonic contributions at large strain amplitude. In this presentation, we classify the nonlinear behavior of complex fluids. We will show that the types of rheological behavior in the nonlinear response can be understood and interpreted by means of a kinetic parameter of a simple network model. The nonlinear behavior of a model will be analyzed in terms of FFT (Fast Fourier Transform) parameters.

Wednesday 6:00 Crystal Ballroom PO37

**Reptation relaxation probed by critical fluctuations in polymer solutions**

Andrei F. Kostko, Mikhail A. Anisimov, Jan V. Sengers, and Igor K. Yudin

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We have performed accurate dynamic light-scattering measurements for solutions of polystyrene in cyclohexane in a wide temperature range near their critical points of mixing. The polystyrene molecular weight varied from 200,000 up to 11,400,000. When the molecular radius becomes of the order of the inverse scattering wave number (or exceeds it), the intensity correlation function is found to be non-exponential due to internal modes of the polymer molecule. We have observed a significant discrepancy between the observed temperature dependence of the decay rate and that predicted by ordinary mode-coupling theory. The temperature dependence of the decay rate exhibits substantial deviations from the theoretical predictions when the characteristic times of critical and internal modes coincide. The values of the measured correlation time become much larger than expected. This dramatic slowing of the critical mode is interpreted in terms of reptation relaxation of long polymer chains. The effect is much more pronounced at large scattering angles, which correspond to small (intramolecular) length scales.

The research has been supported by National Science Foundation Grant No. CHE-9805260.
On constitutive equation of rate type for liquid crystalline polymer – anisotropic viscoelastic fluid
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The liquid crystalline (LC) polymer is an anisotropic viscoelastic fluid. The convected time derivative approach is used to develop the constitutive equation of rate type for LC polymer. Extending the Oldroyd fluid B for the corotational time derivative a constitutive equation of Oldroyd type is developed for the LC polymer. The microrheological effects are described by the macrorheological material functions. In the equation the anisotropic non-linear viscosities, relaxation and retardation times are introduced in order to describe non-linear nature of the material. The general form of the constitutive equation of Oldroyd type is given, which is specialized then for two LC polymer fluid model: LCP - B Fluid. The results show the orientational, anisotropic behaviour of the material functions of LC polymer fluid. In order to test the availability of a constitutive equation, the Poiseuille flow in tube is considered. For the flow the material functions are calculated by the constitutive equation of LCP - B fluid, then the apparent viscosity, first and second normal stress differences are obtained. The results of present investigation are compared in a good agreement with the experimental results by Baek and Larson (1993,1994). The anisotropic retardation time has more important influence on the change of the first and second normal stress differences with shear rates. The rheological behaviour of the LC polymer can be described by the constitutive equation of rate type by using the convected time derivative and introducing the anisotropic material functions.

Calculation of the discrete relaxation spectrum for polymeric materials using a nonlinear regression method
Gholamhossein Sodeifian and Ali Haghtalab
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The relaxation spectrum is an important tool for investigating the behavior of viscoelastic materials. The most popular procedure for determining the relaxation spectrum is the use of a small-amplitude oscillatory shear experiment to obtain the parameters in a multi mode Maxwell model. However, this is an ill-posed problem and its numerical solution is along with difficulties. The determination of the discrete relaxation spectrum by a linear regression approach is widespread in the practice and literature. In this work, a nonlinear regression technique, based on Marquardt-Levenberg procedure, is applied in which the minimization is performed with respect to both the discrete relaxations times and the relaxation moduli. Using this nonlinear optimization the spectrum parameters of a multi-mode Maxwell model were obtained for polymeric materials such as LDPE, HDPE and PS. It has been shown that in comparison with the other methods, the present approach is more efficient and it was found to give a very good fit with the fewest possible parameters.

A solution rheology approach to component dynamics in blends of polyisoprene/1,2-polybutadiene
Shanfeng Wang and Shi-Qing Wang
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A solution rheology approach has been applied to resolve component friction dynamics in mixtures of polyisoprene (PIP)/polyvinylethylene (PVE). This approach consists of separately evaluating rheological properties of entangled "object" solutions of PIP in oligomeric PVE (oVE) and "mirror" solutions of PVE in oligomeric PIP (oIP) at different compositions. By measuring the terminal relaxation times associated with PVE and PIP in the "object" and "mirror" solutions respectively, the friction coefficients $\zeta_{\text{PVE}}(\phi, T)$ and $\zeta_{\text{PIP}}(\phi, T)$ exhibit different temperature and composition dependence. Specifically, the low $T_g$ component, which is PIP in the present case, has a weaker dependence in comparison with the high $T_g$ component, which is PVE. Further analysis supports the idea of co-existence of two consecutive glass transitions in the blends. This observation can be explained by a revised free volume theory (FVT). In this revised theory, each component in the blend may experience a different degree of free volume.
**Effect of boundary conditions on steady rheological behaviour of mesophase pitch**
Dana Grecov, Alejandro D. Rey, and Ae-Gyeong Cheong

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Mesophase pitches are multicomponent discotic nematic liquid crystals, whose characteristic molecular weight is intermediate to low molar mass and polymeric nematic liquid crystals. Mesophase fluids are anisotropic viscoelastic textured materials whose rheological material properties are a function of deformation rates and textural features.

Flow modelling of these fluids is performed using a previously formulated (Singh and Rey, 2000) mesoscopic viscoelastic rheological theory that takes into account flow-induced texture transformations. Predictions for simple shear flow, under non-homogeneous conditions for the apparent shear viscosity and first normal stress differences are presented.

The rheological features are explained using macroscopic orientation effects, which predominate at low shear rates. A systematic investigation of different boundary and initial conditions was performed to characterize their effect on rheological properties. The effect of change in nematical potential on rheological properties of discotic mesophases was also analysed. The model predictions agree well with experiments.

**Combining rheology and SEC to quantitatively characterize long chain branching in an industrial polymer**
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*Solutia, Inc., Springfield, MA 01151*

Long chain branching manifests itself qualitatively through a variety of dilute solution and melt viscoelastic properties. Accurately quantifying these effects has been the subject of many recent studies and continues to be a challenge. In this presentation the problem is approached both theoretically and experimentally, the former by adapting and extending existing models, the latter by applying a variety of analytical techniques. These last include shear rheometry, particularly small amplitude oscillatory shear flows, multi-detector size exclusion chromatography, and related techniques.

The present paper details both the complementary contribution of each technique as well as their individual limitations toward characterizing long chain branching. A case study is presented using poly(vinyl butyral), an important commercial polymer whose end-use properties can be severely influenced by long chain branching. Poly(vinyl butyral) is a "real-world" polymer that is polydisperse with respect to both molecular weight and branching structure.

Branching information, including number and frequency of branches, is obtained via SEC using multi-angle light scattering data and applying the classic theory of Zimm and Stockmayer. In addition, linear viscoelastic properties in the melt are measured via shear rheometry. The differences observed in the flow properties due to branching are consistent with observations already presented in the literature for branched polyethylenes and polybutadienes, e.g., increased zero-shear-rate viscosity, severity of shear thinning, and flow activation energies, along with failure of time-temperature superposition. The linear viscoelastic properties are compared in detail with predictions from recently proposed tube-based models for branched topologies. The resulting fitted branching parameters are compared with those obtained via SEC.

**Pressure gradient rheometer**
Brian M. Tande and Abraham Vaynberg

*Chemical Engineering, University of Delaware, Newark, DE 19716; Analytical Department, Hercules Incorporated, Wilmington, DE 19808*

We describe a novel rheometer designed to measure the pressure gradient of tube flow as a function of rate. By fitting the data with several rheological models, we show that various types of viscous materials may be easily and accurately characterized using this simple device. We present pressure gradient data taken with this rheometer from several common materials, including a Newtonian oil, a commercial toothpaste, and cake frosting. The rheological
parameters (viscosity, yield stress, power law exponent) determined using this method are in good agreement with those found by conventional rotational rheometry. This simple and inexpensive device capable of characterizing diverse materials can be a useful addition to any material characterization laboratory.

Wednesday 6:00 Crystal Ballroom PO44

Rheo-optical FTIR spectroscopic investigation of crystal structure growth and response in semi-crystalline polymers
Rangaramanujam M. Kannan, Michael Sevegney, and Gautam Parthasarathy
Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Novel synthesis methods have made it possible to make polymers with well-defined composition, tacticity, architecture and molecular weight. This provides a tremendous flexibility to engineer products that have tailored properties at the molecular and nanostructural levels. However, quantifying and relating responses at these length scales to macroscopic properties is still a challenging task. We have developed a novel rheo-optical FTIR spectrometer to gain insights into responses at such length scales, by combining conventional mechanical testing with step-scan FTIR spectroscopy. Using polarization-modulation scheme, we monitor the quantitative dichroism spectra of the complex polymer over a wide range of conditions. Two mini rheometers with temperature control are used for small amplitude dynamic oscillatory deformation, and uniaxial extension.

Crystallization process and the response of the crystallites in polypropylenes (PP) can be a strong function of tacticity. The metallocene-catalyzed syndiotactic PP and mixed-tacticity PP crystallize significant slower than commercial i-PP. The slow crystallization kinetics in the metallocene PPs has a significant impact on the mechanical and orientation behavior in films. Rheo-optical FTIR spectroscopy is being used to quantify the responses of the amorphous, crystalline, and the 'mesophase' in these materials. In a semi-syndiotactic PP, the 'mesophase' growth is monitored by the growth of the 791 cm⁻¹, 895 cm⁻¹ peaks with time. These peaks are absent in isotactic PP (i-PP), pure syndiotactic PP (s-PP) and the growth of these peaks correlates well with AFM photographs of the same material. The dynamic change in the FTIR spectrum upon deformation reveals the response of these length scales. It appears that small changes in the tacticity can cause significant difference in the crystal formation, and subsequently to macroscopic properties. Results on i-PP, s-PP, and semi-syndiotactic PPs of varying tacticity will be presented.

Wednesday 6:00 Crystal Ballroom PO45

Actuating properties of soft gels with ordered iron particles: Basis for a shear actuator
Yuxian An¹, Bo Liu¹, and Montgomery T. Shaw²
¹Polymer Program, Institute of Material Sciences, University of Connecticut, Storrs, CT 06269; ²Polymer Program and Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269

Investigated were the actuating properties of soft electrorheological (ER) gels with ordered iron particles. Unlike ER fluids, the particles in gels do not change relative positions; thus structures can be created that will deform in an electrical field. To build such structures, a magnetic field was used to align iron particles during the cure of a liquid silicone prepolymer. The gap between the particles was controlled by swelling the crosslinked material with silicone prepolymer. Iron-particle chains were made with as little as 0.5 % particles and at angles from 0 to 60 ° to the normal of the sample surface. The ER, electrical and actuating properties of these materials were explored using rheometry and dielectrometry. Some examples of the results are as follows: With only 1 volume % particles, the modulus doubles at electrical field of around 2 kV/mm. With particle chain alignment of 45 °, shear stresses of around 140 Pa were measured with a special sandwich-type shear fixture.

Wednesday 6:00 Crystal Ballroom PO46

Squeeze-flow characterization of HDPE melts using a Fizeau interferometer
Edwin C. Cua¹ and Montgomery T. Shaw²
¹Polymer Program, Institute of Material Sciences, University of Connecticut, Storrs, CT 06269; ²Polymer Program and Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269

A novel squeeze-flow apparatus was devised to measure the viscosities of low-MFI HDPE melts at very low shear rates (< 10⁻³ s⁻¹) and stresses (in the order of 10 Pa). The apparatus is contained in a vacuum chamber that can be evacuated down to 10⁻⁸ torr and heated to 300°C. The polymer melt is squeezed with a constant force between a
plano-convex lens top lens and an optical flat that also serves as the chamber window. Changes in the gap between the lens and the flat are detected via Fizeau interferometry, which has a minimum resolution of one-quarter of the wavelength of the laser source used. High spatial resolution, complete freedom from drift and inert sample conditions are necessary for long-term experiments on sensitive materials; these conditions are met by the set-up. Several samples can be run simultaneously and "swapped" into the interferometer without disrupting the flow process.

The data from the squeeze runs were analyzed with a purely Newtonian model and GNF models. With the test resin selected, it was found that extrapolation of the usual dynamic data could result in a severely overestimated zero-shear-rate viscosity.

Wednesday 6:00 Crystal Ballroom

**RheoVision: The correlation between flow and microstructure**

Dirk Eidam, Frederic Bar, and Pierre Reinheimer  
*Rheology, Thermo Haake, Karlsruhe 76185, Germany*

Additional to the well-known rheo-mechanical methods, rheo-optical techniques have become helpful for the understanding of structure dynamics and structure changes. In a new rheometer concept called "RheoVision" a universal air-bearing rheometer has been combined with a microscope-camera-setup. With this combination the rheo-mechanical properties and the observation of microstructures can be correlated. Whereas most of the existing optical methods refer to the molecular level, RheoVision provides information about structural changes within the micrometer range. During a measurement, the rheological behaviour (rotation, oscillation, etc.) is recorded simultaneously with the corresponding image. In this context many samples (e.g. emulsions, gels and foams) from food, cosmetic, pharma and related industries can be characterized. Together with RheoVision a powerful image analyzing programme can be used. Both the behaviour of network structures and the orientation, deformation and possible degradation of aggregates will be monitored. Several examples will be presented and further future developments will be discussed.

Wednesday 6:00 Crystal Ballroom

**New developments for improving the accuracy in temperature control for rotational rheometers**

Joerg Laeuger¹, Monika Bernzen¹, and Gerhard Raffer²  
¹Physica Messtechnik GmbH, Stuttgart D-70567, Germany; ²Anton Paar GmbH, Graz, Austria

Since for almost all samples the temperature has a great influence on the rheological behavior, controlling the temperature with a high precision is crucial to receive reliable rheological data. Although this is a common place statement, in practical measurements inaccurate temperature control is still responsible for a large number of measurement uncertainties and errors. Designing a temperature control unit has to fulfill three main tasks: 1. Setting and measuring the right absolute temperature, 2. having no or almost no temperature gradients, 3. producing no significant temperature overshoots during the control process. Three different temperature control units for different temperature ranges and applications are described which were developed with the aim to fulfill the above mentioned requirements: 1. A peltier temperature control unit with an actively peltier controlled bottom plate and an actively peltier controlled hood (pat. pent.), 2. A electrically heated system with electrically heated bottom plate and electrically heated hood, 3. A convection temperature device based on a combination between electrically heating and convection. For all units a special calibration sensor was developed which in combination with an automatic temperature calibration software module can be used by the individual user to assure that the sample has the accurate temperature. For development purposes a special tool was designed to measure and minimize the horizontal and vertical temperature gradients. Measurements of absolute temperatures and temperature gradients as well as typical measurements are shown for all three temperature control units indicating the excellent performance of the described units.
Recent findings related to the kinetics and thermodynamics of Environmental Stress Cracking of glassy polymers
Alan J. Lesser
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003

Environmental Stress Cracking (ESC) involves the premature crazing and cracking of glassy polymers when they are subjected to nominally acceptable stress levels and certain surface-active agents (e.g., solvents, detergents). ESC has been a chronic problem in industry for more than 50 years. Yet only qualitative, phenomenological descriptions and remedies have been provided in the literature. In this paper, we present recent findings from and ongoing investigation aimed at developing more quantitative tools that predict the ESC response of polymer glasses when subjected to such environments. We discuss both thermodynamic and kinetic aspects of the problem and illustrate conditions upon which thermodynamic instabilities are predicted and kinetics then dictates time to failure. We present concepts to consider in more generalized states of stress and present complementary experiments aimed at isolating the effect of stress state and polymer orientation on the ESC behavior of the glass.

Viscoelasticity of gels obtained from EVA/SBS/motor oil solutions
Anton Santamaría, María E. Muñoz, and María S. Barral
Department of Polymer Science and Technology, University of The Basque Country, San Sebastián, Basque Country E-20018, Spain

Taking advantage of the use of waste liquids, like for instance used motor oils, is a subject of industrial and environmental interest. The formation of thermoreversible gels from solutions of ethylene vinyl acetate (EVA) copolymers in recycled motor oil has been recently reported [1]. Here we present results on viscoelasticity of ternary gels formed from solutions of EVA, SBS copolymers and waste motor oil. Frequency sweeps at a temperature of 25°C show, that for polymer concentrations (1:1 SBS:EVA) above 6%wt., both storage and loss moduli become frequency independent, which is a clear symptom of gel formation. From these measurements a characteristic elastic modulus of the gel, G_e, is obtained for each composition. For systems with a constant total polymer concentration (i.e. 20%wt. SBS+EVA) a rapid increase of G_e (beyond additive rule) is observed with the content of EVA. Temperature sweeps performed at a frequency of 1Hz, reveal that the elastic modulus decreases in a two step process. Two peaks, associated to this G’ decrease, are observed in tan d vs. temperature plots. The peaks correspond respectively to the fusion temperatures of binary EVA/oil gel and SBS/oil gel. The ternary gel resembles an interpenetrating system, where after EVA based network vanishes, SBS based network holds on giving rise to elastic moduli above 10^5 Pa.s.


Does movement during cure affect overall sealant performance?
Carl Buch and Christopher C. White
National Institute of Standards and Technology, Gaithersburg, MD

Current test methods used to evaluate the viability of sealant formulations are based on threshold criteria and incorporate exposure to known stressing factors. The typical protocol involves a static cure followed by serial moisture, temperature, cyclic deformation, and UV exposure. Recent surveys from England, Japan and Germany show that 55% of the 420,000 tons of sealant sold every year will prematurely fail within 10 years. Clearly, the existing test methods are not sufficient. One of the first weaknesses in the existing test method is the lack of a dynamic cure. In this study we have designed, constructed and evaluated instrumentation to measure sealant joint performance under cyclic deformation. This new instrumentation was used to fatigue and monitor sealant performance during dynamic cure. The experimental plan involves casting a large number of samples at one time and subjecting sub sets to dynamic cure at regular intervals of time. The silicone sealant was studied at 7.5% and 25% of joint movement at two speeds: .0635mm/min .127mm/min. The molecular weight between cross-links (Mc) was calculating from the tensile modulus. Large early movement exceeded the adhesive strength of the sealant. For the lower, slower movements, a smooth curve could be drawn for Mc versus time regardless of the movement history.
Intercalation and exfoliation of modified montmorillonite clay in dicyclopentadiene

M. Yoonessi, H. Toghiani, C. Pittman, and W. Kingery

1School of Chemical Engineering and Departments of Chemistry, Mississippi State University, Mississippi State, MS; 2Department of Chemical Engineering, Mississippi State, Mississippi State, MS; 3Mississippi State University, Mississippi State, MS

Organically modified montmorillonite clay was intercalated and exfoliated using sonication in the presence of the non-polar organic monomer, dicyclopentadiene (DCPD). A small amount of more polar Furan was added to compatibilize the matrix with silica layers. XRD was used to follow the d-spacings. Increased sonication time caused the d-spacings to increase. Rheological studies demonstrated non-Newtonian shear thinning behavior of the exfoliated clay/DCPD mixture. With increasing sonication time the viscosity increased, indicating increased exfoliation had occurred. With increasing sonication time, the thixotropic behavior is more pronounced. After intercalation or exfoliation the monomer was cured by (PCp3)2Cl2Ru=CH-C=C(CH3)2 via a living ROMP to create a clay-reinforced nanocomposite.
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Plenary Lectures
Sponsored by a generous contribution from NIST Polymers Division

8:30 AM  Crystal Ballroom

Monday, October 22  
Nonequilibrium thermodynamics applications in rheology
Antony N. Beris  
Chemical Engineering Department, University of Delaware

Tuesday, October 23  
Bingham Lecture  
Modeling of entanglement - past and present
Masao Doi  
Dept. of Computational Science and Engineering, Nagoya University

Wednesday, October 24  
Microrheology of DNA near surfaces
Ronald G. Larson, Lei Li, and Manish Chopra  
Chemical Engineering Department, University of Michigan

Social Program

Sunday, October 21  
Welcoming Reception  
7:00 PM – 9:00 PM  Fellini’s Bar and Grill (Lobby Level)  
Sponsored by a generous contribution from TA Instruments

Monday, October 22  
Society Luncheon  
11:50 AM – 1:30 PM  Crystal Ballroom

Tuesday, October 23  
Business Meeting  
5:30 PM  Cabinet/Judiciary Rooms  
Awards Reception  
7:00 PM – 8:00 PM  Crystal Ballroom Foyer  
Sponsored by a generous contribution from Rheometric Scientific  
Awards Banquet  
8:00 PM  Crystal Ballroom

Wednesday, October 24  
Poster Session Refreshments  
6:00 PM – 8:00 PM  Crystal Ballroom  
Sponsored by a generous contribution from Bohlin Instruments

A generous contribution from Paar Physica USA is used to defray general meeting costs.