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THE SOCIETY OF RHEOLOGY

82^ND ANNUAL MEETING PROGRAM AND ABSTRACTS

Santa Fe Convention Center
Santa Fe, New Mexico
October 24 - 28, 2010

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Meeting Schedule

Monday, October 25, 2010

8:30	K. S. Schweizer (PL1)					
9:20	Coffee					
9:55	SC1	GM1	SI1	FD1	CR1	BF1
10:20	SC2	GM2	SI2	FD2	CR2	BF2
10:45	SC3	GM3	SI3	FD3	CR3	BF3
11:10	SC4	GM4	SI4	FD4	CR4	BF4
11:35	SC5	GM5	SI5	FD5	CR5	BF5
12:00	Lunch					
1:30	SC6	MS1	SI6	FD6	CR6	BF6
1:55	SC7	MS2	SI7	FD7	CR7	BF7
2:20	SC8	MS3	SI8	FD8	CR8	BF8
2:45	SC9	MS4	SI9	FD9	CR9	BF9
3:10	Coffee					
3:35	SC10	MS5	SI10	FD10	CR10	BF10
4:00	SC11	MS6	SI11	FD11	CR11	BF11
4:25	SC12	MS7	SI12	FD12	CR12	BF12
4:50	SC13	MS8	SI13	FD13	CR13	BF13
5:15	SC14	MS9	SI14	FD14	CR14	BF14
5:40	End					
6:30	Society Reception					

Tuesday, October 26, 2010

8:30	T. C. McLeish (PL2)					
9:20	Coffee					
9:55	SC15	MS10	SI15	GM6	SA1	CR15
10:20	SC16	MS11	SI16	GM7	SA2	CR16
10:45	SC17	MS12	SI17	GM8	SA3	CR17
11:10	SC18	MS13	SI18	GM9	SA4	CR18
11:35	SC19	MS14	SI19	GM10	SA5	CR19
12:00	Lunch					
1:30	SC20	MS15	SI20	GM11	SA6	CR20
1:55	SC21	MS16	SI21	GM12	SA7	CR21
2:20	SC22	MS17	SI22	GM13	SA8	CR22
2:45	SC23	MS18	SI23	GM14	SA9	CR23
3:10	Coffee					
3:35	SC24	MS19	NP1	GM15	SA10	CR24
4:00	SC25	MS20	NP2	GM16	SA11	CR25
4:25	SC26	MS21	NP3	GM17	SA12	CR26
4:50	SC27	MS22	NP4	GM18	SA13	CR27
5:15	End					
5:30	Society Business Meeting					
7:00	Awards Reception					
8:00	Awards Banquet					

Wednesday, October 27, 2010

8:30	J. A. Kornfield (PL3)					
9:20	Coffee					
9:55	SC28	MS23	NM1	GM19	SA14	NP5
10:20	SC29	MS24	NM2	GM20	SA15	NP6
10:45	SC30	MS25	NM3	GM21	SA16	NP7
11:10	SC31	MS26	NM4	GM22	SA17	NP8
11:35	SC32	MS27	NM5	GM23	SA18	NP9
12:00	Lunch					
1:30	SC33	MS28	NM6	GM24	SA19	NP10
1:55	SC34	MS29	NM7	GM25	SA20	NP11
2:20	SC35	MS30	NM8	GM26	SA21	NP12
2:45	SC36	MS31	NM9	GM27	SA22	NP13
3:10	Coffee					
3:35	SC37	MS32	NM10	GR1	SA23	NP14
4:00	SC38	MS33	NM11	GR2	SA24	NP15
4:25	SC39	MS34	NM12	GR3	SA25	NP16
4:50	SC40	MS35	NM13	GR4	SA26	NP17
5:15	End					
5:30	Poster Session & Reception					

Thursday, October 28, 2010

8:05	SC41	MS36	NM14	FD15	SA27	GR5
8:30	SC42	MS37	NM15	FD16	SA28	GR6
8:55	SC43	MS38	NM16	FD17	SA29	GR7
9:20	SC44	MS39	NM17	FD18	SA30	GR8
9:45	Coffee					
10:20	SC45	MS40	NM18	FD19	SA31	GR9
10:45	SC46	MS41	NM19	FD20	SA32	GR10
11:10	SC47	MS42	NM20	FD21	SA33	GR11
11:35	SC48	MS43	NM21	FD22	SA34	GR12
12:00		MS44	NM22	FD23		GR13
12:25	End					

Session Codes

BF = Rheology of Natural Materials: Biorheology and Food Rheology
CR = Computational Rheology: Behavior ‘in Silico’
FD = Micro- and Nano-Fluidics
GM = Rheology and Flow of Glass-like Materials
GR = General Rheology
MS = Polymer Rheology: Melts, Solutions and Blends
NM = Nano- and Micro-Rheology: Indentation and Beyond
NP = Complex Fluids: Nanocomposites and Phase Separated Systems
PL = Plenary Lectures
SA = Self-Assembling, Associative, and Gel-like Systems
SC = Suspensions, Colloids and Emulsions
SI = Surface and Interfacial Rheology

Contents

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Sweeney F PL1

Activated relaxation and rheology of glassy materials: From dense colloidal suspensions to amorphous polymers

Kenneth S. Schweizer
University of Illinois, Urbana, IL 61801, United States

Recent progress in developing, within a common predictive framework, theories for the activated barrier hopping dynamics and mechanical properties of dense colloidal suspensions [1] and cold polymer melts and glasses [2] will be summarized. The central concept is a dynamic free energy in the context of a stochastic nonlinear Langevin equation (NLE) approach. Hard spheres literally arrest only upon jamming, and intermittent barrier hopping results in multiple dynamic heterogeneity effects. The mean square force exerted on a particle is the key controlling factor and provides a link between slow dynamics and local structure. External stress weakens the confining dynamic free energy resulting in speeding up of relaxation, modulus reduction, shear thinning, and yielding. The theory has been extended to describe the viscoelasticity of soft colloids (stars, microgels) and coupled translation-rotation activated relaxation of hard nonspherical objects. Deeply supercooled polymer melts and glasses are treated based on a statistical segment level model. Both chemically-specific and universal predictions for segmental relaxation and fragility have been made including the role of chain stiffness and attractive interactions. In the quenched glass the temperature dependence becomes Arrhenius and apparent power law physical aging commences. How these nonequilibrium processes are described, and the construction of a constitutive equation to address the combined consequences of aging, rejuvenation, local plastic flow, and strain hardening on creep and constant strain rate mechanical experiments, will be outlined and representative applications presented.

[1] KSS, E.J. Saltzman: J. Chem. Phys, 119, 1181 (2003); KSS: Curr. Opin. Colloid Interface Science, 12 ,297 (2007); V. Kobelev, KSS: Phys. Rev. E, 71, 021401(2005); M. Tripathy ,KSS: JCP ,130, 244907(2009); R.Zhang, KSS: PRE, 80, 011502(2009). [2] K. Chen, E.J. Saltzman, KSS: J.Physics-Condensed Matter, 21, 503101 (2009); Annual Reviews Condensed Matter Physics, 1, August, 2010.

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Monday 9:55 Sweeney A SC1

Connecting nanoscale motion and rheology of gel-forming colloidal suspensions

Subramanian Ramakrishnan[1], Hongyu Guo[2], James L. Harden[3], and Robert Leheny[4]
[1]Chemical and Biomedical Engineering, Florida A&M University, Tallahassee, FL, United States; [2]Physics, Johns Hopkins University, Baltimore, MD, United States; [3]Physics, University of Ottawa, Ottawa, Canada; [4]Johns Hopkins University, Baltimore, MD, United States

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

Monday 10:20 Sweeney A SC2

Signatures of aging: Comparison between colloidal and molecular glass

Xiaojun Di[1], K.Z. Win[1], Gregory B. McKenna[1], Tetsuharu Narita[2], François Lequeux[2], Srinivasa Rao Pullel[3], and Zhengdong Cheng[3]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]UPMC-ESPCI-CNRS UMR7615, Paris, France; [3]Texas A&M University, College Station, TX, United States

Colloidal systems near to the glass concentration are often taken as excellent models of the molecular glass transition temperature. Yet, one of the most important aspects of the dynamics of molecular glasses, i.e., that of structural recovery in the temperature histories catalogued by

Kovacs, has yet to be elucidated in colloidal systems. In the present work, we take advantage of a thermo-sensitive PNIPAAM colloidal suspension to study the aging behavior near to the glass concentration. We use multi-speckle Diffusive Wave Spectroscopy (DWS). Because, unlike molecular glasses, the thermodynamic variable for this colloidal system is volume fraction and not temperature, we take advantage of the thermosensitive nature of the particles to use temperature to control the concentration. The three classical aging signatures observed in molecular glasses: Intrinsic isotherms, asymmetry of approach, and memory effect, are investigated with this colloidal suspension and the results are compared with those typical of molecular glass. Our results show that: 1) for the intrinsic isotherms, our colloidal system shows dramatic changes in equilibrium relaxation time while the times required to reach the equilibrium state are almost independent of the concentration; 2) for the asymmetry of approach we find a similar but weaker nonlinearity to that observed in molecular glasses; 3) we are also investigating the memory behavior. The three responses will be described in detail.

Monday 10:45 Sweeney A SC3

Anisotropic cooperative structural relaxation in confined colloidal liquids under oscillatory shear

Prasad Sarangapani and Y. Elaine Zhu
Dept. of Chemical and Biomolecular Eng., Univerisity of Notre Dame, Notre Dame, IN 46556, United States

We have investigated the dynamics of confined amorphous “hard-sphere” colloidal suspensions under oscillatory shear using a home-designed micron-gap rheometer interfaced with a confocal microscope. Our systems consist of model hard-sphere colloidal suspensions of micron-sized poly-(methyl methacrylate) (PMMA) particles suspended in density and refractive index matched nonpolar solvents at particle volume fractions from 0.40-0.43. We simultaneously visualize the dynamical response of confined PMMA particles between two solid surfaces at narrow gap spacing of 10-28 particle layers to applied shear deformation. Between a threshold strain of ~6-8% where an applied deformation is sufficient to induce plastic behavior, we find that structural rearrangements are highly anisotropic. Non-affine motion, determined by subtracting the globally uniform strain from the bare particle coordinates, reveals that particles move as cooperatively rearranging groups with a preferred orientation transverse the flow direction. We also find evidence of anisotropy when examining affine motion, where shear-transformation zones have a similar orientation as the clusters of mobile, rearranging groups. Strikingly, we find a strong amplitude and thickness dependence on the degree of anisotropy as well as spatial extent of shear-transformation zones and rearranging regions.

Monday 11:10 Sweeney A SC4

Influence of particle shape on activated dynamics, elasticity and kinetic arrest in dense hard and sticky colloidal suspensions

Rui Zhang, Ryan Kramb, Charles F. Zukoski, and Kenneth S. Schweizer
University of Illinois, Urbana, IL, United States

The naive mode coupling theory (NMCT) of ideal kinetic arrest and the nonlinear Langevin equation theory of activated barrier hopping are generalized to treat the coupled center-of-mass translational and rotational dynamics of uniaxial objects [1]. For colloids that interact via hard core repulsions, the kinetic arrest diagram has three states: ergodic fluid, plastic glass and fully nonergodic double glass, the boundaries of which meet at a dynamical “triple point” corresponding to a most difficult to vitrify state of aspect ratio ~1.43 The NMCT arrest actually signals a crossover to thermally activated transport which is described by two coupled stochastic nonlinear Langevin equations for motion on a dynamic free-energy surface. Multidimensional Kramers theory is applied to determine the reaction coordinate and mean barrier crossing (cage escape) or relaxation time as a function of volume fraction and particle aspect ratio. Application of the center-of-mass version of the theories to recent experiments that probe the dynamical state (fluid, glass, gel) and volume fraction dependence of the shear modulus of dense suspensions of spheres, symmetric dicolloids, and colloidal triangles that interact via tunable repulsive and attractive forces show good agreement [2]. Non-monotonic and particle shape dependent variation of the kinetic arrest boundary with solution ionic strength, universal scaling of the elastic modulus of all repulsive colloids, and a connection with jamming physics is theoretically predicted and experimentally observed. Extensions to treat homogeneously and heterogeneously (Janus) sticky colloids has also been achieved. A rich competition between attractive and repulsive forces in determining kinetic arrest and the alpha relaxation time is found, including the presence of distinctive re-entrancy effects and mixed glass-gel dynamical regimes.

[1] R.Zhang and K.S.Schweizer,Phys.Rev.E,80,011502(2009). [2] R.Kramb, R.Zhang, K.S.Schweizer and C.F.Zukoski, submitted, 2010.

Monday 11:35 Sweeney A SC5

Viscoelasticity, dynamic fragility and soft jamming in glassy suspensions of soft colloids

Jian Yang and Kenneth S. Schweizer
University of Illinois, Urbana, IL, United States

Simplified mode coupling theory and the nonlinear Langevin equation theory of activated barrier hopping are applied to models of dense suspensions of many arm stars and crosslinked microgels that interact via tunably soft repulsive forces. For both systems the slow glassy dynamics is a sensitive function of both volume fraction and interaction strength or reduced temperature. No activated dynamics regime is predicted below a critical single particle repulsion strength. In the activated hopping regime the dynamic fragility is a sensitive function of repulsion strength with soft colloids behaving as strong glasses. For many arm star polymers, the onset volume fraction for thermally-driven hopping dynamics is a non-monotonic function of the number of arms, the activation barrier grows roughly linearly with arm number, and the shear modulus is an arm number dependent apparent power law function of volume fraction. Microgels are modeled as interacting via a Hertzian contact repulsion of variable softness. The alpha relaxation time in the activated regime is predicted to vary strongly with suspension volume fraction and temperature. However, these dependences can all be collapsed onto two distinct universal curves consistent with a recent scaling ansatz motivated by jamming physics arguments. At very high volume fractions the pair correlation function near contact of both soft colloidal systems goes through a maximum. This defines a crossover (soft jamming) concentration beyond which stars strongly interpenetrate and microgels osmotically deswell, resulting in a new viscoelastic regime where barriers saturate and the modulus scales roughly linearly with volume fraction. Comparison of the theoretical results with recent experiments and computer simulations has been performed.

Symposium GM
Rheology and Flow of Glass-like Materials

Organizers: Grigori Medvedev and Leon Govaert

Monday 9:55 Sweeney B GM1

Constitutive modeling of the finite anisotropic elasto-viscoplastic behavior of oriented polymers

Theo A. Tervoort and Markus Hütter
Department of Materials, ETH Zurich, Zurich, Zurich 8093, Switzerland

It is well-known that the covalently bonded macromolecular chains in polymeric solids can be oriented, resulting in anisotropic materials. For example, application of polymer processing techniques, such as injection molding or film blowing, typically results in products with anisotropic properties.

Traditionally, one of the most used tools to describe the onset of plastic deformation in anisotropic materials is the yield criterion of Hill. More recently, it was shown that for modeling the finite macroscopic deformation behavior of solids, the elastic part of the deformation gradient is a suitable measure of the state of deformation, particularly so for anisotropic materials. In such a description, the evolution equation describes how the affine accumulation of elastic strain is reduced by a so-called plastic velocity gradient tensor. Typically, constitutive relations for the plastic velocity gradient tensor rely on phenomenological macroscopic arguments, resulting in a large number of material constants in case of anisotropic materials.

In this work, we illustrate a procedure to relate the plastic velocity gradient tensor to the rapid microscopic fluctuations of the elastic deformation gradient [1]. In this way, assuming that these fluctuations are of transversely anisotropic character, we are able to restrict the tensorial structure of the plastic velocity gradient tensor, thereby drastically reducing the number of material parameters. The anti-symmetric part of the plastic velocity gradient tensor, the so-called “plastic spin”, naturally arises in our treatment, and does not require any special constitutive assumptions. This new approach will be compared to experimental anisotropic yield data of uniaxially oriented polymer films of polycarbonate and a thermotropic liquid crystalline polyester.

Reference: [1] Hütter, M.; Tervoort, T. A., Adv. Appl. Mech. 2008, 42, 253-317.

Monday 10:20 Sweeney B GM2

Theory of physical aging, strain softening, plastic flow and strain hardening in polymer glasses

Kang Chen[1] and Kenneth S. Schweizer[2]
[1]Materials Research Laboratory, University of California-Santa Barbara, Santa Barbara, CA, United States; [2]University of Illinois, Urbana, IL 61801, United States

We have developed a force-based statistical mechanical theory of segmental dynamics, activation barriers, kinetic vitrification, physical aging, and rheology in deeply supercooled polymer melts and nonequilibrium glasses [1]. The approach is based on nanometer scale density fluctuations as the key structural variable and the concept of a dynamic free energy within a nonlinear Langevin equation description. Constant strain rate and stress responses have been studied based on a constitutive equation that assumes deformation does not modify density fluctuations at relatively low strains. In the quiescent quenched glass the relaxation time follows an Arrhenius temperature dependence, and grows on intermediate aging time scales as a temperature-dependent power law. Modest deformation weakens dynamical constraints and accelerates relaxation resulting in dynamic yielding and local plastic flow. A non-entropic theory predicts strain hardening in the post-yield regime based on prolongation of the alpha time triggered by chain stretching or compression which suppresses density fluctuations. Quantitative comparisons with experiments on PMMA reveal good agreement. The theoretical approach has now been generalized to include rejuvenation effects associated with mechanically-induced enhancement of density fluctuations near yielding. The competing consequences of aging and rejuvenation results in overshoots or yield peaks in stress-strain curves which depend systematically on temperature, pre-aging time, and strain rate. An apparent erasure of aging in the plastic flow hardening regimes is predicted. The nonadditive consequences of aging, rejuvenation and strain hardening on the segmental relaxation and dynamic strain in creep experiments has also been studied, and the results contrasted with recent experiments of Ediger, Caruthers, and others.

[1] K.Chen, E.J. Saltzman, K.S. Schweizer: J. Physics Condensed Matter, 21, 503101 (2009); Annual Reviews of Condensed Matter Physics, 1, August, 2010.

Monday 10:45 Sweeney B GM3

Strain hardening and its relation to Bauschinger effects in oriented polymer glasses

Dirk Senden[1], Johannes Van Dommelen[2], and Leon Govaert[1]

[1]Polymer Technology, Eindhoven University of Technology, Eindhoven, The Netherlands; [2]Mechanics of Materials, Eindhoven University of Technology, Eindhoven, The Netherlands

The nature of strain hardening in glassy polymers is investigated by studying the mechanical response of oriented polycarbonate in uniaxial extension and compression. The yield stress in extension is observed to increase strongly with pre-deformation, whereas it slightly decreases in compression; a phenomenon usually referred to as the Bauschinger effect. Moreover, oriented specimens tend to display significantly increased strain hardening in extension, whereas it nearly vanishes in compression.

Although traditional constitutive models for glassy polymers have successfully incorporated rubber-elastic theories to quantitatively describe the strain hardening response of these materials, the present study demonstrates that this success is limited to cases in which the loading increases monotonically. In reversed loading, model predictions strongly deviate from experimental observations. Consequently, these models are unable to capture the Bauschinger effect, implying that they are also not capable of describing the mechanical response of oriented glassy polymers.

A solution is found in the introduction of a viscous contribution to strain hardening in terms of a deformation-dependent flow stress. It is shown that this viscous contribution can originate from a deformation-induced change in either the activation volume or the rate constant. The latter occurs in polycarbonate, for which the yield kinetics (yield stress vs. logarithm of strain rate) are observed to shift along the logarithmic strain rate axis upon plastic deformation.

An extension of the 1-D concept of a deformation-dependent flow stress to 3-D and its incorporation in the Eindhoven Glassy Polymer model is discussed, and preliminary results are presented.

Monday 11:10 Sweeney B GM4

Evaluation of the Dyre shoving model using dynamic data near the T_g

Ben Xu and Gregory B. McKenna

Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

The temperature dependence of the dynamics of glass-forming systems remains an important fundamental problem in glass physics. Here we use literature data1, reanalyzed with the BSW2 model of complex fluid dynamics to evaluate the Dyre shoving model3 that relates the temperature dependence of viscosity to the infinite frequency shear modulus and its temperature dependence. In Dyre's model, the free energy barrier for a "flow event" is attributed to the work done in shoving aside the surrounding molecules; the free energy barrier is proportional to the glassy modulus, which increases as the temperature decreases. In our work, the glassy modulus was obtained by the extrapolation of KWW4 and BSW function fits to zero time or infinity frequency, respectively. It was found that the glassy modulus obtained from the BSW function for m-toluidine1 over the temperature range 186.2 K to 192.2 K can be expressed by Dyre's model, while those obtained by KWW function cannot.

[1] S.A. Hutcheson, G.B. McKenna, J. Chem. Phys. 129,074502 (2008). [2] M. Baumgärtel, A. Schausberger, H.H. Winter, Rheol. Acta. 29:400-408 (1990). [3] J. C. Dyre, N. B. Olsen, T. Christensen, Physical Review B. 53, 5 (01996). [4] G. Williams and D. C. Watts, Trans. Faraday Soc. 66, 80 (1970); F. Kolrausch, Pogg. Ann. Phys. 12, 393 (1847).

Monday 11:35 Sweeney B GM5

Modeling rate-dependent plasticity with microstructure

Markus Hütter and Lambert van Breemen

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The modeling of viscoplasticity in amorphous solids is addressed. As a key ingredient in macroscopic modeling approaches, a dynamic variable is used to describe the elastic part of the material deformation. To close the model, a constitutive relation is needed to describe the relaxation of the elastic deformation upon the onset of yielding. Elaborate ansatzes for the relaxation term have been made in literature that allow for accurate modeling of complex deformations [1]. In this work, we do not attempt to improve on these successful, purely macroscopic, ansatzes. Rather, the goal is to model the dynamics of the microstructure explicitly as is believed to be relevant for the viscoplastic deformation.

In amorphous solids, the relevant structural features and length scales responsible for viscoplastic deformation are difficult to identify. Falk and Langer have proposed a model for amorphous metals [2,3], employing so-called shear transformation zones (STZ). The model accounts for the number density of such zones and for their average orientation [3]. We discuss the implications that arise from formulating the STZ model in a nonequilibrium thermodynamics framework [4]. In so doing, we identify the thermodynamically admissible flexibility for accounting for the microscopic processes resulting in the macroscopic viscoplastic deformation, and re-examine Langer's model. Finally, we discuss in what sense the STZ model can be used to also describe the viscoplastic deformation of polymer glasses. Particularly, it seems feasible to link the STZ model to experimental findings about cooperative chain-backbone orientation, i.e. intramolecular interactions, in polycarbonate upon the onset of yielding [5].

[1] Klompen ETJ et al., Macromol. 38, 6997 (2005); [2] Falk ML, Langer JS, Phys. Rev. E 57, 7192 (1998); [3] Langer JS, Phys. Rev. E 77, 021502 (2008); [4] Öttinger HC, Beyond Equilibrium Thermodynamics (Wiley, 2005); [5] Lunn AC, Yannas IV, J. Polym. Sci. Pol. Phys. Ed. 10, 2189 (1972).

Symposium SI
Surface and Interfacial Rheology

Organizers: Ophelia Tsui and Lenore L. Dai

Monday 9:55 Coronado/DeVargas SI1

Near surface dynamics of polymeric and molecular glasses: When does a surface glass transition make sense?

James A. Forrest[1], Dongping Qi[2], Chad Daley[2], Zahra Fakhraai[3], and Mark D. Ediger[3]
[1]Physics and Astronomy, University of Waterloo, Waterloo, On N2L 3G1, Canada; [2]University of Waterloo, Waterloo, On N2L 3G1, Canada; [3]University of Wisconsin-Madison, Madison, WI 53706, United States

There is a mounting evidence that the surface of glassy materials exhibits enhanced dynamics. This has important technological consequences, and may help elucidate the origins of vitrification. Over the past few years we have used nanoparticle embedding and annealing of nanoscale surface roughness to probe the surface dynamics of both polymeric (PS,PMMA) and non-polymeric (TNB) glasses. We find that all surfaces we looked at exhibited enhanced when the bulk of material was glassy. The difference between the temperature dependence of this surface mobility and that of the same material in bulk appears to be highly material dependent. The nanoparticle embedding experiments are able to determine a length scale of the surface effect.

Monday 10:20 Coronado/DeVargas SI2

Two-particle interfacial microrheology at polymer-polymer interfaces

Yanmei Song and Lenore L. Dai
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We continue to develop two-particle interfacial microrheology and have applied it to study the interfacial viscoelastic properties of immiscible polydimethylsiloxane (PDMS) - polyethylene glycol (PEG) interfaces. The interfacial storage and loss moduli are measured over a wide frequency range; at low frequencies, the interfaces are dominated by viscous responses. The interfacial viscosity, estimated based on the Cox-Merz rule, falls between the bulk viscosities of two individual polymers. Surprisingly, the interfacial relaxation time, calculated from the crossover of the storage and loss moduli, is found to be an order of magnitude larger than that of the PDMS bulk polymers. The effects of tracer particle size (40 nm to 1.0 um) and surface chemistry (hydrophilic vs. hydrophobic) have also been studied and shown minimum influences on two-particle interfacial microrheology.

Monday 10:45 Coronado/DeVargas SI3

Using real-time DNA imaging/rheometry to demonstrate the molecular mechanisms of wall slip in entangled fluids: Interfacial chain disentanglement versus chain desorption

Pouyan E. Boukany[1], Shi-Qing Wang[2], and L. J. Lee[1]
[1]Department of Chemical Engineering, The Ohio State University, Columbus, OH, United States; [2]Department of Polymer Science, The University of Akron, Akron, OH 44325, United States

Using a combination of confocal microscopy and rotational rheometer, we obtain first molecular level evidence of wall slip during shear in entangled DNA solutions. Conformational images of stained DNAs were captured during shear for both strong and poor interfacial interactions respectively. Simultaneous rheometric and velocimetric measurements were carried out as well. Upon a sudden startup shear with the Weissenberg number Wi > 1.0, the stress decline after its initial rise was found to correlate with occurrence of wall slip. In the case of strong interactions at the wall/DNA interface, adsorbed DNA chains remained coiled till after the stress maximum when the molecules start to stretch and elongate at the surface after disentanglement from coiled bulk chains. At higher Wi, the DNA molecules close to surface exhibit tumbling behavior when they have become fully disengaged (i.e., freed) from the entanglement network of the bulk. Beyond this regime, bulk shear-inhomogeniety starts to develop across the gap. In the case of weak surface interactions between solid wall and DNA, massive wall slip takes place as evidenced by the moving coiled DNA molecules at the wall surface. Evidently, here chain desorption was the mechanism for wall slip.

Monday 11:10 Coronado/DeVargas SI4

The role of symmetric grafting copolymer on the suppression of drop coalescence

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In this study, we analyze the rheological properties of “symmetric” blends of Polybutadiene(PBd) and Polydimethylsiloxane(PDMS) with a symmetric grafting $\text{PBd-COO}^-\text{NH}_3^+\text{PDMS}$ copolymer as compatibilizer. The zero shear viscosity of the PBd and PDMS were exactly matched. The blends were prepared by varying the volume fraction of PBd and PDMS between 20:80 and 80:20 and with 0.1 or 1 wt% of compatibilizer. With PBd as the continuous phase,viscosity is only slightly lower than a suspension of rigid spheres, suggesting that the compatibilizer immobilizes the interface almost completely. With PDMS as continuous phase, the rheological properties are less strongly affected, suggesting less effective immobilization. These results are similar to the previously published results(Velankar et al,J. Rheol. **51**,669(2007))using PIB/PDMS. In the present work, we further explore the role of the compatibilizer by studying the effects on coalescence.

Flow induced coalescence of a pair of these drops with compatibilizer was studied at the level of individual drops using 4-roll mill. With PBd as the continuous phase, there are two critical interface concentrations of copolymer,Γ_{c1} and Γ_{c2}. For interface concentrations between these two values, $\Gamma_{c1} < \Gamma < \Gamma_{c2}$, the grafting copolymer effect on coalescence is independent of the coverage and is almost the same as the copolymer effect with PDMS as the continuous phase. For $\Gamma > \Gamma_{c2}$, however, in the system with PBd as the continuous phase, coalescence is suppressed, at least on the experimental time scales. We suggest Marangoni effects as the main mechanism for suppression of coalescence in the former case ($\Gamma_{c1} < \Gamma < \Gamma_{c2}$), while steric effects appear to be the main mechanism for the latter case ($\Gamma > \Gamma_{c2}$). When PDMS forms the continuous phase, we did not find a level of copolymer coverage that can totally suppress the coalescence.

Monday 11:35 Coronado/DeVargas SI5

Viscosity of polystyrene nanometer films

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In the past 15 years, the glass transition temperature, T_g, of a variety of polymer films has been found to deviate from the bulk T_g when the film thickness was decreased below ~100 nm. Since T_g is the temperature at which a polymer transforms from the solid-like, glassy state to the liquid state on heating, the dynamics of those films has been suggested to alter with the T_g. Specifically, a decrease (increase) in the T_g is supposed to accompany an enhancement (retardation) in the film's dynamics. On the other hand, a large number of experiments have found inconsistency with this prediction. One frequently cited reason is that the measured dynamic property may not be directly related to the glass transition. Viscosity is a dynamic property traditionally used to characterize the dynamic slowing down occurring at the glass transition of a material. In this contribution, we introduce a technique recently developed by our group to measure the viscosity of polymer films down to nanometer thicknesses. This technique is based on monitoring the dynamics of surface capillary waves on a film as it equilibrates upon heating. We have employed this technique to measure the viscosity of polystyrene films supported by silicon with film thickness from 2.3 nm to 79 nm. The viscosities obtained from the 79 nm films, where the T_g is the same as the bulk, exhibit excellent agreement with the bulk viscosity. But as the film thickness is decreased below ~20 nm, the viscosity of the films decreases noticeably with decreasing film thickness. We also find that the temperature dependence of the viscosity of the films fits well to the Vogel-Fulcher-Tamman relation, with the fitted values of the Kauzmann temperature showing a good consistency with the observed thickness dependence of the films' T_g. Altogether, our results show that the viscosity of polystyrene films supported by silicon is in good consistency with their T_g.

Symposium FD
Micro- and Nano-Fluidics

Organizers: Siva Vanapalli and Anubhav Tripathi

Monday 9:55 Peralta/Lamy FD1

Cooperative effects of surfactant and viscoelasticity in microscale thread formation

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When a droplet breaks up, threads can form in the necking region if polymers are dissolved in the bulk, or if surfactant is present at the interface. In the first case, polymer elasticity stabilizes the thread against breakup. In the second case, surfactants concentrate at the neck during pinching, forming a high curvature tip. A local extensional flow can easily draw a thin thread from this tip. In microfluidic droplet generation, thread formation offers a way to generate droplets much smaller than the characteristic device size, overcoming a fundamental limitation of these methods.

We use a microfluidic flow focusing geometry to examine thread formation in the presence of dissolved surfactants and polymers. In these experiments, water droplets are formed in an immiscible outer phase of oil. Span80 surfactant is dissolved in the oil, and polyethylene oxide (PEO) of varying molecular weight is dissolved in the water. We consider two basic scenarios. In the first, the viscosity ratio is too large for surfactant-mediated thread formation, or tipstreaming, to occur and we observe that viscoelastic threads form during droplet breakup. The viscoelastic thread length increases with increasing molecular weight. In the late stages of breakup, the thread undergoes exponential self-thinning and a polymer relaxation time can be obtained.

In the second case, the viscosity ratio and surfactant concentration are selected such that tipstreaming occurs in the absence of viscoelasticity. When polymer is dissolved in the inner liquid, we observe viscoelastic thread formation for most PEO molecular weights. However, at a moderate polymer molecular weight, $M_w \sim 3\times10^5$ g/mol, we observe cooperative effects in which the presence of both surfactant and polymer leads to significantly longer threads than are formed with polymer alone. We interpret these results in terms of competing timescales for convection/stretching, surfactant mass transport, and polymer relaxation.

Monday 10:20 Peralta/Lamy FD2

Effect of confinement on droplet deformation in microfluidic hyperbolic contractions

Molly K. Mulligan and Jonathan P. Rothstein

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A microfluidic device was used to create emulsions of aqueous droplets in an oil matrix phase. Droplets of deionized water, surfactant solutions and aqueous particle suspensions were created in oil using a flow focusing device. The morphological developments of these drops was then studied under a series of different extensional and mixed shear and extensional flow conditions were studied. Once formed, droplets were driven through a hyperbolic contraction, resulting drop deformation in a nearly homogeneous extensional flow. Droplet deformation was quantified for each of the droplet types. The effects of confinement on droplet deformation were also studied. Confinement was found to increase drop deformation for all systems studied. After passing through the hyperbolic contraction droplets over 50 µm in radius were confined. Evidence of tail streaming (a phenomena likened to tip streaming) was seen during the extensional flow and continued as the drop was confined for the surfactant solutions. As the drop transitioned from pure extensional flow to shear flow from confinement, a transition from one to two tails was made. Surfactants and particles change the interfacial tension of the droplets. Comparisons were made between the deformation of water, surfactant and particle laden droplets.

Monday 10:45 Peralta/Lamy FD3

Effect of confinement on drop-drop interaction in shear flow

Patrick D. Anderson

Materials Technology, TU Eindhoven, Eindhoven, The Netherlands

Many applications of microfluidic devices rely on the creation of separated drops or structures in flow used, e.g. in biological testing and also in microreactors. These devices are small, the transport takes place through narrow channels typically in the order of 10-100µm, which is also the size of the cells and drops. Wall interactions can significantly alter the flow and induce specific flow patterns and drop deformations. In this work the effect of a parallel wall confinement on drop-drop interaction in shear flow is computationally studied. A boundary integral method is applied in which the Green's functions are modified to include wall effects. The method is first validated by comparing with other computational techniques, but also with recently published experimental findings by the group of Moldenaers at Leuven. The results show that compared to unconfined conditions a slight degree of confinement only decreases the orientation angle at which the drops approach prior to coalesce. For more confined conditions, the critical capillary number up to which coalescence can occur, increases, and hence confinement promotes coalescence. For an intermediate range of confinement ratios the drops approach each other, but remain separated because of the strongly altered flow field.

Monday 11:10 Peralta/Lamy FD4

Microfluidic production of self-organized droplet arrays in a fluidic network with hydrodynamic traps

Swastika S. Bithi and Siva A. Vanapalli

Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

We assess the capability of a microfluidic device containing hydrodynamic traps to produce self-organized arrays of Newtonian droplets. The hydrodynamic resistance of the network and the hydrodynamic resistance of individual droplets, guide the movement of droplets inside the network. The observed trapping and break-up of droplets are classified into four different behaviors: 1) by-passing, 2) no trapping-squeeze through, 3) breakup-induced non-uniform trapping and, 4) uniform trapping. We present a phase diagram that identifies the optimal conditions for storing nanoliter-scale droplets on the microfluidic device. We present an indirect approach to predict the bounds for hydrodynamic resistances of the moving and the trapped drops. Using these indirect estimates we are able to predict the flow rate conditions for optimal trapping of droplets. We vary three design parameters: trap shape, trap size and entrance length to the trap. The effects of these parameters on droplet traffic and trapping efficiency will be presented.

Monday 11:35 Peralta/Lamy FD5

Making adhesion independent of rheology: Microfluidic and structural control of adhesion in soft visco-elastic surfaces

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Adhesion or the lack of it in nature is often controlled by surface texture, as in anti-stick shark skin and in strongly adhering gecko foot, rather than by visco-elasticity, as in man-made soft adhesives. This talk will summarize some of our recent results on: (a) the role of visco-elasticity in pattern formation,[1] and (b) the role of surface and sub-surface patterns in adhesion[2] of soft visco-elastic surfaces. The surface patterns in a visco-elastic film can be spontaneously self-organized by application of an external field1 or by its controlled cohesive failure. The resulting surface texture has a profound influence on the adhesive strength of the surface to the extent of making non-stick surface of a sticky material. Even more interestingly, adhesive strength can be greatly modulated by imbedding of micro-air pockets and oil-filled micro-channels in the interior of a soft elastic film.[2] These results show an intimate relation between adhesion and structure at soft interfaces and point to potential technological applications in fabrication of both anti-stick coatings as well as strong, reusable "structural" adhesives. The structural adhesives harness thermodynamic factors, rather than the kinetic factors such as visco-elasticity, to modulate the adhesive strength. Thus, such structural adhesives are equally effective in wet environments.[2]

References: [1] Electric field induced patterns in soft visco-elastic films: from long waves of viscous liquids to short waves of elastic solids, Phys. Rev. Lett. 102, 254502 (2009). [2] Micro-fluidic adhesion induced by sub-surface micro-structures, Science, 318, 258 (2007); A bioinspired wet/dry microfluidic adhesive for aqueous environments, Langmuir 26, 521 (2010).

Symposium CR
Computational Rheology: Behavior 'in Silico'

Organizers: Rajesh Khare and Daniel J. Lacks

Monday 9:55 O'Keeffe/Milagro CR1

Structural signatures of mobility on intermediate time scales in a supercooled fluid

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We use simulations to explore how particle displacements on intermediate time scales in supercooled fluids correlate to their dynamic structural environment. The fluid we study, a mixture of hard spheres, exhibits dynamic heterogeneities a bifurcated single-particle displacement distribution, i.e., subpopulations of immobile and mobile particles. Immobile particles, during the course of their displacements, exhibit stronger average pair correlations to their neighbors than mobile particles, but not higher average coordination numbers. We discuss how the correlation between structure and single-particle dynamics depends on observation time.

Monday 10:20 O'Keeffe/Milagro CR2

Deformation of polystyrene melts near T_g: A molecular dynamics study

Yongchul Chung and Daniel Lacks
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Dynamic behavior of polymers near the glass transition temperature (T_g) remains to be one of the unsolved mysteries in condensed matter physics. Polymer dynamics drastically change near the Tg with miniscule changes in the temperature, and this results in a long relaxation time associated with material properties of the polymer such as Young's Modulus. Due to such long-time scale dynamic behavior and associated large computational cost and time, the use of atomistic investigation tool, e.g., molecular dynamic simulation, to interrogate the polymer dynamics near T_g has been limited. Recently, Kremer and co-workers have developed the coarse-grained model for polystyrene (PS), and the investigation of long-term dynamics of polymers has become possible with substantially less computational cost and time. We've investigated the dynamics and relaxation of deformed PS melts near T_g using molecular dynamic simulation based on this coarse-grained model. From this simulation results, molecular trajectories are analyzed to determine the Kohlrausch-Williams-Watts parameters to elucidate the hidden links between deformation, relaxation time and system properties.

Monday 10:45 O'Keeffe/Milagro CR3

Brownian dynamics simulations of carbon nanotubes breaking during sonication

Guido Pagani[1], Micah J. Green[1], Philippe Poulin[2], and Matteo Pasquali[1]
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The extraordinary mechanical, thermal, and electrical properties of carbon nanotubes (CNTs) are well-known; however, the processing of CNTs into high-performance macroscopic materials is hampered by CNTs' poor solubility in virtually all common aqueous and organic solvents. CNTs naturally tend to form insoluble bundles and ropes due to van der Waals interactions. One of the most common approaches to liquid-phase dispersion is ultrasonication, which breaks the bundles apart. Stabilizing agents such as surfactants and polymers are then used to prevent the CNTs from reaggregating. However, a number of experiments indicate that the average length of CNTs in solution decreases with sonication time; this is due to CNT breaking due to the extreme flow field around cavitating bubbles. We couple Brownian Dynamics simulations of CNTs with a model for the formation and collapse of bubbles during sonication. These simulations show that CNTs are prone to breakage when they become oriented in a direction tangent to the bubble wall during bubble growth; when the bubble collapses, such CNTs become compressed and can break. This contradicts previously-suggested mechanisms for CNT shortening. The simulations suggest phase diagram for nanotube breakage as a function of length and stiffness; we compare simulation results to experimental data for the scaling of average length as a function of sonication time.

Monday 11:10 O'Keeffe/Milagro CR4

Micromechanical constitutive modeling of the finite deformation of semicrystalline polymers

Amin Sedighiamiri[1], Leon Govaert[1], and Johannes Van Dommelen[2]
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The plastic deformation of polyethylene is a very complex process due to the operation of a variety of mechanisms at different levels. Double yield points are a common phenomenon in polyethylene, which are observed during both tensile and compressive deformation modes. Several possible mechanisms have been proposed to explain double yield, e.g. crystallite thickness distribution, partial melting-recrystallization process and operation of fine and coarse slips in the first and second yields, respectively. The mechanical performance of semicrystalline polymers, as characterized by elasto-viscoplastic deformation, strongly depends on their underlying microstructure. Here, a micromechanically based constitutive model is used to study the complex deformation mechanisms and structural evolution in these materials. The model represents the microstructure as an aggregate of layered composite inclusions, consisting of a crystalline lamella, which is mechanically coupled to its adjacent amorphous layer. The crystalline phase is modeled as anisotropic elastic with plastic flow governing by crystallographic slip. The shear rate of each slip system is related to the corresponding resolved shear stress via an Eyring flow rule. The amorphous phase is assumed to be isotropic elastic with a rate dependent plastic flow and strain hardening resulting from molecular orientation. The uniaxial tension and compression of polyethylene is studied. The model provides a tool to study texture development and the basic mechanisms of plastic deformation in semicrystalline polymers. The presented model mimics this complex behavior, however the model only employs fine slip mechanisms and there is no coarse slip and lamellar fragmentation effect presented in the model. It is observed that near the second yield point a change in the active slip mechanisms occurs and transverse slip systems become effectively active, whereas the (100)[001] chain slip was the dominant active slip system in the first yield point.

Monday 11:35 O'Keeffe/Milagro CR5

A computational study of shear banding in reversible associating polymers

Arlette R. Baljon[1], Joris Billen[1], and Joris Stegen[2]
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A novel hybrid MD/MC simulation technique is employed to study the rheological properties of telechelic polymers*. When enough end-groups of these molecules connect to each other, they form a reversible gel. At low temperature or high concentration, the unsheared system is arrested. After application of a uniform shear, it yields and subsequently flows. Two or more shear bands can be observed in the flow profile, a phenomenon also observed in recent experimental studies**. The stress fluctuates erratically over time. These macroscopic observations are correlated with changes in the microstructure, such as chain orientation. A slight difference in chain orientation between both shear bands is detected. The topology of the network differs between the two shear bands, as well as between those and the unsheared system. Fluctuations in the position of the interface between the shear bands occur as well. They resemble phenomena observed in wormlike micelles. We are currently investigating if they are related to the dynamics of the reversible bonds. Creep response under constant stress will be investigated and reported as well.

This work is supported by the NSF under Grant No. DMR0517201.

* Baljon et al, J. Chem. Phys. 126, 044907 (2007). ** Sprakel et al, Phys. Rev. E. 79, 056306 (2009).

Symposium BF
Rheology of Natural Materials: Biorheology and Food Rheology

Organizers: Danilo Pozzo and Peter Fischer

Monday 9:55 Kearney BF1

The viscoelasticity of living cells

Claire M. Anderson and Gerald G. Fuller
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Cell mechanical properties depend primarily on the cytoskeleton, a multifunctional network which plays a key role in cell shape and motility. The cytoskeleton is one of the first cell components to be modified by disease, thus cell mechanical properties provide a diagnostic tool for early detection and diagnosis of cancers and other diseases. Our research involves the construction of a cell monolayer rheometer capable of measuring the average mechanical properties of a monolayer of cells. In this device, cells are deposited between two parallel coverslips and allowed to adhere to both the top and bottom plates. The top coverslip is then sheared while a force transducer measures the applied stress. This allows measurement of the viscoelastic modulus of the cell population, as well as stress relaxation and creep behavior. Many tissues in the body consist of uniaxially aligned cells, thus it is of particular interest to study highly oriented materials using our cell monolayer rheometer. To accomplish this we have developed a technique for orienting cells on glass substrates coated with oriented collagen fibers. The procedure involves spreading a molecular solution of collagen at the air-water interface of a Langmuir trough to induce fiber formation, followed by compression-induced orientation of the fibers and transfer onto glass substrates via Langmuir-Blodgett technique. Cells cultured on such

substrates use topographical cues to elongate along the direction of the collagen fibers. Our cell monolayer rheometer is then used to apply shear strain to the oriented monolayer of cells. The measured viscoelastic modulus, relaxation time, and other mechanical properties may then be related to the direction of the shearing motion relative to the axis of cell orientation, thereby providing a detailed picture of how oriented cells behave under strain.

Monday 10:20 Kearney BF2

Effects of metastatic potential on internal cell mechanics

Diana Goldstein and Daphne Weihs
Faculty of Biomedical Engineering, Technion-Israel Institute of Technology, Haifa, Israel

One of the most important factors determining cancer aggressiveness is the metastatic potential of malignant cells. Variations in metastatic potential are manifested in cellular mechanics. Cells with higher metastatic-potential are typically softer and detach more readily from their substrate, as compared to cells with low metastatic potential. In general, metastatic cells can detach from the original tumor, penetrate into blood vessels, and eventually attach at new sites; hence, higher metastatic potential of the cells results in enhanced likelihood for a secondary tumor. All of those processes involve changes in intracellular mechanical-dynamics and specifically dynamic remodeling of the cytoskeleton. Moreover, molecular motors typically exhibit enhanced activity in higher metastatic potential cells and that activity affects the density of the intracellular microenvironment. Therefore, many chemotherapeutic drugs have been designed to target cytoskeletal filaments, such as microtubules, slowing cellular function and reducing metastasis formation.

We combine intracellular particle-tracking with cell biology techniques, to elucidate mechanical responses of metastatic breast-cancer cells to perturbations. In intracellular particle-tracking, the motion of fluorescent sub-micron particles internalized into cells provides a measure of the dynamics of the internal structural density and local mechanics. We apply treatments separately targeting energy levels within the cell, cytoskeleton remodeling dynamics, and molecular motors activity. We show that intracellular mechanics of human, metastatic breast-cancer cells vary as a function of their metastatic potential. Those cells vary in morphology, dynamics, and time-dependent responses. We discuss the correlation between intracellular mechanics and metastatic potential in terms of probe-microenvironment density and cell activity.

Monday 10:45 Kearney BF3

Photorheological fluids and biophotoresists based on biopolymers

Vishal Javvaji[1], Aditya G. Baradwaj[1], Gregory F. Payne[2], and Srinivasa R. Raghavan[1]
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[2]*Univesity of Maryland Biotechnology Institute, Center for Biosystems Research, College Park, MD, United States*

Photorheological (PR) fluids, i.e., fluids whose viscosity can be altered by light, are of interest in applications ranging from sensors to microfluidic devices. In an effort to create simple and low-cost PR fluids, we have designed such systems using only well-known commercially available surfactant molecules or nanoparticles. In this talk, we report yet another class of PR fluids based on biopolymers. We combine the biopolymer alginate with an insoluble calcium salt and a photoacid generator (PAG). When irradiated with UV light, the PAG generates acid, which reacts with the salt and generates calcium ions. The latter, in turn, crosslink alginate chains and give rise to a gel. The same concept of UV-triggered crosslinking has been extended to other polysaccharides as well. In addition, photogelation of the biopolymer can be conducted on thin films rather than in the bulk. This allows us to exploit the alginate system in a manner akin to a photoresist.

Monday 11:10 Kearney BF4

Photorheology studies of collagen crosslinking pertinent to corneal tissue engineering

Joyce Huynh[1], Viet Anh Nguyen Huu[1], Matthew Mattson[1], Daniel Schwartz[2], and Julia A. Kornfield[1]
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[2]*Ophthalmology, University of California at San Francisco, San Francisco, CA 94143-0730, United States*

Therapeutic crosslinking of protein is of interest for the treatment of diseases associated with inadequate mechanical stability of tissues. For example, photoactivated crosslinking of collagen is used to treat Keratoconus, a condition in which the cornea progressively protrudes and visual acuity is lost. Specifically, riboflavin is used as a photosensitizer that is activated using UV irradiation. Here we apply photorheology to characterize the interplay of riboflavin concentration and UV intensity in determining the rate of collagen crosslinking. From a 500 µm thick sheet of collagen gel (2.5 g gelatin from bovine skin, 6.5 mL Dulbecco's phosphate buffered saline and 1ml of riboflavin solution to achieve the desired concentration), an 8-mm diameter sample was cut and loaded onto a rheometer with a home-built irradiation accessory. The storage modulus was measured as a function of time as the sample received UV irradiation. Collagen control samples without either riboflavin or irradiation showed no increase in modulus. The rate of modulus increase ranged from 0 to 40 Pa/min for various samples containing 0-0.5% riboflavin receiving 0-6 mW/cm2 irradiation. Of particular interest, photorheology revealed the favorable range of riboflavin concentration such that UV light penetrates adequately into the sample and sufficient photosensitizer is present at depth to optimize crosslinking throughout the thickness of the material. Thus, photorheology can be used as a tool to evaluate the trade-offs among therapeutic parameters (drug concentration, light intensity and duration of irradiation) to optimize collagen crosslinking relevant to treatments that strength tissue using light-activated crosslinking agents.

Monday 11:35 Kearney BF5

Rheological advancement of insulin aggregation and misfolding

Kiersten M. Batzli and Brian J. Love
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We are investigating insulin, an amyloidogenic protein associated with type 2 diabetes, as a model protein by which to study the kinetics of aggregation to better understand the pathways of amyloid diseases. We have used rheology to study the gelation kinetics of bovine insulin protein in solution (2% w/v) as a function of temperature (65-80°C) and ramp rate (0.1, 1 and 10°C/min). Insulin was heated to a specific range of temperatures to induce aggregation which was observed as a rise in complex viscosity and gelation resulting in “soft” gels. The dynamic viscosity data was subjected to power law analysis in order to determine the gelation temperature (T_{gel}) and log-Boltzmann sigmoidal analysis to determine the gelation time (t_{gel}). It was found that t_{gel} decreased with increasing temperature. Experiments conducted at lower ramp rates show that gelation begins at approximately 60°C. Studies using ramp rates of 1°C/min suggest a two-stage process of gelation, a first rapid gelation to ~0.1 Pa-s as the temperature reaches 60°C, followed by a progressive increase in $\eta(t,T)$ reaching a plateau at ~1.0 Pa-s. We will present on the temperature dependence of insulin aggregation, as well as investigations of the inhibition of aggregation by introduction of BSA, Tween 80 and rifampicin.

Monday Afternoon

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Monday 1:30 Sweeney A SC6

Self similarity in electrorheological behavior

Manish Kaushal, Anoop K. Patel, and Yogesh M. Joshi
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In this work we discuss self similarity in creep flow behavior of suspension of Poly aniline (PANI) particles in silicon oil under application of electric field. Suspension of PANI in silicon oil, a model electrorheological fluid, shows enhancement in elastic modulus and yield stress with increase in the magnitude of electric field. Under creep flow field, application of greater magnitude of electric field reduces strain induced in the material while application of greater magnitude of shear stress at any electric field enhances strain induced in the material. Although, electric field and shear stress act in opposite manner, time evolution of strain after appropriate shifting on time and strain axes show superposition demonstrating self similarity in electrorheological behavior. Observed electric field - shear stress - creep time superposition suggests that the creep flow behavior of electrorheological fluid under smaller electric field strengths and greater shear stresses over shorter duration is equivalent to long term behavior at greater electric field strengths and smaller shear stresses. We conclude by discussing similarities between observed electric field - shear stress - time superposition and recently observed Stress - aging time - creep time superposition in aging soft glassy materials.

Monday 1:55 Sweeney A SC7

Dispersion and rheology of polymer coated graphene

Sriya Das, John L. Shelburne, Ahmed S. Wajid, and Micah J. Green
Chemical Engineering, Texas Tech University, Lubbock, TX, United States

Liquid phase exfoliation and dispersion of graphene, i.e. single layer graphite, is a critical challenge for bulk processing of graphene based materials and devices. Here we demonstrate the in situ formation of localized polymer coatings on the graphene surface in solution. These polymer coatings do not disrupt the pristine structure or superior properties of the graphene sheets; instead, these coatings allow for stable, aggregation resistant graphene dispersions. We monitor dispersion quality and stability by measuring shear thinning in the dilute concentration regime before and after freeze drying and redispersion.

Monday 2:20 Sweeney A SC8

Yielding of colloidal glasses under large amplitude oscillatory shear (LAOS)

Frederic Renou[1], Andreas Poulos[1], Nick Koumakis[1], Joerg Stellbrink[2], and George Petekidis[1]
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The understanding of yielding and flow of a colloidal glass under large amplitude oscillatory shear (LAOS) represents a motivating challenge. Monitoring the higher harmonics in the stress signal by Fourier-Transform (FT) rheology may provide useful insight on the progressive transition from linear to nonlinear viscoelastic response and the mechanisms involved during shear induced melting. Here we study the process of yielding in a colloidal glass formed of star-like micelles with LAOS and interrogate the nonlinear intracycle stress response by FT analysis and decomposition to an orthogonal set of Chebyshev polynomials. Such approach provides a robust framework enabling us to map out a rich phenomenology of intracylce nonlinearities that may relate to distinct physical mechanisms. We find that the nonlinearities during yielding are represented in the form of intracylce shear-thickening/thinning and strain-hardening/softening in the viscous and elastic response respectively. We argue that the underlying mechanisms are cage breaking and reformation as well as stress storing and relaxation within the period of oscillatory shear which are affected by an interplay between shear and Brownian motion. Finally, to access the influence of the polymeric arm interpenetration and the soft interparticle potential of such star-like micelles we compare their response with that of hard sphere glasses.

Monday 2:45 Sweeney A SC9

Delayed yield of colloidal gels

Joris Sprakel, Stefan B. Lindstrom, and David A. Weitz
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Under a constant stress, heterogeneous solids can suddenly and unpredictably fail after a period of apparent stability. Such delayed failure has been observed in a wide variety of solids, ranging from construction materials as steel, concrete and wood, to soft solids employed in many food

and coating products. In this contribution we study this delayed failure in heterogeneous soft solids formed from attractive colloidal particles, and show that delayed yield occurs in two distinct regimes. Using a transient network model, we explore the origin of these two regimes and will reveal that the two regimes differ by the nature of the microscopic degenerative processes that preceeds the macroscopic failure. Finally, we will we argue that, without further assumption, the same network approach predicts the rate-dependent yielding of these heterogeneous materials under constant rate of deformation.

Monday 3:35 Sweeney A SC10

A scaling theory for the drainage time of the thin film between two elastic spherical capsules or vesicles pushed against each other by a constant force

Arun Ramachandran and L. Gary Leal
Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA 93117, United States

We present a scaling theory based on the analysis of A. K. Chesters [Chem. Eng. Des. Res. 69, 259-270 (1991)] that describes the time required to drain the thin, suspending fluid film that forms between two deformable capsules or vesicles as they are pushed towards each other by a constant force. As the force applied on the capsules/vesicles increases, the radius of the thin film increases. This is expected by analogy with prior work, both theoretical and experimental, on the drainage time between two colliding drops. However, the key difference between capsules or vesicles and drops is that while the pressure in the thin film is independent of the force for drops, it increases with the applied force for vesicles/capsules. A consequence of this effect is that capsules and vesicles show a decrease in the drainage time with the pushing force, which results in the prediction that in a shear flow, the number of doublet formation events increases with the shear rate. Both trends are exactly opposite to what is expected and observed for deformable drops.

Monday 4:00 Sweeney A SC11

The dynamics of a lipid vesicle in simple shear flow

Hong Zhao[1] and Eric S. Shaqfeh[2]
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We have performed direct numerical simulation (DNS) of a lipid vesicle in simple shear flow at zero Reynolds number. The lipid membrane is modeled as a two dimensional incompressible fluid with Helfrich surface energy as a response to bending deformation. A high-fidelity spectral boundary integral formulation is used to solve the flow and membrane interaction system; the spectral resolution and convergence of the numerical scheme are demonstrated. The DNS results are in reasonable agreement with high-order perturbation theories when predicting the critical internal-external fluid viscosity ratio for the transition from steady state tank-treading to “trembling” and finally to tumbling motions at different flow shear rates. We combine our DNS with a linear stability analysis to demonstrate the characteristics and “exact” phase transition boundary between tank-treading and trembling motions. In addition, our DNS reveals a family of time-periodic and out-of-shear-plane vesicle motion patterns, where the orientation of principle axes follow orbits that resemble but are fundamentally different from the classical Jeffery orbits of rigid particles due to the vesicle’s deformability. We discuss the stability of these out-of-shear-plane motions. Finally, the particle stresslets in different flow regimes are calculated, and the consequence for the rheology of a dilute mixture of vesicles is analyzed with a focus on the dynamics as one crosses the phase transition boundaries.

Monday 4:25 Sweeney A SC12

Dynamics of suspensions of elastic capsules flowing in confined geometries

Pratik Pranay, Kushal Sinha, and Michael D. Graham
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Modeling the behavior of fluid-filled capsules (a simple representation of red blood cells and vesicles), is not only important to understand biological processes, such as blood flow in the microcirculation, but also to help design and improve microfluidic devices for characterizing such particles. The present work describes simulations of large numbers of deformable capsules in Newtonian and viscoelastic fluids in confined geometries. Our algorithm incorporates a General-Geometry-Ewald-Like method (GGEM) for efficiently calculating hydrodynamic interactions (O(N)) in an immersed-boundary method. This allows for a detailed description of the particle interface combined with a large degree of freedom to model the complex geometry. With our algorithm, we have addressed several issues. The ability to quickly simulate large number of particles enables examinations of not only the behavior of single particle, but also exploration of collision dynamics and concentration and confinement effects (capillary flows) on suspensions of such particles. The effect of addition of long-chained polymer molecules in blood flow, known to affect hemodynamics, is also investigated. Preliminary results show that the effect of polymer is significant in single particle migration and pair collisions. Through our simulations we aim to gain a fundamental understanding of the viscoelastic effects on blood flow in the microcirculation

Monday 4:50 Sweeney A SC13

The effect of vesicle deformability on the adhesive interactions between vesicles

Arun Ramachandran and L. Gary Leal
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Understanding the phenomenon of adhesion between vesicles is important for several biologically relevant processes and also for vesicle-based formulations such as fabric softeners, shampoos, creams, etc. Adhesive interactions between the constituent bilayers in vesicles can be directly measured using the surface forces apparatus, the atomic force microscope and the biomembrane force probe. In these methods, however, the interacting bilayers are supported on surfaces (e.g. mica sheet) and cannot be deformed, while in a suspension, vesicles composed of the same bilayers can deform by stretching or bending, and can also undergo changes in volume. Adhesively interacting vesicles can thus form flat regions in the contact zone, which will result in an enhanced total favorable energy of interaction as compared to undeformed, rigid vesicles. The calculations presented in this paper compare the energy of non-deforming, spherical vesicles and deforming vesicles. For vesicles with constant internal volume, we show that even very weak adhesive interactions between fixed bilayers can result in significantly deep energy minima for vesicles due to the flattening in the contact region, which can exceed the interaction between rigid vesicles by more than a factor of 10. If the osmotic exchange of water across the vesicles in the presence of an osmotically active solute is also taken into account, which takes place on a somewhat longer time scale, the vesicles can undergo further deformation (flattening), which further enhances the adhesive interaction between them. Finally, osmotic equilibration of ions and solutes, which occurs on an even longer time scale, can lead to further enhancement of the adhesion energy. The results of the analysis could explain why even very weak attractive forces may lead to depletion-induced flocculation of vesicles and their eventual separation from the suspending fluid by gravity, in spite of the fact that these interactions cannot even be measured on typical supported-bilayer devices.

Monday 5:15 Sweeney A SC14

The viscoelasticity of low viscosity ink jet suspensions

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This presentation describes recent work concerning the way fluid viscoelasticity influences ink filament break up and print head performance. Two series of model ink jet fluid were investigated. A first series was a base viscosity matched mixture of solvents and mono disperse polystyrene and the second series was again viscosity matched and built from mixing carrier ink jet fluids with pigment particles and surfactant. High frequency viscoelastic measurements were performed using a Piezo Axial Vibrator (PAV) rheometer developed by Professor Pechhold in Ulm University (Germany), and this enabled linear viscoelasticity high frequency to be obtained in the range 1hz-10khz. PAV data measurements showed the development of viscoelasticity for the fluids as a function of polymer and the particle loading. The data demonstrated that both the presence of polymer and particles can induce viscoelasticity within the fluid; although the form of this viscoelasticity was different depending on whether it was polymer or particle loading. The physical origin of viscoelastic effects produced by the presence of polymer or particles are different, and this results in a different high frequency limiting slope for the G' data. Additional non linear extensional behaviour was obtained using the “Cambridge Trimaster” filament stretching apparatus which, coupled with a high speed camera, enabled nonlinear stretch and break up to be observed. The behaviour of both particle and polymer were different. Finally ink jet performance for both series of fluids will be presented and compared.

Symposium MS
Polymer Rheology: Melts, Solutions and Blends

Organizers: Shi-Qing Wang and Marie-Claude Heuzey

Monday 1:30 Sweeney B MS1

A study on the flow, failure and rupture mechanisms of branched polyethylene in controlled-stress uniaxial extensional flow

Joao Maia and Ricardo Andrade
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Failure of polymer liquids under flow has been the subject of a relatively strong computational, theoretical and experimental effort over the years, despite which a clear picture of the phenomenon is still nonexistent. For example, there are still arguments in the literature whether the maximum in engineering stress, also known as the Considère limit for failure, is a point of true yielding of the polymer network or simply a purely elastic mechanical instability and if this onset of yielding also corresponds to the true onset of non-homogeneous deformation, as expressed for example by necking.

The main aim of this work is to contribute to the ongoing discussion on this matter by studying the transient and steady-state responses of a branched polyethylene melt undergoing pure uniaxial extensional deformation under constant-stress conditions. In particular we will analyze its failure and rupture behavior in both the viscoelastic and purely elastic deformation regimes of deformation.

This work was done using a new dual controlled-stress/rate extensional rheometer for high viscosity systems that our group recently developed[1]. Due to its unique combination of geometrical set-up and feed-back control loop it is possible for the first time to perform

experiments on polymer melts both in controlled rate and controlled stress modes up until the point of physical rupture, which is not the case with other instruments such as the SER or the Munstedt type of rheometers. The instrument designated the Controlled Stress/rate Extensional Rheometer, CSER, is again an adaptation to a rotational rheometer.

[1] JM Maia et al., "A new dual controlled stress/rate extensional rheometer for high viscosity systems", AIP Conference Proceedings - XVth International Congress on Rheology (2008), ISBN 978-0-7354-0549-3, p. 1111-1113.

Monday 1:55 Sweeney B MS2

Reversible large amplitude planar extension of soft elastomers

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The newly developed planar elongation fixture, designed as an add-on to the filament stretch rheometer, is used to measure reversible large amplitude planar elongation on soft elastomers. The concept of the new fixture is to elongate an annulus by keeping the perimeter constant. The deformation on the cylindrical probe is measured using digital imaging, and it is found that the diameter drops a few percent only compared to the initial diameter. Additionally it is found that a new approximation to the Doi-Edwards (DE) model, without independent alignment, captures the experimental data very well. In particular it is observed that this new approximation reproduces the order of magnitude of the deformation on the cylindrical probe. In fact it is demonstrated that the deviation from an ideal planar extension of the cylindrical probe is highly sensitive towards the choice of strain tensor. When analyzing the measured stress data, it is observed that there is some elastic recovery when reversing the flow. This is analyzed calculating the amount of work needed during the deformation, and it is observed that the sample itself contributes with work upon flow reversal.

Monday 2:20 Sweeney B MS3

Uniaxial extensional flow behavior of oligomeric sulfonated polystyrene melts

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The uniaxial extension properties of the alkali metal salts of oligomeric sulfonated polystyrene (SPS) ionomers were investigated and compared to that of well-entangled PS homopolymers. The oligomeric SPS had a weight-average molecular weight of 4,000 g/mol and a narrow polydispersity index of 1.06, which is below the entanglement molecular weight of PS. Yet, as reported previously, these oligomeric SPS ionomers show similar linear viscoelastic characteristics to those of entangled polystyrene melts. Uniaxial extension experiments were carried out to examine nonlinear rheological properties. Unlike an entangled PS melt that has a uniform entanglement network structure and responds to sudden extension with a comparable elastic modulus, these SPS melts undergo increasingly stiffer elastic deformation at increasing applied Hencky rates. The point of yielding at the engineering stress maximum occurs at a common, rather low, Hencky strain, nearly independent of the stretching rate in contrast to PS melts. Although both PS melts and SPS ionomers yield upon rapid extension, the pathways toward the disintegration of the network are rather different. In the former it occurs when no further chain extension can be supported by the intermolecular gripping force, whereas in the latter the network appears to break down at a comparable level of extension. The extrusion behavior of SPS is remarkably different as well, further pointing to the fact that such associative polymers are much weaker networks than networks due to chain entanglement.

Monday 2:45 Sweeney B MS4

Investigation of the rheological behavior of polymer melts in equibiaxial elongational flows

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Department of Chemical & Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States

Equibiaxial elongational deformations, where a fluid element is stretched equally in two directions while it contracts in the third direction, occurs in numerous technologies that include the processing of synthetic polymers and foodstuffs. Despite this importance, the rheological behavior of complex fluids in equibiaxial elongational flow is largely unexplored. Recently, we have demonstrated that limitations caused by uncontrolled lubricant thinning encountered in the Lubricated Squeezing Flow (LSF) technique are resolved in the novel Continuous Lubricated Squeezing Flow (CLSF) technique developed in our laboratory. To our knowledge, CLSF is the only experimental technique capable of generating large and homogeneous equibiaxial deformations in complex fluids. Here, we investigate the behavior of polymer melts with the goal of understanding the relationship between molecular architecture (molecular weight distribution and chain branching) on rheological behavior in constant strain rate deformations. Experimental results will be compared to predictions from molecular models for linear and branched polymers.

Monday 3:35 Sweeney B MS5

Slip-link simulations of entangled polymers in planar extensional and planar mixed flows with comparison to experiments

Amit Kushwaha[1] and Eric S. Shaqfeh[2]

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The non-equilibrium dynamics of entangled polymers is still an open problem in rheology. The presence of topological constraints or entanglements in an entangled system results in interesting rheological properties which are qualitatively different from dilute polymer solutions. In contrast to the dilute solutions which are relatively well understood, the modeling of entangled polymers for “fast flows”, in particular, is complicated due to the interplay between many dynamic chain mechanisms including reptation, tube-length fluctuations, constraint renewal/release, and chain stretch. Recent experimental data of the extensional viscosity of monodisperse polystyrene melts (Bach et al. 2003, Luap et al. 2005) has revealed a failure in the available models for entangled polymers. The experimental data shows an exponent of -0.5 in the extensional thinning region, in contrast to the DE/DEMG models prediction of -1. In the present work, we have extended a slip-link based model which was originally proposed by Masubuchi et. al. (J. Chem. Phys. 2001) to simulate planar extensional flow using Kraynik-Reinelt boundary conditions. Based on our extended model, we present a physical explanation for the failure of DE/DEMG models in predicting the correct thinning exponent. We explain the dynamics behind extensional thinning based on the orientation and stretch distributions of chains and propose that chain orientation plays an important role in thinning dynamics. We also present a detailed comparison of our planar extensional viscosity simulations to the experimental data of Sridhar et. al. We also extend the model to planar mixed flows and compute the birefringence of entangled system to understand the effect of flow type on the chain orientation characteristics. Finally, we discuss certain properties of the mesoscopic slip-link model and their direct effect on our rheological predictions including the presumed constant constraint renewal/release frequency and the decrease in number of entanglements for fast flows.

Monday 4:00 Sweeney B MS6

Melt extensional viscosity for polymer processing of PVC and PLA

Catheryn L. Jackson[1], Paul D. Van Rheenan[2], and Kevin J. Calzia[3]

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The extensional viscosity of polyvinylchloride (PVC) and polylactic acid (PLA) polymers modified with different processing aids was measured using the extensional viscosity fixture (EVF) for the ARES Rheometer. The processing aids studied were high molecular weight acrylic additives used at a 3 -12% level to improve the melt strength of the polymers. The PVC samples were fully formulated as used in solid PVC foam production, but without the blowing agent. Processing aids to be compared include conventional acrylic Paraloid™ K-series and Paraloid™ SureCel™foam cell stabilizing processing aids. Significant differences were seen in the strain hardening behavior of these two materials, which allow fabrication of lower density foam and thicker foam boards. PLA is a biodegradable plastic material blown or extruded into films for packaging applications. For PLA, the melt strength can be significantly increased by adding Paraloid™ BPMS-250 and 260, allowing faster processing rates. Experimental data showing the effect of prestretch conditions, rate, temperature and other variables for both the PVC and PLA examples obtained using the EVF will be presented.

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Monday 4:25 Sweeney B MS7

Examining the coil-stretch transition in flexible polymers

Rangarajan Radhakrishnan and Patrick T. Underhill

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The behavior of polymer solutions in elongational flow is important in many applications. An especially important property is the dramatic strain rate hardening resulting from the coil-stretch transition. Predictions of the coil-stretch transition and hysteresis made by DeGennes, Hinch, and others have been verified by visualizing single molecules of double-stranded DNA (ds-DNA). The same behavior has not yet been directly observed in single molecule studies of synthetic polymers or more flexible biopolymers such as single-stranded DNA. Current theories of flexible polymers predict these other polymers will behave in a similar way to ds-DNA. However, we have very recently predicted that these other polymers could have dramatically different behavior; the coil-stretch transition can be eliminated under some conditions.

For this purpose, we have altered the common bead-spring chain polymer models and simulated their response in flow using Brownian dynamics (BD). This new model we developed allows us to capture the importance of flexibility, entropic elasticity, hydrodynamic interactions, and solvent quality in an accurate and efficient way. This would have not been possible using conventional methods of including excluded volume as a repulsive interaction potential between beads; such a model would require such a large number of beads interacting that it would not be computational tractable. From our theory and BD simulations, we find that excluded volume interactions can have a dramatic effect on the coil stretch transition for long flexible polymers.

Monday 4:50 Sweeney B MS8

Dynamics of moderately entangled ring polymers

Rossana Pasquino[1], Simon Rogers[1], Frank Snijkers[1], George Sakellariou[2], Nikos Hadjichristidis[2], Taihyun Chang[3], Dimitris Vlassopoulos[4], and Michael Rubinstein[5]
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Recently it was shown that entangled ring polystyrenes relax their stress in a self-similar manner. Moreover, critical fractionation emerged as a process of great significance, necessary for understanding ring dynamics. Pure rings were shown to be extremely sensitive to linear chains "contaminants". These results were explained by invoking entropy maximization arguments and ideas from percolation theory. Here, we extend this work and attempt at addressing a number of open issues. We present preliminary results of a large international, interdisciplinary effort in this direction: we use 1,4-polyisoprene rings of molar masses in the range 25-60 kg/mol, prepared under different conditions (mainly good solvent). We confirm the earlier findings whereas at the same time present nonlinear rheological data (damping functions and stress transients) in comparison to linear polyisoprenes. We also discuss some dynamic light scattering data and compare against linear chains, showing the peculiarities of the ring conformation and their consequences.

Monday 5:15 Sweeney B MS9

The linear rheological responses of dense branched brush polymer

Miao Hu[1], Gregory B. McKenna[1], Yan Xia[2], Julia A. Kornfield[2], and Robert H. Grubbs[2]
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We examined the linear rheological responses of a series of dense and regular branched brush polymers. Different degrees of polymerization (DP = 200, 400 and 800) monodisperse polymers were synthesized from the ω-Norbornenyl macromolecule (as main chain) with 1.4kg/mol, 4.4kg/mol and 8.7kg/mol of polylactide side chains. The master curves for these brush polymers were obtained by time temperature superposition (TTS) of the dynamic moduli from the glassy plateau region to the terminal flow region. Two different relaxation processes can be observed for those samples with the higher molecular weight, slightly entangled, side chains. The dilution parameter a which is defined as the second plateau modulus divided by the rubbery plateau modulus is larger than what is expected by the hierarchical theory. We would further examine the basic ideas in the hierarchical theory proposed by McLeish [1, 2] and compare the results with theoretical predictions.

[1] S. T. Milner and T.C.B. McLeish, Macromolecules, 1997, 30, 2159-2166 [2] T.C.B. McLeish et al., Macromolecules, 1999, 32, 6734-6758.

Symposium SI
Surface and Interfacial Rheology

Organizers: Ophelia Tsui and Lenore L. Dai

Monday 1:30 Coronado/DeVargas SI6

Viscoelastic and structural changes of human Meibomian lipids with temperature

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The outermost layer of the tear film may play an important role in tear film stability via lipid mechanical properties. These mechanical properties are a result of lipid structure and organization. We seek to establish the range of viscoelasticity and structure found in stable tear films to ultimately identify which properties are important for stability in the tear film. Samples of human Meibomian lipids (ML) were collected via manual expression of ~15 glands in the lower lid of healthy volunteers with no clinical symptoms of dry eye. ML was stored at -20°C. Material was spread without solvent in a Langmuir trough and interfacial mechanical properties of ML monolayers were monitored using an interfacial stress rheometer. After compression monolayers were held at a fixed surface area while temperature was increased at 0.2°C/min. Crystalline structure of bulk Meibum was probed by small angle x-ray scattering (SAXS) between 25 and 45°C; grazing incidence x-ray diffraction (GIXD) measured order of ML monolayers at 25°C. At 15 mN/m and 18°C, ML monolayers were elastic with high surface moduli values, 2-7 mN/m. As the monolayers were heated to 35°C the surface viscous modulus decreased to 0.02 mN/m and the surface elastic modulus disappeared ~30°C. SAXS showed that bulk ML are crystalline with lamellar packing ~49Å, roughly the length of the lipids. As temperature increased peak intensity decreased and was absent by 45°C. Preliminary GIXD showed that ML monolayers form a tilted lattice with spacing ~4.85 Å. We have shown there is an association between structure and mechanical properties of ML. Moreover, the dramatic changes in interfacial viscoelastic properties are clinically relevant. If the melt temperature of lipids in dry eye individuals is altered (because, for example, of compositional differences), delivery of the lipids from the gland to the tear film and mechanical stabilization of the tear film may be modified in a manner that leads to instability.

Monday 1:55 Coronado/DeVargas SI7

Interfacial microrheoloy of phospholipid monolayer with cholesterol at the air-water interface

KyuHan Kim, Siyoung Q. Choi, Joseph A. Zasadzinski, and Todd M. Squires
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We describe a relationship between the domain structure and the surface dynamic properties of phospholipid monolayers with cholesterol at the air-water interface. Phospholipid monolayers with cholesterol can be served as a model system for biological interfaces, such as lung surfactant layers and leaflets of cell membranes. Furthermore, as a low amount of cholesterol is added to pure phospholipid monolayer, dramatic change of domain structure can be observed while its isotherm does not indicate any difference. We expect the dramatic change of domain structure induced from cholesterol can also affect on the surface dynamic properties. Accordingly, we developed a novel technique which exerts torque on the micro-fabricated disk probe by applying external magnetic field with a sufficient sensitivity to measure the surface dynamic properties as well as direct visualization of dynamics of domain structures. As a result, we found that the linear viscoelasticity of phospholipid monolayer decreases dramatically with a small amount of cholesterol.

Monday 2:20 Coronado/DeVargas SI8

Surface aging in blood serum using active microrheology

Prajnaparamita Dhar and Joseph A. Zasadzinski
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The magnetically driven motion of 300 nm diameter Nickel rods shows the surface viscosity of blood serum at an air-serum interface increases from 10^{-9} to 10^{-5} Ns/m over two hours while the surface pressure saturates in minutes. The increase in surface viscosity is not accompanied by a corresponding increase in elasticity. Differences in the surface properties of blood serum may be attributed to the formation of a monomolecular film of albumin, the most abundant hydrophobic protein in blood. The orders of magnitude change in the surface viscosity suggests that the protein film anneals with time, resulting in a more densely packed film leading to increased resistance to shear. The nanometer dimensions of the rods provide the same sensitivity as passive microrheology with an improved ability to measure more viscous films with faster response times.

Monday 2:45 Coronado/DeVargas SI9

Bulk and surface yield stress in a concentrated monoclonal antibody solution

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For various fundamental scientific and technologically motivated reasons, concentrated protein solutions (protein concentrations exceeding 50 mg mL) are model systems for inquiry into yield stress phenomena. In nature, proteins are found at very high concentrations (that favor yield, i.e., solid-like behavior) in physiological environments. Highly concentrated biopharmaceutics (protein drugs; typically concentrated monoclonal antibody, mAb, solutions) are increasingly applied to treat different diseases. An understanding of the bulk rheology of concentrated mAb solutions in the zero shear limit is important for designing drug delivery strategies. In addition, since proteins are, of course, amphiphilic, and hence surface active molecules, two dimensional (interfacial) viscoelastic measurements offer deep insights into the interfacial stability of proteins. Proteins are susceptible to unfolding-induced instability at interfaces. Interfacial viscoelasticity measurements can also shed light on the mechanisms by which surfactants stabilize protein molecules in solution. Therefore, experimental measurements of bulk and surface viscoelasticity of a mAb solution (mAb concentration = 100 mg/mL) have been performed on a stress-controlled rheometer. Linear and non-linear shear viscoelasticity were studied in the bulk by oscillatory and steady shear. Shear viscoelasticity at the air/water interface was measured using the Double Wall Ring of Fuller, Franck and Vermant. In addition to a bulk yield stress in this mAb solution, a yield stress at the air\water interface was also measured; the latter has an unambiguous signature in surface creep compliance measurements. The bulk and surface viscoelasticity of this mAb solution will be critically interrogated and reconciled with earlier bulk rheology data on mAb solutions (from the pharmaceutical sciences literature). Tentative ideas about the origins of the bulk and surface yield stress in concentrated protein solutions will also be offered in this presentation.

Monday 3:35 Coronado/DeVargas SI10

Interfacial rheology of single-wall carbon nanotube membranes

Erik K. Hobbie
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Thin membranes of single-wall carbon nanotubes (SWNTs) show considerable promise for a number of potential applications. The high conductivity and shape anisotropy of the nanotubes enable the formation of conductive quasi-2D networks at remarkably low surface density, and the mechanical characteristics of the individual SWNTs can be outstanding. Recent advances in the separation of SWNTs by length and electronic type allow for the production of films and coatings with precisely tunable properties, and the tremendous potential of these films for flexible-electronics applications demands a deeper understanding of the coupling between deformation and microstructure. Compressive wrinkling has emerged as a powerful tool for measuring the modulus of thin polymer films supported by soft flexible substrates, and we use this approach here to study the nonlinear deformation of membranes assembled from SWNTs that have been purified by length or electronic type (metallic vs. semiconducting). Our measurements reveal a material that is remarkably stiff under infinitesimal deformation but softens dramatically at finite strain. We link this strongly non-linear behavior to an upward shift in percolation threshold triggered by strain-induced nanotube alignment, an effect correspondingly apparent as an anisotropic decrease in conductivity. We extract the modulus and yield strain as a function of nanotube surface density and film thickness and compare these with theoretical models of percolation in anisotropic 2D rigid-rod networks.

This work is supported by the National Science Foundation through CMMI-0969155.

Monday 4:00 Coronado/DeVargas SI11

Structure and rheology of fiber-laden membranes via integration of nematodynamics and membranodynamics

Alejandro D. Rey and Yogesh K. Murugesan
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This talk presents a study of the structure and dynamics of rigid fiber-laden deformable curved fluid membranes based on an viscoelastic model that integrates the statics of anisotropic membranes, the planar nematodynamics of fibers and the dynamics of isotropic membranes. Fiber-laden membranes arise frequently in biological systems, such as the plant cell wall and in protein-lipid bilayers. Based on the membrane's force and torque balance equations and the fiber's balance of molecular fields, a viscoelastic anisotropic model that provides the governing equations for the membrane's velocity and curvature and the fiber structure (fiber orientation and order) is found. A Helmholtz free energy that incorporates the tension/bending/and torsion membrane elasticity, the Landau-de Gennes fiber ordering, and fiber order-membrane curvature interactions is used to derive elastic moments, torques, and stresses. The corresponding viscous stresses and moments include the Boussinesq-Scriven contributions as well as bending, torsion, and rotational dissipation. A spectral decomposition leads to the main viscoelastic material functions for anisotropic fluid membranes. Applications of the rheological model to cylindrical growth and cylindrical axial stretching show that competing curvo-phobic, curvo-philic interactions under extensional flow predict transitions between axial and azimuthal fiber arrangements, of interest to cellulose fiber orientation in plant

Monday 4:25 Coronado/DeVargas SI12

Dynamic moduli of nematic liquid crystal polymers with tangential anchoring

Eric P. Choate and M. Gregory Forest
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We apply anchoring conditions to a nematic liquid crystal polymer system so that the major director lies parallel to the plates of a shear cell, and then we apply a small amplitude shear flow at an arbitrary angle to the direction of the anchoring. We use a Doi-Marrucci-Greco tensor model with one dimensional spatial heterogeneity to predict the storage modulus and viscosity. If the anchoring direction lies in the flow-flow gradient plane (in-plane anchoring), the system effectively reduces to Leslie-Ericksen theory. If the anchoring is aligned with the flow vorticity axis (logrolling anchoring) the solution is also analytically solvable. For the oblique angles in between in-plane and logrolling, we can solve the system numerically. The viscosity is smaller for logrolling anchoring than in-plane anchoring, and we observe that logrolling anchoring thins above a critical frequency, unlike in-plane anchoring. The storage modulus for in-plane anchoring is slightly larger than logrolling for low frequencies; however in-plane anchoring plateaus at lower frequency than logrolling, allow the logrolling case to be two-to-three orders of magnitude larger than in-plane for higher frequencies.

Monday 4:50 Coronado/DeVargas SI13

Modeling dynamics and rheology of droplets of liquid crystal polymers using kinetic theories

Qi Wang[1], M. Gregory Forest[2], and Xiaofeng Yang[1]
[1]Mathematics, University of South Carolina, Columbia, SC, United States; [2]Department of Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States

We present a kinetic theory for droplets of liquid crystal polymers immersed in a viscous fluid. Due to the interfacial interaction between the host viscous matrix and the liquid crystal polymer droplets, two symmetric anchoring conditions may occur: tangential and homeotropic. We develop a new kinetic theory based model to study the interfacial nematic structure at the interface and the morphology of the droplet in equilibrium and under shear flows. The new model can resolve the defect structure near the interface explicitly and capture how these defects deform under shear. This new kinetic approach establishes a paradigm to study interfacial dynamics of droplet of complex fluids.

Monday 5:15 Coronado/DeVargas SI14

Nanomechanical properties in ultrathin polymer films: Measurement on rectangular vs circular bubbles

Shanhong Xu and Gregory B. McKenna
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Confinement effects on the mechanical properties of ultrathin polymer films were investigated by a bubble inflation technique developed in our lab. Prior studies of ultrathin films of poly(vinyl acetate) (PVAc) and polystyrene (PS) were performed on circular bubbles of different diameters. In this study creep behaviors of ultrathin films of PS were investigated on rectangular bubbles. The thicknesses of the thin films for rectangular bubbles range from 20 to 40nm. The modulus of the thin film rectangular bubbles was analyzed by exact solutions and an approximation method. The mechanical properties of the thin films with the same thickness for circular and rectangular bubbles are compared and we find that the rubbery plateau compliance is geometry independent.

Symposium FD
Micro- and Nano-Fluidics

Organizers: Siva Vanapalli and Anubhav Tripathi

Monday 1:30 Peralta/Lamy FD6

Micro fluidic slug flow separation of two phase immiscible liquids

Malcolm R. Mackley[1], David Agar[2], Frederik Scheiff Scheiff[2], and Nuno Reis[1]
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This presentation describes recent work carried out concerning the way micro slugs of oil in water flowing within a plastic Micro Capillary Film (MCF) can be separated using a branched flow consisting of a hydrophobic and hydrophilic stream. Micro slugs of oil in water were created by sidestream injection of water into a 600 micron diameter capillary made from plastic. Slug formation was characterised as a function of flowrate and also viscosity ratio of the two fluids and both parameters were were found to be important. A hydrophilic metal needle was introduced into the plastic MCF to form a downstream flow junction and flow conditions were discovered where the oil slugs would flow down the hydrophobic channel and the aqueous stream along the hydrophilic channel. A pressure balance model was developed to help describe and understand the results. The separation strategy appears novel and could be of use in separating immiscible fluid suspensions if the fluids can form slugs within appropriate diameter microchannels. The process is particularly sensitive to viscosity ratios and surface tension.

Monday 1:55 Peralta/Lamy FD7

Lubricated extensional flow in a microchannel

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Many of the fluids used in microfluidic devices have complex microstructures and exhibit viscoelastic properties. Few conventional techniques are available, however, to characterize these fluids in extension and at the high shear rates relevant to microfluidic applications. We have developed a technique for estimating the extensional flow resistance of dilute polymer solutions using a lubricated converging-channel flow. The channel has a hyperbolic profile, and the viscous or viscoelastic core fluid is lubricated by a less viscous Newtonian fluid introduced at the channel entrance. The velocity field is found from a combination of particle image velocimetry data, the flow rate, and the locus of the fluid/fluid interface. Extensional viscosity is estimated from the pressure in the channel or from a balance of stresses at the interface.

A viscous Newtonian fluid (η = 60 mPa.s), lubricated by de-ionized water (η = 0.9 mPa.s), was tested first, and the lubricant produced a large decrease in the pressure drop. When a small amount (50 ppm, 200 ppm, or 500 ppm) of polyethylene oxide ($M_w \sim 4{,}000{,}000$) was dissolved in the core fluid, the viscosity barely increased but the core flow separated from the sidewalls upstream. An instability generated at high flow rates was eliminated by using an immiscible lubricating fluid. With a stable core flow, the extensional rate was evaluated from the flow rate and the interfacial locus.

The technique promises to yield measurements of extensional viscosity as a function of strain as well as strain rate, and thus to be useful in characterizing complex biological fluids such as Matrigel and Collagen Type I, at various temperatures and for fluid volumes on the order of 10^{-2} ml.

Monday 2:20 Peralta/Lamy FD8

An immersed boundary method for flowing DNA through microfluidic devices

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We have developed an immersed boundary method that allows fast calculation of Brownian dynamics of polymer chains and other particles in complex geometries with fluctuating hydrodynamics. This method is based on general geometry Ewald method which solves the Stokes's equation with distributed regularized point forces with O(N) operations. The implementation is verified against Hasimoto's solution of point force in periodic boundary domain and exact solution for the problem of uniform flow around a solid sphere. Fluctuating hydrodynamics is introduced into the calculation using a midpoint algorithm and Chebyshev polynomial approximation which are both proposed by Fixman. This approach is applied to the flow-driven actuation of a tethered λ-DNA molecule which functions as a soft nanomechanical switching element for microfluidic devices. Comparisons with previous results of electrostatic-driven actuation case has been made.

Monday 2:45 Peralta/Lamy FD9

Controlled DNA tethering and stretching with microfluidics for single-molecule electronics

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DNA molecules have been recently explored as powerful scaffolds for creating molecular wires. Metallized DNA scaffolds can lead to reliable electrical contacts to single organic molecules forming arrays of single-molecule electronic devices. One of the critical steps in the process is to control the tethering and stretching of DNA molecules. In this work, we develop reproducible surface chemistry for tethering DNA at tunable density and flow processing for controlled DNA stretching and alignment. Enzymatic cleavage of λ-phage DNA has been used to create a series of tethered DNA chains of various lengths and the effect of shear rates on flow/extension behavior of this series has been investigated using designed microfluidic channels and single molecule fluorescence microscopy. Flow dynamics of different length DNA chains is further compared to Brownian Dynamic simulations of the Kratky-Porod chain through lengths as small as 4 microns. Furthermore, we demonstrate the controlled stretching and double tethering of thiol functionalized DNA molecules (10 kbp) between pre-defined gold electrodes. Subsequent metallization of the DNA scaffolds could eventually lead to reliable and reproducible metal contacts to single organic semiconducting molecules of interest. This progress represents an important step towards efficient fabrication of large scale single-molecule electronic devices.

Monday 3:35 Peralta/Lamy FD10

Separation of macromolecules by their size: The mean span dimension

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Size Exclusion Chromatography (SEC), also referred to as gel chromatography, gel filtration, has evolved into one of the most prevalent separation techniques for synthetic and natural polymers, including proteins and carbon nanotubes. There are also micro-/nano-fluidic sorting devices that mimic SEC separation. However, despite a wide usage of such separation devices, an ambiguity about the separation principle remains unsolved. We introduce here the concept of the molecular mean span dimension. It will be demonstrated how this property is related to the separation principle of microfluidic devices (including SEC) that separate molecules based on size. General polymer architectures are constructed from three types of fundamental subchains , namely, 1) connector, 2) arm and 3) loop. We then derive general results for the mean span of arbitrary polymer architectures including stars, Pom-Poms and rings. New analytical results are given for stars. It is demonstrated that the mean span concept provides improved understanding of the separation principle in SEC.

Monday 4:00 Peralta/Lamy FD11

Rheo-optics and μ-PIV for probing the high deformation rate rheological behavior of worm-like micelles in complex microscale flows

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On account of the small lengthscales associated with microfabricated devices, microfluidic rheometry may be used to observe the response of viscoelastic fluids undergoing very large deformation rates (10^2-10^4 s^{-1}) even for moderate volumetric throughputs. In our experiments, we combine micro-particle image velocimetry (μ-PIV) and a full-field birefringence system to study two different worm-like micellar solutions as they flow through microscale geometries. By adapting a commercial birefringence microscope (the ABRIO system (CRi., Inc.)) to enable time-resolved pixelwise measurements of extinction angle and retardance in the fluid, we obtain highly spatially resolved measurements of the evolution of the average stress and molecular conformation in a micellar solution undergoing strong deformations. These measurements are coupled with μ-PIV kinematic measurements to probe the behavior of worm-like micellar solutions in complex geometries characteristic of flows in inkjet heads and porous media.

First, we observe the shear-banding and shear-thinning of CPyCl:NaSal and CTAB:NaSal micellar solutions in steady Poiseuille flow through a rectilinear channel. Then we build on previous work with polymer solutions (Oliveira *et al*., 2007, and Soulages *et al*., 2009) to observe the corresponding behavior in extension-dominated flows in converging and T-shaped microchannels. We characterize the steady flow and onset of viscoelastic flow instabilities in order to gain insight into the spatiotemporal dynamics of the non-linear viscoelastic behavior of worm-like surfactant systems.

Monday 4:25 Peralta/Lamy FD12

Irreversible gelation of wormlike micelle solutions in microfluidic devices

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The formation of flow-induced gel-like structures in surfactant solutions containing wormlike micelles have previously been observed in macroscopic flow under applied shear in dilute solutions of cetyl-trimethylammonium bromide (CTAB) and sodium salicylate (NaSal). However, the observed gel-like phase transition is short-lived once the applied flow is stopped and reversibly disappears. Recently, irreversible gelation was achieved by applying high shear and extensional flows within a packed bed of microbeads in a microfluidic device [1]. We present here a further investigation of the irreversible flow-induced gelation of dilute solutions of CTAB/NaSal in microfluidic devices with microfabricated arrays of microposts with varying post diameters and inter-post spacing. The onset of gelation at various concentrations and applied shear rates will be examined to determine the extent of this phenomenon. Additionally, different surfactant systems that behave similarly to wormlike micelles will be investigated.

Reference: [1] Vasudevan, M., et al., *Irreversible nanogel formation in surfactant solutions by microporous flow.* Nature Materials, 9(5), 436-441, 2010.

Monday 4:50 Peralta/Lamy FD13

Shear induced ordering of defect textures arising from the undulation instability of layered fluids

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The undulation instability is a characteristic structural instability in lamellar fluids. In thermotropic smectic liquid crystals, sinusoidal undulations grow to form disordered arrays of parabolic focal conic defects [1]. By the simultaneous application of dilatation and shear, highly ordered defect arrays can be formed. Such highly ordered micron scale focal conic defect arrays have been used as lithographic templates [2].

While the undulation instability is well understood, the growth of the nonlinear instability leading to the formation of focal conic defects is not. We examine the nonlinear growth of defects using a custom-built shear cell with plate separations of 100 to 500 microns. We examine the annihilation and growth of defects in the presence of simultaneous dilatation and shear, as well as in pure compression and expansion without shear. We examine the effect of sample thickness on the growth and ordering of defects and on the scaling of defect sizes. We characterize the long range order of the defect textures using the radial and angular components of the pair distribution function. When defects are disordered, we observe that application of shear induces partial ordering.

We use polarization microscopy to reveal the three-dimensional structure of the ordered array of defects. In simple shear flow, we observe that defects move as rigid bodies surrounded by layers of viscous liquid. The defects are not centered about the midplane of the sample, and they do not span the entire sample thickness. These observations provide important information about the rheology of defect-ridden smectics.

[1] Rosenblatt C, Pindak R, Clark N et al (1977) J. Physique 38, 1105-1115. doi:10.1051/jphys:019770038090110500. [2] Kim Y, Lee J, Jeong H et al (2010) Adv. Mater. Advanced online publication doi: 10.1002/adma.200903728.

Monday 5:15 Peralta/Lamy FD14

Intermittent dynamics in particle-tracking bio-microrheology

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In active biological systems, such as living cells, probe particles experience Brownian motion combined with active transport, due to intracellular processes. That can lead to trajectories of local diffusion and trapping, punctuated by segments of active transport. Analyzing such a trajectory as a single unit masks the intermittent nature of the motion. Moreover, directly applying the generalized Stokes-Einstein relation in out-of-equilibrium systems is incorrect and returns inaccurate rheological parameters. We present an image-processing based approach able to segment intermittent trap-escape trajectories, allowing quantitative analysis of active phases. We then evaluate intermittent dynamics of particle motions in active systems and discuss subsequent results of our algorithm, defining controlling parameters, such as particle size and camera frame rate.

Symposium CR
Computational Rheology: Behavior 'in Silico'

Organizers: Rajesh Khare and Daniel J. Lacks

Monday 1:30 O'Keeffe/Milagro CR6

Performance of mesoscale modeling methods for predicting microstructure, mobility and rheology of charged suspensions

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In this presentation we examine the accuracy and performance of a suite of discrete-element-modeling approaches to predicting equilibrium and dynamic rheological properties of polystyrene suspensions. What distinguishes each approach presented is the methodology of handling the solvent hydrodynamics. Specifically, we compare stochastic rotation dynamics (SRD), fast lubrication dynamics (FLD) and dissipative particle dynamics (DPD). Method-to-method comparisons are made as well as comparisons with experimental data. Quantities examined are equilibrium structure properties (e.g. pair-distribution function), equilibrium dynamic properties (e.g. short- and long-time diffusivities), and dynamic response (e.g. steady shear viscosity). In all approaches we deploy the DLVO potential for colloid-colloid interactions. Comparisons are made over a range of volume fractions and salt concentrations. Our results reveal the utility of such methods for long-time diffusivity prediction can be dubious in certain ranges of volume fraction, and other discoveries regarding the best formulation to use in predicting rheological response.

Monday 1:55 O'Keeffe/Milagro CR7

Determination of local viscoelastic properties of confined polymer melts from molecular dynamics simulations

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The nanoscale rheological properties of complex fluids are governed by the molecular topology as well as the specific chemical interactions in the system. Molecular modeling can explicitly account for the molecular structure and the detailed interactions in the system and thus provides a unique tool for systematic investigation of the nanoscale viscoelastic behavior. In this work, we analyze the usage of molecular dynamics simulations for performing active nanorheology to obtain the local rheological properties of confined polymer melts. Specifically, the viscoelastic properties of a confined polymer melt are determined by analyzing the medium response to the oscillatory motion of a probe particle in the polymer melt. The system parameters that play an important role in the application of the technique are identified. Results will also be presented for the variation of the local viscoelastic properties as a function of the chain topology and the distance from the confining surface.

Monday 2:20 O'Keeffe/Milagro CR8

Molecular scale simulation correlations to rheological characteristics of complex mixtures

Peter H. Koenig[1], Bruce P. Murch[1], Pierre Verstraete[2], Kelly L. Anderson[1], David M. Eike[1], John D. Shaffer[1], and Michael L. Hilton[3]
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We want to probe how molecular structure of ingredients in complex mixtures impact certain macroscopic rheological characteristics. We have developed simulation analysis tools that allow us to extract a set of new quantitative descriptors from molecular scale dynamics simulations of surfactant mixtures. Such descriptors enable the construction of empirical models that relate surfactant compositions to rheological properties operating at a much larger scale. This lets us explore composition mixtures and demonstrate trends that are at times non-obvious. We would also like to use more explicit multi-scale models, but this is a challenging process due to the many orders of magnitude of length- and time scales involved. We recognize that measured rheological characteristics derive from complex mechanisms operating at scales well beyond those accessible to molecular scale simulations. There remain significant gaps in simulation capabilities explicitly bridge time and size scales from molecular to macroscopic scales. The more direct correlation models can fill this gap for some contexts.

Monday 2:45 O'Keeffe/Milagro CR9

Effect of interparticle and particle-wall hydrodynamic interactions on effective viscosity of a cylinder-bound suspension

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For an unconfined dilute colloidal system, Einstein's equation expresses the change in effective viscosity as proportional to the solute volume-fraction. However, for a conduit-bound dense suspension, this relation has to be modified. Then, the change in rheological properties is not linearly proportional to the volume-fraction due to interparticle flow interactions, and the linear dependence has to be replaced by a power series expansion. Moreover, in such systems, the rheology depends on geometry manifesting the influence of particle-wall hydrodynamic interactions on the macroscopic transport. In this talk, we present results describing effective viscosity of a suspension as function of volume-fraction and conduit-radius to illustrate the effect of interparticle and particle-wall flow interactions on rheology. For this purpose, the hydrodynamic friction and mobility tensors of many-sphere system inside a cylinder are first computed by using a new Stokesian dynamics algorithm. These tensors are incorporated in many-body Smoluchowski equation to find the steady-state distribution of number density of the spheres in parabolic flow. Then, the effective viscosity of the medium is related to the additional pressure drop induced by freely suspended bodies with steady-state density distribution. Finally, we express the viscosity as a power series expansion of volume-fraction with geometry-dependent expansion coefficients, and plot these coefficients as functions of cylinder to sphere size-ratios for different Peclet number. We also consider transient flow-rate in the channel, and solve unsteady Smoluchowski equation to find the temporal variation in number density inside the channel. We explore the shear induced structural changes in the configuration of colloidal particles to understand shear thickening behavior in narrow conduits. Then, the time-dependent effective viscosity is calculated for unsteady systems with different size-ratios and Peclet numbers.

Monday 3:35 O'Keeffe/Milagro CR10

Simulation of red blood cell aggregation and blood rheology

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Blood rheology is mainly governed by viscoelastic properties of red blood cells (RBCs), their concentration and interactions. In experiments, a shear-thinning behavior of blood is generally found. However, at low shear rates or in equilibrium RBCs tend to aggregate and form rouleaux structures which resemble coin stacks. RBC aggregation results in a significant increase of blood viscosity at low shear rates and in a subsequent increase in the blood flow resistance in vessels, where the flow is relatively slow. We model blood as a suspension of individual RBCs which incorporate realistic RBC membrane properties and aggregation interactions. Blood rheology as well as the effect of RBC aggregation is investigated through numerical simulations of RBC suspension using the dissipative particle dynamics method. The results are compared with available experiments showing good quantitative agreement.

Monday 4:00 O'Keeffe/Milagro CR11

Experiments and models to understand polyurethane foam processing

Rekha R. Rao[1], Lisa A. Mondy[1], Mathew C. Celina[2], Douglas B. Adolf[2], Jamie M. Kropka[2], and Edward M. Russick[2]
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We are developing production-level foam process model for chemically blown polyurethane. This foam has two major simultaneous competing reactions, the polymerization of the reactive resins and carbon dioxide gas formation that creates the foamed material. The kinetics of the resin cure were evaluated using a dry polyurethane precursor, as water is essential to carbon dioxide formation reaction, in order to separate the polymerization and blowing reactions, which both consume primary isocyanate groups. The kinetics of the foaming reaction was measured by tracking volume evolution with time in both the curing system and a model system with a constant viscosity. This allowed us to compare the rate of gas expansion in a material with evolving viscosity and elasticity to one with constant values, which can give us an estimate of how much gas volume is lost due to bubble pressurization. Rheology was performed on the dry polyurethane system in order to quantify the effects of cure and temperature on the continuous phase viscosity. Rheology of the foam was carried out to understand the effect of gas fraction on the flow of polymer and verify whether or not the effects of the disperse phase and continuous can be decoupled in the viscosity model. A finite element model was developed combining the equations of motion, an energy balance, a density model to represent the foam blowing reaction, and a rate equation for the polymerization reaction. This was combined with a level set method to track the location of the free surface as it evolves in time. The model is compared to experimental flow visualization data.

Monday 4:25 O'Keeffe/Milagro CR12

Stabilized finite element approximation of flows of viscoplastic liquids inside a cavity

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In this work, a numerical investigation of inertia effects in flows of viscoplastic liquids inside a cavity is performed. The conservation equations of mass and momentum are solved using a stabilized finite element approximation, which employs a multi-field Galerkin least-squares strategy in terms of extra-stress, pressure and velocity. This methodology improves the classical Galerkin stability by adding mesh-dependent terms, which are functions of the residuals of flow governing equations. The viscoplastic behavior of the fluid is modeled by the regularized SMD equation (Souza Mendes e Dutra, 2004). The velocity and extra-stress fields are obtained for different rheological parameters, flow conditions (inertia and inertialess) and aspect ratios. Moreover, the yielded/unyielded regions are determined. Two distinct unyielded regions are observed, one close to the walls (stagnant flow) and another close to the lid cavity (plug-flow zone). The unyielded zones decrease as we increase the power-law index and the lid cavity velocity. In the inertia flows, the advective effects move the plug-flow regions to the right and bottom walls. The effect of the cavity aspect ratio was also investigated, and it is observed that larger stagnant regions are formed for deeper cavities.

Keywords: viscoplastic liquids, regularized models, SMD fluid, multi-filed formulations, GLS method.

Souza Mendes, P.R., and Dutra, E.S.S., 2004, "Viscosity Function for Yield-Stress Liquids", Applied Rheology, Vol. 14, pp. 296-302.

Monday 4:50 O'Keeffe/Milagro CR13

A simulation-based approach to obtain the constitutive equation for waxy crude oil systems

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Increased oil exploration and production activity from deep-water fields have brought flow assurance issues to the forefront. New frontiers in Flow Assurance deal with the development of strategies that allow for continuous flow of oil in adverse conditions, such as the presence of waxes, hydrates, and/or asphaltenes. In waxy crude oils, wax starts to precipitate out of solution as the temperature falls below the Wax Appearance Temperature (WAT). This wax-oil mixture forms a gelling system, with aspherical wax particles aggregating to form a percolated network structure in the oil and the concomitant appearance of a yield stress.

We study the gelling wax-oil system by using dissipative particle dynamics (DPD). DPD is a particle-based simulation technique originally developed to study colloids. The technique is similar to molecular dynamics, in which particle interactions are given by a known potential form. DPD provides the flexibility to tune the potential form and parameters to represent the desired system. The original formulation of DPD allows simulating fluids with Schmidt number (Sc) of order 1, whereas typical liquids have Sc ~ $O(10^3)$. An extension of DPD, incorporating the Lowe-Andersen thermostat (DPD-LA), allows the simulation of fluids with Sc ~ $O(10^5)$.

In the present study, we use this DPD-LA scheme to investigate the rheology of a wax-oil system. We studied the rheological response at various wax concentrations and shear rates. Preliminary results show an Arrhenius-like behavior of the viscosity above the WAT in agreement with experiments. A progressive deviation from Arrhenius-like behavior is observed as the temperature goes below the WAT. We compare results for the viscosity with predictions of available empirical continuum models, e.g. Pedersen's model.

Monday 5:15 O'Keeffe/Milagro CR14

Submerging flows of non-Newtonian impinging jets

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When a fluid jet impinges onto a shallow pool of fluid, a variety of behaviors may occur around the impact region. One example is mounding, where the fluid enters the impact region faster than it can flow away, forming a mound of fluid above the main surface. For some operating conditions, this mound can destabilize and buckle, entraining air in the mound. Other behaviors include submerging flow, where the jet impinges into an otherwise steady pool of liquid, entraining a thin air layer as it enters the pool. This impact region is one of very high shear rates and as such, complex fluids behave very differently than do Newtonian fluids.

In this work, we characterize this range of behavior for Newtonian and non-Newtonian fluids. We model the fluid as a Bingham-Carreau-Yasuda fluid, which exhibits the full range of pseudoplastic flow properties throughout the impact region. Additionally, we study viscoelastic effects through the use of the Giesekus model. Both 2-D and 3-D numerical simulations are performed using a variety of finite element method techniques for tracking the jet interface, including Arbitrary Lagrangian Eulerian (ALE), diffuse level sets, and a conformal decomposition finite element method (CDFEM). The presence of shear-thinning characteristics drastically reduces unstable mounding behavior, yet can lead to air entrainment through the submerging flow regime. We construct an operating map to understand for what flow parameters stable and unstable submerging flows will occur and how the fluid rheology affects these behaviors. This study has many implications in high-speed industrial bottle filling applications.

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

Symposium BF
Rheology of Natural Materials: Biorheology and Food Rheology

Organizers: Danilo Pozzo and Peter Fischer

Monday 1:30 Kearney BF6

The confined flow of red blood cells past a wall-bound leukocyte

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The micron-scale rheology of blood, due to its cellular character, plays a critical role in the phenomenology of the microcirculation. For example, as part the inflammation response, white blood cells (leukocytes) bind nearly statically to the vessel wall before transmigrating across the endothelium. We will present quantitative simulations of the forces exerted on a wall bound leukocyte due to the red blood cells flowing by. The simulation tool is based on a fast boundary integral formulation, which permits the red cells to both be realistically flexible and approach to very close separation distances. Comparisons with experiments on the effective viscosity for flow in small tubes demonstrate that this is a reasonable quantitative model for confined cell-scale blood flow. The red blood cells are modeled as membranes enclosing a Newtonian hemoglobin solution with an also Newtonian plasma outside of them. The elastic membranes are flexible in shear and bending, but have a strong resistance to surface dilatation. The no-slip condition is applied on the leukocyte as well as the vessel walls. We will show that for vessel diameters less that 20 microns, the particulate nature of blood due to the presence of individual red cells significantly affects the magnitude of the forces that the leukocyte experiences, transiently increasing well above a simple-homogeneous fluid prediction. For a tube hematocrit of 25% and a spherical protrusion with a diameter three-quarters times that of the tube, the average forces are increased by about 40% and the local forces by more than a factor of two relative to forces from an effective-viscosity homogenized blood. Different flow configuration are considered and analyzed.

Monday 1:55 Kearney BF7

Probing the nonlinear response of collage gels using confocal rheology

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Branched Type I collagen fiber networks provide extracellular support in mammalian tissues. The intricate network structure can succumb to partial or complete tearing under sufficient applied strain. Under small shear strains, in vitro collagen gels exhibit strain-stiffening while maintaining overall network integrity. Higher shear strains lead to network failure through discrete yielding events. We perform rheology and confocal-rheology experiments to fully elucidate the strain-stiffening and yielding behavior in these highly nonlinear materials. We apply continuous shear strains to collagen gels confined within the rheometer at fixed gaps. We observe that sheared collagen in the strain-stiffening and yielding regime has an apparent modulus that is strongly dependent on the collagen thickness. Moreover, using confocal rheology, we are able to simultaneously quantify the collagen network morphology in the nonlinear regime. These results have broad implications for the interpretation of rheological data of extracellular matrix proteins and for the design of biomimetic scaffolds.

Monday 2:20 Kearney BF8

Morphological and rheological characterization of chitosan anisotropic gels

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In this work the formation of chitosan anisotropic (liquid crystalline) gels was investigated. Chitosan, poly[β-(1-4)-linked-2-amino-2-deoxy-O-glucose], is a derivative of chitin used in several biomedical applications were biodegradability is important. The biomedical interest in these liquid crystalline systems lies in the possibility of mimicking the structure of the main component of the extra-cellular matrix in connective tissues, collagen type I, which has analogous liquid crystalline ordering in acidic solutions. Malic and chloridric aqueous solutions with different concentrations of chitosan (0 - 6 wt%) were prepared and the gel formation was followed by rheological measurements. In fact, by measuring the complex modulus, and its components, in function of the angular frequency, at ambient temperature, we were able to determine the concentration above which a crossover between the values of G' and G" occurs, indicating a sol-gel transition. This transition was also observed in steady state measurements of the viscosity in function of the shear rate. The concentration, c*, at which the gel is formed was found to be dependent on the acid used, the malic aqueous solutions presenting higher c*. Finger-prints texture typical of cholesteric mesophases were observed by Polarised Optical Microscopy (POM) and the helical pitch was determined from POM images.

Monday 2:45 Kearney BF9

Mixing and conveying high solids biomass using rheological modifiers

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Rising global demand for energy combined with an increasing appreciation for the environmental consequences of petroleum-based fuel use is motivating research and development of more carbon-neutral, widely accessible sources of renewable energy. Particularly critical to the transportation industry is an abundant source of renewable liquid fuels. A likely feedstock in the production of fuel ethanol is lignocellulosic biomass. Many processes designed to convert lignocellulosic materials to liquid fuel require operations in which biomass slurries are heated (e.g. the NREL process). Reducing the amount of water present in those slurries lowers operating costs associated with heating and makes such processes more economical.

Processing biomass at high solids concentration leads to a number of difficulties that are not present in dilute systems. Concentrated biomass acts as a Bingham fluid with a yield stress that increases rapidly with solids concentration. This behavior makes pumping and transporting the process slurry difficult if not impossible. In addition, the mixing required to obtain adequate rates of mass transfer when introducing reactants into the slurry is severely inhibited.

Prior work on fiber suspensions has shown that controlling the magnitude of yield stresses of biomass slurries is possible using small amounts of high molecular weight polymers. We examined the rheological behavior of biomass with polymer additives as a function of process conditions using torque rheometry. Temperature, pH, solids concentration and biomass type (e.g. corn stover vs. switchgrass) were considered as process variables. Biomass pH and solids concentration significantly affect polymer efficacy. Unusual behavior in the form of a non-monotonic increase of stress with strain rate was observed which can be modified with the addition of polymer. We will also describe more recent experiments in which those rheological modifiers are exploited to facilitate extrusion of biomass at high solids concentrations.

Monday 3:35 Kearney BF10

Rheology modification and enzyme kinetics of high solids cellulosic slurries

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Chemical additives that reduce the yield stress and viscosity of pretreated corn stover slurries and also enhance the kinetics and overall conversion of cellulose during enzymatic saccharification were explored. Additives included polymers, proteins, and nonionic, anionic, and cationic surfactants. Rheological measurements assessed changes in the yield stress of the suspensions, and enzymatic saccharification experiments were conducted to assess the effect of the additives on enzyme kinetics. For high-solid slurries with an insoluble solids content of about 20%, a 3- to 4-fold reduction in the yield stress was observed upon addition of 2% (w/w) cetylpyridinium chloride (CPCl), cetyl trimethylammonium bromide (CTAB),sodium dodecylbenzene sulfonate (NaDBS), and sodium dodecyl sulfonate (SDS). However, the presence of bovine serum albumin (BSA) at the same concentration doubled the yield stress. Although NaDBS and SDS were both very effective at reducing the yield stress, their presence was very detrimental to the saccharification kinetics, cutting cellulose conversions from 80% to less than 20% over one week due to chemical inhibition of the enzymes. However, the surfactants CPCl and CTAB synergistically reduced the yield stress and increased the relative extent of cellulose conversion by up to 35% during the first 24 h of saccharification. It is hypothesized that the increased rate of saccharification observed with the presence of CPCl and CTAB are associated with the decreases in the suspensions' yield stresses, which in turn may affect the uniformity of mixing within the saccharification reactors. Of the modifiers tested, CPCl and CTAB appear to be the most efficacious, as they both reduce the yield stress at concentrations as low as 0.1% (w/w) and improve the kinetics of enzymatic saccharification. Lastly, the economic implications of rheology modifiers in a hypothetical lignocellulosic biomass-to-ethanol pilot facility are discussed.

Monday 4:00 Kearney BF11

Biomass suspension rheology as a predictor of susceptibility to enzymatic hydrolysis

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Ligno-cellulosic biomass can be biochemically converted to sugars, which can further be transformed to renewable fuels and chemicals. However, process design and economic objectives require an understanding of slurry flow behavior coupled with efficient conversion. Concentrated suspensions of dilute acid pretreated corn stover (PCS) have a significant yield stress that decreases as enzymes break down cellulose into soluble sugars. In fact, the yield stress of enzymatically hydrolyzing biomass is less than pretreated biomass at the same solids concentration. A natural hypothesis is that hydrolyzing biomass is breaking down into smaller particles compared to diluted slurries. However, we show particle size reduction alone neither decreases slurry yield stress over a wide range of solids concentrations, nor increases enzymatic digestibility. This correlation is potentially interesting because robust measures to accurately predict biomass susceptibility to enzymatic hydrolysis are correlative and indirect. We posit that the connection between yield stress and enzymatic hydrolysis is robust because the enzymes act as Brownian surface probes to characterize surface chemistry while rheology provides a bulk measure of inter-particle interactions. Enzyme adsorption on microcrystalline cellulose is compared with yield stress to determine if rheology could be a fast and affordable in-line predictor of enzymatic conversion.

Monday 4:25 Kearney BF12

Dyphagia - when rheology is hard to swallow

Adam S. Burbidge, Jan Engmann, and Chris J. Pipe
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The human mouth and throat form a complex, but effective bio-mechanical system which allows us to breathe, eat and drink through the same physiological inlet. Unsurprisingly for such a complex system, different types of failure may occur such that food or beverages may enter the airway. For healthy individuals, this may merely provoke a coughing reaction, whereas for those with serious malfunctions, the consequences can be serious and even lead to aspiration pneumonia, which in many cases is fatal. Current medical practice often prescribes ‘thickened’ fluids as a treatment for such individuals, but the question of ‘which is the optimal fluid?’ for a particular condition remains largely unanswered. Shear thinning, extensional or viscoelastic properties of dysphagia treatments are currently not considered by medical practitioners because they are not sufficiently familiar with these concepts. In this paper, we will discuss the physiology and fluid mechanics of swallowing and in particular consider the kinetics of drainage in the human pharynx.

Monday 4:50 Kearney BF13

Effects of acidification on the rheology of rennet induced curd made from buffalo milk: A comparison with cow’s milk

Imtiaz Hussain, Alan Bell, and Alistair Grandison
Food and Nutritional Sciences, University of Reading, Reading, United Kingdom

Oscillatory dynamic rheology was used to measure the curd firmness (G*), overall viscoelasticity (tan d) and total yield stress (s) of the rennet induced curds made from pasteurized whole buffalo milk at differing pH values (6.6- 5.6). The dynamic moduli (G', G") increased with increasing time after chymosin addition at initial pH values of 6.6 to 6.0 and attained maximum value after 90 minutes. This is may be due to reduction in electrostatic repulsion of the micelles and a slight decrease in the total amount of the casein bound calcium. The maximum gel strength obtained after 90 minutes and decreased with decreasing pH from 6.0 to 5.6. This is assumed to be due to the excessive loss of casein bound calcium from casein micelles at the lower pH values. Loss tangent increased with the reduction in milk pH during the acidification process. After 95 minutes of chymosin addition, rennet curds were subjected to constant low shearing force to break up the system. The measured yield stress is an indicator of the overall interaction of the curd components and below pH 6.0 decreases with decreasing pH. This resulted in a significant loss of casein bound calcium associated with the loss of “cross linking” between the casein micelles. The structure and casein bound calcium in the actual casein particles are major determinants for the production of good quality buffalo curd. It is postulated that any alteration of casein micelle structure will result in changes to the physicochemical and rheological properties of buffalo rennet curds with subsequent changes in the overall quality of mozzarella produced. Key words: rennet induced curd, pH, buffalo milk; casein bound calcium, dynamic moduli

Monday 5:15 Kearney BF14

The rheology and processing of swallowing starched based fluids

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This presentation describes recent work on rheology and processing related to swallowing starched based thickened fluids that are used for some patients that suffer from a throat disorder known as Dysphagia. Two commercial Dysphagia fluids were rheologically characterised in terms of their shear thinning. linear viscoelastic behaviour and also extensional filament stretching response. A model “Cambridge throat” was designed

and constructed in order to mimic the action of the tongue forcing fluid into the back of the throat. The apparatus resulted in essentially a constant stress rheometer that squeezed fluid through a flexible membrane into a geometry that resembled the back of the throat. For a given torque applied to the “mechanical” tongue, the residence time of fluid within the throat increased with increasing viscosity and viscoelasticity. The residence time appears to be important in relation to the response time of the person to movement of the epiglottis, which is a “flap” that directs air down the wind pipe and fluids to the stomach. Using high speed photography it was possible to identify how different levels of viscoelasticity influenced fluid drop break up within the back of the throat.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Sweeney F PL2

A random walk in rheology

Tom C. McLeish

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Rheology is an inherently multidisciplinary subject of great richness. It encompasses methods of enquiry from engineering to theoretical physics, from chemistry to computing. Its students travel from the complex world of industrial development as much as from the more systematising schools of universities. It is also a field continually on the move itself, growing, for example, deeper roots into the molecular and microscopic structures responsible for its fascinating macroscopic phenomena. In this almost-random walk from the point of view of one of its disciples, we will take a look at some examples of the surprising understanding that such mixed communities of researchers can produce when working together, at some unusual places in which polymer rheology turns up unexpectedly, and at some extraordinary present puzzles that point to a fascinating future.

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Tuesday 9:55 Sweeney A SC15

Dilation and capillary forces in dense shear thickening suspensions

Eric Brown and Heinrich M. Jaeger

James Franck Institute, The University of Chicago, Chicago, IL 60637, United States

Some densely packed suspensions and colloids exhibit Discontinuous Shear Thickening in which the shear stress jumps dramatically at some shear rate. We performed rheometry and video microscopy measurements on a variety of dense suspensions including cornstarch in water and 100 micron glass spheres in mineral oil to determine the mechanism for Discontinuous Shear Thickening. By comparing fixed gap and fixed normal force measurements we show that the stress jump does not occur without positive normal forces so is not due to an increase in viscous interactions. Dilation is observed along with shear thickening as an apparent roughness of the surface. The scale of the stress jump is shown to roughly match, for a wide variety of suspensions, the ratio of surface tension divided by a radius of curvature equal to the particle size. These results suggest that the shear thickening comes from confinement by capillary forces at the liquid-air interface which provide a confining stress when the suspension is dilated. At higher packing fractions above the jamming transition, particles are also observed to penetrate the fluid surface and a yield stress is observed to have the same stress scale, suggesting the same confining stress sets the strength of the jammed state.

Tuesday 10:20 Sweeney A SC16

Shear-induced structural reordering of a model nanoparticle system with tunable interactions

Aaron P. Eberle[1], Norman J. Wagner[1], and Nicos S. Martys[2]

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Nanoparticle and colloidal gels, flocculated suspensions, and attractive driven glasses are of fundamental scientific interest and pose challenges to industrial formulation and application because of the hierarchy of structures that connect particle properties to bulk material properties. In many cases the processing of these materials relies on the fact that the underlying structure may be reversibly broken down by flow. As a result their rheological behavior is of technological relevance to process design optimization, and can exhibit complex behaviors such as solid-like linear viscoelasticity, thixotropy, aging, yielding, hysteresis, and shear localization. Much is known about the fractal and fractal-like microstructure of low density gels under static conditions and the dissolution of the network as a result of flow, but less is known about concentrated systems. In this work, we explore the shear induced structural reordering of a nanoparticle dispersions with tunable attractions using small-angle neutron scattering (SANS) in combination with a novel 1-2 plane shear cell. The model system is composed of silica spheres which have a relatively thin grafted oligomeric surface layer that provides steric stability in a good solvent, but contributes to a reversible, short range attraction in poor solvents. The SANS scattering profiles are analyzed in combination with the steady shear rheology. The strength of attraction is found to have a profound impact on both the rheology and local nanostructure. The experimental results are compared directly to dissipative particle dynamics (DPD) simulations. The goals of this study are to identify the hierarchical structures that quantitatively relate the state or phase of the system, interparticle potential, and particle properties to the bulk rheology.

Tuesday 10:45 Sweeney A SC17

Experimental investigation of the sedimentation behavior of concentrated suspensions in non-Newtonian fluids under simple shear flows

Narongsak Tonmukayakul[1], Jeff Morris[2], and Jason E. Bryant[1]
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Settling of noncolloidal particles in non-Newtonian fluids is relevant to the understanding of particle transport by well-technology fluids used in the oilfield-service industry. The key issue is that the liquid rheology influences particle settling, and this affects the design of fracture stimulation processes. Effective proppant suspension requires supporting the weight of solids of high relative density (with typical proppant) over long distances in a pressure-driven flow through a subsurface fracture, and relies strongly on viscosity and/or elasticity of the suspending fluid. It has been shown [B.H. van den Brule and G. Gheissary, 1993] that the settling velocity is significantly reduced by elastic force (e.g., presence of normal stress difference) and shear rate. In this work, we experimentally characterize settling velocity and sedimentation behavior of spherical particles in several non-Newtonian fluids under static and imposed shear conditions. The liquids considered are high viscosity Boger fluids, aqueous solutions of xanthan gum, aqueous guar solutions reversibly cross-linked by borate ions, and finally a surfactant solution. The rheological properties of the liquids without solid loading are determined by small amplitude oscillatory sweep, and in steady shear where both viscosity and first normal stress difference are measured. The settling of particles is studied in a transparent Couette cell. The results reveal how under shear, the viscosity (typically but not always shear thinning) and elasticity in the fluid affect settling rate. The settling rate increased with increasing shear rate for xanthan gum and surfactant solutions, which are predominantly shear thinning. For Boger and highly cross-linked guar samples, where elasticity effects are stronger, the settling rate decreases with increasing imposed shear rate. A simple physical model and scaling analysis based upon the model are presented to explain the observed role of elasticity and shear thinning on the settling.

Tuesday 11:10 Sweeney A SC18

Capillary forces in suspension rheology

Erin Koos and Norbert Willenbacher
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When a small amount (less than 1%) of a second immiscible liquid is added to the continuous phase of a suspension, the rheological properties of the mixture are dramatically altered from a fluid-like to a gel-like state. The yield stress and viscosity increase by several orders of magnitude as the volume of the second fluid increases. This transition is attributed to the capillary forces of the two fluids on the solid particles, and in an analogy to wet granular materials[1], two distinct states are defined: the “pendular state” where the secondary fluid preferentially wets the particles; and the “capillary state” where the secondary fluid wets the particles worse than the primary fluid. We find that both states are associated with a transition in the suspension from a fluid-like to gel-like state. While the pendular state has been partially studied[2], very little is known about the capillary state. This research investigates the capillary state in detail and provides evidence that the capillary forces dominate the behavior.

This phenomenon is demonstrated in several different particle and fluid combinations. The transition to a gel-like state using two fluids occurs for particle volume fractions as low as $\phi = 0.10$ – much lower than for wet granular materials. This research demonstrates that the addition of a second immiscible fluid to particle suspensions is able to create stable suspensions when settling would otherwise occur, generate a variety of rheologically tunable fluids that are completely reversible and adjusted by temperature, as well as controlling the formation of an extremely strong network of particles at lower particle concentrations, which may be used as a template for the manufacture of porous ceramics or foams.

[1] N. Mitarai and F. Nori. Advances in Physics, **54(1)**, 1-45 (2006). [2] S.V. Kao, L.E. Nielsen and C.T. Hill. Journal of Colloid and Interfacial Science, **53(3)**, 367-373 (1975).

Tuesday 11:35 Sweeney A SC19

Structural instability in sedimentation through polymer solutions

Ronald J. Phillips[1] and Laurence Talini[2]
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When particles sediment through polymer solutions, it is often observed that the particle distribution becomes non-homogeneous. In some cases, it has been found that vertical, particle-rich columns form in a regular pattern, a development that can be described as a structural instability that dramatically changes the sedimentation rate. We hypothesize that the columns form as a result of competition between a “viscoelastic attraction” that brings particles together, and the dispersive influence of their chaotic trajectories, that keeps them apart. To account for the attraction, we have generalized the Rotne-Prager-Yamakawa theory for hydrodynamic interactions to account for weak elasticity. The new attraction term, together with a Fickian dispersion term, yield a conservation equation governing particle concentration. The conservation equation predicts that a homogeneous suspension microstructure can become unstable to fluctuations under many conditions of interest. The predicted time for column formation and the thickness of the columns compare well with experimental data obtained by particle image velocimetry (PIV) in Xanthan solutions.

Symposium MS
Polymer Rheology: Melts, Solutions and Blends

Organizers: Shi-Qing Wang and Marie-Claude Heuzey

Tuesday 9:55 Sweeney B MS10

A full-chain stochastic tube model for entangled polymeric liquids at high shear rates

Joontaek Park, David W. Mead, and Morton M. Denn
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We have modified the full-chain stochastic tube model developed by Xu et al. [J. Rheology (2006) 50:477-494] to simulate entangled melts and solutions of linear polymers at high shear rates. This model, which has only one adjustable parameter equivalent to the Rouse time, successfully describes shear and normal stress data at low to moderate rates, but the model deviates systematically from data at high rates. The algorithm for re-entanglement has been modified to reduce the deviation in the calculated viscosity at high rates. The discussion focuses on the structural changes in terms of the constraint renewal mechanism, the effect of a non-uniform drag coefficient of chains, and the entanglement density.

Tuesday 10:20 Sweeney B MS11

Dielectric relaxation as an independent examination of relaxation mechanisms in entangled polymers using the discrete slip-link model

Ekaterina Pilyugina and Jay D. Schieber
Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States

Dielectric spectroscopy is often used as a complementary tool for investigating the relaxation properties of a viscoelastic medium. The method is to apply a small electric field to polymers with permanent dipoles and the response of the system is investigated by measuring the relaxation of the dielectric permittivity ε. If the polymer chain has permanent dipoles, then the dielectric response should reflect the structural properties of the investigated polymer. For example, it has been shown that for so-called type-A polymers, where the dipoles are parallel along the backbone of the chain, the complex dielectric permittivity $\varepsilon(\omega)$ is proportional to the Fourier transform of the autocorrelation function of the chain's end-to-end vector $R(t)$. Also, comparison of the experimentally measured relaxation modulus $G(t)$ with the autocorrelation function of the end-to-end vector for linear monodisperse type-A polymers has shown a relationship between these two functions for linear polymers, namely, $G(t)\sim R(t)^2$. However, this relationship is based on assumptions about the relative contributions of constraint release and chain sliding dynamics to the relaxation modulus. Previous comparisons of contributions to the relaxation modulus of monodisperse and bidisperse linear chains showed significant differences between tube and slip-link theories. Molecular probe rheology experiments [C. Liu *et al.*, Macromol., 2006, **39**(21), 7415-7424] are in agreement with slip-link theory predictions, and not tube models. Dielectric relaxation can provide an additional independent check on the contributions of these two relaxation mechanisms. Also of interest is star-branched polymers where tube theories typically cannot explain both dielectric and viscoelastic behavior simultaneously [H. Watanabe, *Macromol. Rapid Commun.* 2001, **22**, 127-175].

Tuesday 10:45 Sweeney B MS12

Rheo-dielectric behavior of entangled linear and star polyisoprene

Hiroshi Watanabe and Kazushi Horio
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Rheo-dielectric behavior was examined for entangled linear and star-branched cis-polyisoprene (PI) under steady shear as well as LAOS. PI has the type-A dipoles, and the rheo-dielectric signal detected in the shear-gradient direction detects fluctuation of the end-to-end vector (for linear PI) and end-to-branching point vector (for star PI) in this direction. The rheo-dielectric relaxation behavior was quite insensitive to the shear for linear PI, while moderate decreases of the relaxation time and intensity were noted for star PI. This difference may be related to a difference of the dynamic tube dilation behavior of linear and star PI at equilibrium. Under LAOS, the oscillation of the rheo-dielectric signal due to the oscillation of the conformational distribution function was detected for both linear and star PI.

Tuesday 11:10 Sweeney B MS13

Large amplitude oscillatory shear responses of star polymers in solution

Jung-Eun Bae[1], Kwang Soo Cho[1], and Ji Ho Youk[2]
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[2]Departemt of Advanced Fiber Engineering, Inha University, Incheon, Republic of Korea

We investigated nonlinear viscoelasticity of solutions of star polymers under large amplitude oscillatory shear compared with those of linear counterparts. In analysis of LAOS data, we applied strain-frequency superposition which was developed by Cho et al. for solutions of linear polymers. We used the plots of logarithm of normalized elastic stress amplitude as a function of normalized viscous stress amplitude. The normalized stress amplitudes are defined as the ratio of stress amplitude in nonlinear regime to the product of linear viscoelastic modulus and strain amplitude. As for the entangled solutions of linear polymers, the slopes of the plot are about 3 irrespective of frequency, molecular weight and concentration while those of star polymers are different from 3. We propose that the slope can be used for identification of chain topology.

Tuesday 11:35 Sweeney B MS14

Analysis of entangled polymer bidisperse blends and molecular probe rheology experiments with the discrete slip-link model

Renat N. Khaliullin, Jay D. Schieber, Teresita Kashyap, and David C. Venerus
Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States

We present an application of a single-chain mean-field model to entangled linear blends. Slip-links instead of tubes are employed. The entanglements on a chain are destroyed by two coupled relaxation processes: called sliding dynamics (SD); and relaxation of the environment, called constraint dynamics (CD). CD are implemented by destruction and creation of the entanglements in the middle of the chain in a way statistically self consistent with SD, completely avoiding Rouse dynamics.

Here we compare DSM to experimental data as well as the Park and Larson tube model. Our self-consistent implementation of constraint dynamics avoids factorization assumptions, or tube dilation processes, so no new parameter, such as the Struglinski-Graessley parameter is necessary. Also, in previous work we pointed out variations in experimental data from lab to lab, that result in different plateau moduli and relaxation timescales. Therefore, we performed LVE measurements on three monodisperse polystyrene samples and their binary blends. Both DSM and the Park and Larson tube model compare very well with the experimental data.

We then use the DSM to analyze the molecular probe rheology experiments of Liu et al. By examining the dynamic modulus of blends of very long and short entangled chains, those authors concluded that constraint release plays a significant role in molecular weight scaling of the longest relaxation time. Here we show that their analysis neglects constraint dynamics of the long chains and, therefore, does not lead to the correct conclusion. Moreover, we show that a correct analysis can be used to distinguish between tube and slip-link models. Namely, probe rheology can be used to estimate a sum of relaxation from sliding dynamics and constraint dynamics. Since the dynamic modulus of monodisperse systems measures a product of these two processes, the combination of the two experiments can be used to distinguish between sliding and constraint dynamics. Only DSM can describe both experiments.

Symposium SI
Surface and Interfacial Rheology

Organizers: Ophelia Tsui and Lenore L. Dai

Tuesday 9:55 Coronado/DeVargas SI15

Mechanical properties of recombinant protein interfaces

Varvara Mitropoulos, Peter Fischer, and Erich J. Windhab
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Proteins form a strong viscoelastic network at the liquid/liquid or air/liquid interface due to their high surface activity. The nature of the proteins participating in network formation affects the stability and deformability of the viscoelastic adsorption layer. However, the prediction of the mechanical behavior of a protein adsorption layer with respect to the protein structure and properties remains elusive. To face this challenge we applying a protein system composed of recombinant, size-consecutive individuals, which share a structure only differing in an integer amount of a helix-loop-helix motive. Their modular structure allows comparison between differently sized proteins by maintaining the same folding aspects; a comparison, which is not possible with conventional food grade proteins due to their largely differing structures. With our system we aim a systematic approach to the protein adsorption layer formation process and the construction of tailor made capsules with adjustable viscoelasticity.

Tuesday 10:20 Coronado/DeVargas SI16

A new, microfluidic method for compressible and incompressible interfacial rheology

Jeffrey D. Martin, Kendra A. Erk, and Steven D. Hudson
Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

Drop deformation and rupture, emulsion viscoelasticity, coalescence - nearly all of the properties and performance of emulsions - are governed and influenced by interfacial rheology. Generally, dilatational and shear properties are both relevant, and different techniques are required for the measurement of each property. Here, we lay the foundation for a new technique that measures the dynamics of droplet interfaces directly. Specifically, we use microfluidics, particle velocimetry, and shape analysis to probe the interfacial rheology of surfactant-stabilized aqueous drops in oil. The natural language for flow of droplet interfaces is spherical harmonics, which importantly form two types - compressible and area incompressible. We excite the lowest order drop circulation modes of each type and their magnitudes directly indicate the respective dilatational and shear mobilities. Velocimetry at two points only in the drop is sufficient to determine the amplitude of these two fundamental modes. Investigation of small drops is of interest for their relevance to emulsion applications, and to improve force sensitivity. A variety of interfacial behaviors is demonstrated using different surfactants and concentrations.

Tuesday 10:45 Coronado/DeVargas SI17

Flow accelerates coupling reactions at polymer interfaces

Jie Song[1], Randy H. Ewoldt[2], and Chris Macosko[1]
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We show that extensional flow at the interface between two immiscible polymer melts can greatly accelerate interfacial coupling reactions. We demonstrate this through the effect of flow on adhesion between functionalized polyethylenes (PEs) and thermoplastic polyurethane (TPU). Maleic anhydride (MA), hydroxyl (OH) and secondary amine (NHR) functionalized PEs were synthesized via reactive extrusion and blended into non-modified PE. These were laminated and coextruded with TPU to make bilayer samples and adhesion determined by T-peel tests. NHR functionalized PE showed dramatic adhesion improvement with low concentration. For all functionalized PEs adhesion was found to increase proportional the square of interfacial copolymer coverage. With simple lamination this coverage increases linearly with time but for coextrusion the increasing area due to extensional flow must be also considered as it dilutes the functional groups. Interfacial coupling reaction in coextrusion was found to be much faster in comparison with lamination at the same effective time. Extensional strain at the interface is believed to accelerate coupling by forcing functional groups into the interface.

Tuesday 11:10 Coronado/DeVargas SI18

Block copolymers at the oil-water interface

Inbal Preker and Moshe Gottlieb
Chemical Engineering Department, Ben Gurion University, Beer Sheva 84105, Israel

The interfacial activity of amphiphilic block copolymers plays a significant role in industrial applications and processes and in biological systems. The main goal of the present work is to examine the relation between the structural properties of the polymers and their interfacial activity as reflected by surface pressure and interfacial rheology. Amphiphilic block copolymers composed of poly(ethylene oxide) as the hydrophilic block and poly(dimethyl siloxane) as the hydrophobic block were examined. The effect of the hydrophobic/hydrophilic blocks sizes ratio on the interfacial behavior was investigated along with the effect of the polymers architecture (diblock copolymers versus triblock copolymers). The interfacial tension reduction and the interfacial dilatational rheology modulus were examined by using pendant drop apparatus combined with pulsating drop modulus. Interfacial shear rheology was determined by means of the magnetic needle and double ring methods (carried out in collaboration with Prof. Jan Vermant, KU Leuven). An optimal ratio between the hydrophobic/hydrophilic blocks sizes which leads to maximal interfacial tension reduction was observed

Tuesday 11:35 Coronado/DeVargas SI19

Surface cleaning using polymer solution and other non-Newtonian fluids

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The removal of contaminants is an important step in production process of many industries, such as high-precision optical lenses, magnetic storage media, solar cells, and semiconductor devices. The present study examines a novel cleaning process effective for micron or smaller particulate contaminants, involving the use of semidilute aqueous polymer solutions rinsed off by an impinging water jet. Unlike many existing removal processes, this continuous process generates limited and nonhazardous aqueous waste. We have investigated the particle removal mechanism with a model system of silica particles on glass substrates. First, we constructed an experimental set-up to image particle removal in situ using differential interference contrast microscopy, which enables particle imaging down to the nanometer scale. Using a high-speed camera, we determined the relevant timescales for removal is on the order of milliseconds. We also developed a quantitative technique to evaluate removal efficiency by using fluorescently dyed silica particles and a fluorescent 2D scanner. We found that effective particle removal requires the cleaning solution to be highly elastic, including high molecular weight polymer solutions, Boger fluids, and worm-like micelle solutions. Newtonian solutions such as low molecular weight polymer solutions and glycerol-water show very low particle removal abilities. There is a direct correlation between the extensional viscosities of the cleaning solution and the particle removal efficiency. It is also necessary for the rinsing flow to contain an extensional component. A purely shear flow shows limited efficiency while a siphoning process shows very high efficiency. Thus, we propose that when the microstructures of the cleaning solutions are stretched, a dramatic increase in tensile resistance coupled with extensional flow is responsible for achieving particle removal. This is further supported by high-speed videos showing that the particles are “plucked away” from the surface instead of “rolling away.”

Symposium GM
Rheology and Flow of Glass-like Materials

Organizers: Grigori Medvedev and Leon Govaert

Tuesday 9:55 Peralta/Lamy GM6

Shear banding in soft glassy materials

Suzanne M. Fielding[1] and Michael E. Cates[2]
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Following brief introductions separately to the topics of (i) shear banding in complex fluids and (ii) the rheology of soft glassy materials, we present several recent approaches aimed at modelling shear banding in soft glassy materials, as observed experimentally in colloids, emulsions, star polymers, and other soft glasses. In particular we consider (a) a spatially aware version of the “soft glassy rheology model” and (b) simplified fluidity models. Particular focus will be placed on on the effects of sample ageing and flow protocol in leading to differing degrees and types of shear banding.

Tuesday 10:20 Peralta/Lamy GM7

Rheology of complex urethane adhesives

Suraj S. Deshmukh[1], Valeriy Ginzburg[1], Norbert Wiese[2], Gary Jialanella[3], Sunil Chaudhary[4], and Chris Christenson[4]
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Highly filled viscous urethane adhesives are used in a wide range of applications wherein their flow behavior is critical for optimum performance. Rheological characterization of these systems having a time, temperature, humidity and composition dependent yield stress using traditional stress or shear rate sweeps on a controlled stress rheometer can lead to erroneous results. Further complications arise due to high normal stresses, inertia and slip layers at larger deformations. Typically, performance is controlled using quality checks such as melt indexer-like tests and Brookfield viscosity measurements. We will describe new techniques to understand the fundamental flow behavior of these systems using oscillatory shear flow and mixed shear-extensional flow experiments. Experiments on a host of instruments including stress and strain controlled rheometers and mechanical test frames will be described including their advantages and limitations in characterization of these complex urethane systems. Further, we will describe a yield stress model in conjunction with statistical modeling to better correlate the fundamental rheological properties such as yield stress, plastic viscosity and relaxation time with the flow behavior.

Tuesday 10:45 Peralta/Lamy GM8

Rheology and dynamics of soft glasses

Praveen Agarwal and Lynden A. Archer
Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States

We report on the linear and non-linear viscoelasticity of a class of self suspended colloidal suspensions. Termed Nanoscale ionic materials (NIMs) these suspensions are created by densely grafting organic polymers (polyethylene glycol (PEG), polystyrene (PS), or polyisoprene (PI)), to the surface of inorganic nanoparticles. We find that these materials manifest a spectrum of rheological features ranging from simple Newtonian and non-Newtonian fluid behavior to more complex soft glassy rheology, which can be tuned via the core particle size, volume fraction, and tethered polymer molecular weight and graft density. For systems in the Newtonian limit, we investigate the effect of particle volume fraction and corona polymer molecular weight on viscosity, modulus, and relaxation dynamics in the suspensions. For materials that exhibit soft-glassy rheology we study the effect of temperature and shear strain on structure and dynamics. Rheological studies of both classes of materials reveal multiple new effects. For example in the Newtonian case we find that, unlike star-branched molecules, the suspension viscosity in NIMs is a decreasing function of corona polymer molecular weight. In the soft-glassy limit, we report that shear strain accelerates relaxation in a manner analogous to temperature in normal fluids. Further, we find that this acceleration leads to unusual time-strain-superposition (TSS) behavior, which appears to be a generic feature of soft glasses.

Tuesday 11:10 Peralta/Lamy GM9

Time-aging time-stress superposition in soft glass under tensile deformation field

Asima Shaukat, Ashutosh Sharma, and Yogesh M. Joshi
Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India

Many industrially important visco-plastic soft materials, which show thixotropic behaviour, are usually out of thermodynamic equilibrium due to physical jamming of their constituents. In many applications, such materials routinely encounter extensional flows engendered by normal stresses. The strong deformation history dependence exhibited by these materials makes it difficult to predict long time rheological behaviour. In this work, we employ aqueous suspension of Laponite, a model soft glassy material, to demonstrate self similarity in time evolution under the tensile deformation field. We study the deformation behaviour of thin films of aqueous suspension of Laponite when subjected to a creep flow

field generated by a constant engineering normal stress. Aqueous suspension of Laponite demonstrates aging behaviour wherein it undergoes time dependent enhancement of its elastic modulus as well as its characteristic relaxation time. However, under application of the normal stress, the rate of aging decreases and in the limit of high stress, the aging stops with the suspension now undergoing a plastic deformation. Overall, it is observed that the aging that occurs over short creep times at small normal stresses is same as the aging that occurs over long creep times at large normal stresses. This observation allows us to suggest an aging time - process time - normal stress superposition principle, which can predict rheological behaviour at longer times by carrying out short time tests. This methodology can be used for the understanding and processing of this class of materials.

Tuesday 11:35 Peralta/Lamy GM10

A constitutive law for the flow of soft glasses

Jyoti Seth[1], Clémentine Locatelli[2], Michel Cloitre[2], and Roger Bonnecaze[1]
[1]Department of Chemical Engineering and Texas Materials Inst, The University of Texas at Austin, Austin, TX 78712, United States; [2]Soft Matter and Chemistry, ESPCI ParisTech, Paris 75231, France

Soft glasses encompass a broad class of concentrated dispersions made of soft and deformable particles jammed into an amorphous structure. They can be as diverse as concentrated emulsions, colloidal pastes, multi-lamellar vesicles, star polymers, copolymer micelles and clay suspensions. In spite of important differences in constituents and architecture, many soft glasses exhibit generic dynamical properties intermediate between solid and liquid. They behave like weak elastic solids at rest but yield and flow with a complex dependence on shear rates. The prediction of the flow properties of soft glasses is the key to success in many applications but at the same time it remains a formidable challenge.

Here we propose a micromechanical 3-d model which quantitatively predicts the non-linear rheology of soft glasses. We consider that the squeezed particles deform elastically and slip one past the other instead of being advected as in conventional suspensions. We derive constitutive equations for the shear stress and normal stress differences, which result from a subtle interplay between elastohydrodynamics interactions among the particles and the alteration of the dynamic structure under flow. These predictions, which have no adjustable parameters, are successfully validated with experiments on concentrated emulsions, polyelectrolyte microgel pastes, and block copolymer micelles, which highlight the universality of the flow properties of soft glasses.

Symposium SA
Self-Assembling, Associative, and Gel-like Systems

Organizers: Ferenc Horkay and Matthew W. Liberatore

Tuesday 9:55 O'Keeffe/Milagro SA1

Some minimal models of network elasticity

Jack F. Douglas
Polymers Division, NIST, Gaithersburg, MD 20899, United States

Classical network elasticity theories are based on the conception of flexible volumeless network chains fixed into a network in which there are no excluded volume interactions between the chains and where the chains explore accessible configurations by thermal fluctuations. The limitations of this approach are clear from the observation that unswollen rubbery materials are nearly incompressible, reflecting the existence of strong intermolecular interactions that restrict the polymer chains to an exploration of their local molecular environments. The imposition of a deformation to these solid rubbery materials then necessitates a consideration of how local molecular packing constraints become modified under deformation and the impact of these changes on the macroscopic elasticity of the material as a whole. The simple 'localization model' of rubber elasticity, introduced by Gaylord and Douglas (GD), provides an attractive minimal model for the network elasticity of rubbers having strong intermolecular interactions in the dense polymer state. The properties of this model are summarized and compared to observations on rubbery materials where both the cross-linking density and swelling are varied. The model is extended to describe networks of stiff chains and networks having junctions formed through reversible association.

Tuesday 10:20 O'Keeffe/Milagro SA2

Swelling behavior and rheological response of porous, sponge-like hydrogels

Ronald C. Hedden, Jun Zhao, and Lan Ma
Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

Porous hydrogels have been widely studied as biomedical, biomimetic, super-absorbent, and stimuli-responsive materials. Porosity can be engineered into hydrogels to achieve rapid changes in the macroscopic volume swelling ratio in response to environmental conditions; to control the rate of release of a drug or other chemical agent; to affect mechanical response; or to mimic the structure and/or mass transfer characteristics of living tissue. Experimental methods are needed to measure pore size, water concentration within the gel phase, and the volume fraction of porosity in the swollen state. An analytical method has been developed which combines equilibrium swelling measurements and ultra small-angle scattering (USANS) invariant analysis to characterize sponge-like hydrogels containing micrometer-scale pores. The method was first demonstrated with hydrogels of poly(hydroxyethylmethacrylate), poly(HEMA), which had (1 to 30) micrometer pores generated by water-extraction of a polymeric porogen (40 to 80 mass %). [Iannuzzi, M. A.; Reber, R.; Lentz, D. M.; Zhao, J.; Ma, L.; Hedden, R. C. Polymer 2010, 51, 2049-2056.] The collection of USANS data for invariant analysis is faster and simpler than that required for neutron contrast-variation methods. However, a limitation of the invariant analysis is the need to extrapolate I(q) data to q=0 and q=infinity, requiring both high quality data and a good fit to a scattering model. The rheological response of sponge-like hydrogels differs significantly from that of non-porous gels, due to the stress-induced flow of water through the interconnected pores and channels. Two series of porous hydrogels, which have typical pore volume fraction of 0.3 to 0.8, have been characterized in compression and shear: rigid poly(hydroxyethylmethacrylate) gels, and ultra-soft poly(acrylamide) gels.

Tuesday 10:45 O'Keeffe/Milagro SA3

Deciphering the relationship between structure and rheology for poly-thiophene organogels

Kathleen Weigandt, Greg Newbloom, and Danilo C. Pozzo
Chemical Engineering, University of Washington, Seattle, WA 98195, United States

Conjugated polymers, such as polythiophenes, are known to form fibrilar structures when solvent quality is reduced. At high concentrations, solutions of conjugated polymers will also self-assemble and form elastic networks of interconnected fibers. This talk will describe a systematic evaluation of the structure of these networks covering a wide range of length scales (0.1 - 10,000 nm) using scattering techniques (SAXS and SANS). The complementary characterization of the mechanical (rheology), optical and electronic properties of the organogels allows us to also formulate structure-property relationships for this new class of materials. The talk will also discuss the implications of our findings in the context of the design of novel organic electronic and photovoltaic technologies.

Tuesday 11:10 O'Keeffe/Milagro SA4

Rheology of associating block copolymer protein hydrogels

Fan Wan, Shane Scott, Stephen E. Fischer, and James L. Harden
Physics, University of Ottawa, Ottawa, Ontario, Canada

We present studies of hydrogel networks formed by self-assembly of associating block copolymer proteins. These designer proteins consist of a hydrophilic, disordered coil domain linked to an amphiphilic beta sheet domain. The association of the beta sheet domains into extended linear aggregates protects their hydrophobic faces from the aqueous environment. This assembly process leads to the formation of hydrogel networks of amyloid-like fibers. We discuss the dependence of hydrogel viscoelasticity on solution conditions (concentration, ionic strength, pH and temperature) and make connections with the thermodynamic behaviour and microstructure of these materials.

Tuesday 11:35 O'Keeffe/Milagro SA5

Nonlinear stress-strain behavior of nematic elastomers using relative rotations

Harald Pleiner[1], Helmut R. Brand[2], and Andreas Menzel[3]
[1]Max Planck Institute for Polymer Research, Mainz, Germany; [2]Theoret. Physik III, University Bayreuth, Bayreuth, Germany; [3]Department of Physics, University of Illinois, Urbana, IL, United States

As a recent development in the area of side-chain liquid single crystal elastomers, the mate- rials are exposed to an external field of large amplitude to drive them into the nonlinear regime. Then, a second external field is superimposed. The small-amplitude response to this second external field is recorded under the influence of the first, large-amplitude external field. Current experimental work includes small-amplitude shear measurements [1] as well as dynamic light scattering measurements [2] on prestretched nematic SCLSCEs. In the latter case, essentially the response to externally imposed electromagnetic fields is recorded. We investigate the response of prestretched nematic side-chain single crystal elastomers to superimposed external shear, electric, and magnetic fields of small amplitude. The prestretching direction is oriented perpendicular to the initial nematic director orientation, which enforces director reorientation. Furthermore, the shear plane contains the direction of prestretch. In this case, we obtain a strongly decreased effective shear modulus in the vicinity of the onset and the completion of the enforced director rotation. For the same regions, we find that it becomes comparatively easy to reorient the director by external electric and magnetic fields. These results were derived using conventional elasticity theory and its coupling to relative director-network rotations [3,4]. Our results are interesting from an experimental and an applied point of view for the potential use as actuators, in particular for swollen nematic elastomers [5,6].

References: [1] P. Martinoty, International Liquid Crystal Elastomer Conference, Ljubljana, 2007. [2] A. Petelin, M. Copic, European Conference on Liquid Crystals, Colmar, 2009. [3] A.M. Menzel, H. Pleiner, H.R. Brand, J. Appl. Phys. 105, 013503 (2009). [4] A.M. Menzel, H. Pleiner, H.R. Brand, Eur. Phys. J. E 30, 371 (2009). [5] Y. Yusuf et al., Phys. Rev. E 71, 061702 (2005). [6] K. Urayama, S. Honda, T. Takigawa, Macromol. 38, 3574 (2005).

Symposium CR
Computational Rheology: Behavior 'in Silico'

Organizers: Rajesh Khare and Daniel J. Lacks

Tuesday 9:55 Kearney CR15

Residual mass for the immiscible liquid-liquid displacement of two visco-plastic material in a plane channel

Jackson F. Freitas[1], Edson J. Soares[1], and Roney L. Thompson[2]

[1]Department of Mechanical Engineering, Universidade Federal do Espírito Santo, Vitória, Espírito Santo, Brazil; [2]Department of Mechanical Engineering, Universidade Federal Fluminense, Rio de Janeiro, Rio de Janeiro, Brazil

The motion of two immiscible visco-plastic materials in a capillary plane channel is analyzed for the case in which the flow conditions and the interactions between the liquids and the solid surface maintain the displaced fluid attached to the wall. An elliptic mesh generation technique, coupled with the Galerkin Finite Element Method is used to compute the velocity field and the configuration of the interface between the two fluids. Examples of important applications where this kind of problem appears are the oil recovery processes from porous media and the cementation of oil wells, where the liquid film of the displaced material that remains attached to the rocks plays a significant role on the efficiency of the operation. Typically, because of the high viscosity levels and slow displacement velocities involved, these kind of processes occur with negligible inertial effects. Besides that, especially in oil recovery, as a consequence of the small length scale, the capillary forces have a fundamental importance on the physics of the phenomenon. We can find in the literature interesting investigations involving non-Newtonian liquid-liquid displacement. However, in the most of them, the interfacial tension was neglected. The objective of the present work is to present results for the thickness of the displaced liquid film attached to the channel walls as a function of the non-Newtonian properties of the two fluids considered for a large range of capillary number and viscosity ratio.

Tuesday 10:20 Kearney CR16

Dynamics of bead formation and breakup in weakly viscoelastic jets

Arezoo M. Ardekani, Vivek Sharma, and Gareth H. McKinley

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

Understanding the instability and breakup of polymeric jets is important for a wide variety of applications including inkjet printing, and spraying of fertilizers and paints. Even though these fluids are only weakly viscoelastic, the transient extensional viscosity and thus the jetting and breakup processes are affected by presence of small amount of polymer. In this study, we investigate the growth and evolution of surface-tension-driven instabilities of a weakly viscoelastic jet using both experiments and numerical simulations. The initial growth of disturbances can be predicted using linear instability analysis for small perturbations. A viscoelastic jet is initially more unstable when compared to a Newtonian fluid of the same viscosity and inertia. However, as the radius of the jet thins under the action of surface tension, elastic stresses grow and become comparable to the capillary pressure, leading to formation of a uniform thread connecting two primary drops. We show that by understanding the physical processes that control the temporal evolution of the jet profile, it is possible to extract transient extensional viscosity information even for very low viscosity and weakly-elastic liquids. This is particularly useful since filament-stretching and capillary breakup elongational rheometers face challenges for low-viscosity elastic polymer solutions. Computational rheology studies of jet breakup also enable us to deconvolute the competing and highly nonlinear roles of finite jet inertia (as parameterized by the Weber number We) and finite molecular extensibility (as parameterized by the FENE parameter b) on macroscopic observables such as the jet breakup length.

Tuesday 10:45 Kearney CR17

Active and hibernating turbulence in channel and boundary layer flow of Newtonian and polymeric fluids

Li Xi[1], Shinji Tamano[2], and Michael D. Graham[3]

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Turbulent channel flow of Newtonian and drag-reducing polymer solutions is simulated in channel flow and boundary layer flow geometries. Simulations in the minimal channel geometry reveal that, even in the Newtonian limit, there are intervals of "hibernating" turbulence that display many features of the universal maximum drag reduction (MDR) asymptote observed in polymer solutions: weak streamwise vortices, nearly nonexistent streamwise variations and a mean velocity gradient that quantitatively matches experiments. As viscoelasticity increases, the frequency of these intervals also increases, while the intervals themselves are unchanged, leading to flows that increasingly resemble MDR. Simulations in larger channel flow domains as well as turbulent boundary layers reveal spatiotemporally localized regions of active and hibernating turbulence, with hibernating turbulence becoming dominant as the level of viscoelasticity (and drag reduction) increases.

Tuesday 11:10 Kearney CR18

Effects of viscoelasticity on the inertial wake in flow past a circular cylinder

David H. Richter[1], Gianluca Iaccarino[1], and Eric S. Shaqfeh[2]
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Using our three dimensional, time dependent finite volume code developed to compute non-Newtonian flows over a large range of Reynolds number (Re), we performed simulations of viscoelastic flow past a circular cylinder. Our focus was on elucidating elastic effects on transition to turbulence in a three dimensional base flow. The FENE-P constitutive model was used to describe the presence of polymers, and the numerical method employed was such that a large range of rheological parameters (polymer length L, dimensionless Weissenberg number (Wi), and polymer concentration β in the FENE-P model) could be probed.

Full simulations at a Re = 300 indicate that viscoelasticity can have a profound stabilizing effect on the wake. At low polymer extensibilities (L = O(10) in the FENE-P model), modest changes to the wake structure are seen, but at higher, more realistic L (L = O(100)), the highly three dimensional mode B instability structure seen in Newtonian flows is completely suppressed. To better quantify this effect and identify the mechanism causing it, a Floquet linear stability analysis was performed for the two dimensional, time-periodic wake. The code was modified to solve the linearized FENE-P equations with a specified perturbation spanwise wavenumber. Instability growth rates were then obtained for a wide range of spanwise wavenumbers and rheological parameters, and comparisons with full nonlinear simulations will be presented and discussed.

Finally, to further probe the effect of polymer viscoelasticity on the transitioning wake behind a circular cylinder, viscoelastic flows at a Re = 3900 were also computed. In this range of Re for Newtonian flows, the shear layer present immediately behind the cylinder has transitioned. With the addition of viscoelasticity, however, even at low polymer extensibilities, the shear layer is stabilized and the wake structure reverts back to a state which is similar to the mode B instability seen in Newtonian flows at a much lower Re.

Tuesday 11:35 Kearney CR19

Modeling of dual cylinder wind-up extensional rheometers*

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Polymer extensional flow is the one of the most important deformation in polymer processing. It is the dominant deformation in melt-spinning, bottle-blowing, and roll-coating. Because the molecular structure of the polymeric system strongly influences the extension viscosity, extensional flow measurements are useful for polymer characterization. The Sentmanat extensional Rheometer[1] is an new testing platform for the study of polymers and elastomers in extensional flow. This technique employs a dual wind-up drum technique to perform an uni-axial extensional deformation during experiments. This miniature unit requires small amount of material and has been designed in such a manner that it can be used for polymer melt and soft elastomers characterization over a very wide range of temperatures and kinematic deformations and rates. In order to validate the reliability of this testing platform a finite element technique based on a Lagrangian kinematics description of the 3D time-dependent flow of K-BKZ type fluids [2] is used to simulate extension flow of both cylindrical and strip shaped sample in the SER. Here the purpose is to discuss the potential deviations from ideal uni-axial deformation, based on theoretical ideal configurations. Our simulation can setup a theoretical based ‘safe’ geometry range of samples for SER experiments. Furthermore, the simulations are able to capture flow instabilities in stress relaxation, which have been experimentally observed [4].

References: [1] M.L. Sentmanat, Rheol Acta, 43:657--669, 2004. [2] J.M.R. Marín, H.K.Rasmussen, J. Non-Newtonian Fluid Mech, 156 (3) , p. 177-188. [3] K.Y, J.M.R. Marín, H.K.Rasmussen, O.Hassager, J. Non-Newtonian Fluid Mech, 165 (1) , p. 14-23. [4] Y.Wang, P.Boukany, S.Wang, X.Wang, Physical Review Letters, 99, 237801 (2007).

* The title of this submission has been modified to remove the name of a commercial product or company to bring the title into compliance with SOR policy.

Tuesday Afternoon

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Tuesday 1:30 Sweeney A SC20

Rheology and microscopic particle dynamics in hard sphere glasses during start-up flow

Nick Koumakis[1], Marco Laurati[2], Stefan Egelhaaf[2], and George Petekidis[1]
[1]IESL, FORTH, Heraklion, Crete 71110, Greece; [2]Condensed Matter Physics Laboratory,, Heinrich-Heine University, Duesseldorf, Germany

The rheology and particle dynamics of hard sphere colloidal glasses during a step rate experiment are investigated with a combination of classical rheometry and particle tracking via confocal microscopy. Colloidal glasses as well as concentrated suspensions below the glass transition volume fraction were submitted to start-up flows at different shear rates. A typical stress overshoot was observed in rheological step rate tests. As a constant shear rate is imposed the sample exhibits an initial elastic response during which the stress is building up due to cage deformation until the yield strain is reached. When the imposed strain exceeds the yield strain significant cage breaking takes place leading to stress relaxation. The magnitude of the stress overshoot decreases with decreasing shear rate due to an interplay between the shear induced deformation and Brownian motion relaxing the distorted structure. At low Pe numbers where Brownian motion takes over the stress overshoot disappears. The particle mean square displacements under shear during such start up flow are measured by confocal microscopy. In this way we manage to link the macroscopic rheological response with the microscopic particle motions during the stress overshoot and subsequent relaxation regime. The results are also compared with Mode-coupling theory predictions and computer simulations results for such flows.

Tuesday 1:55 Sweeney A SC21

Microstructure evolution in near-hard-sphere particle suspensions

Bu Xu, Changbao Gao, and James F. Gilchrist
Department of Chemical Engineering, Lehigh University, Bethlehem, PA, United States

Microstructure formation in sheared suspensions is key to understanding the their rheological behavior. Thus far, little experimental evidence is available to reveal the dynamics of microstructure. In this work, silica microsphere suspensions under pressure-driven flow are studied using dynamic confocal laser scanning microscopy. The pair distribution function, a measure of microstructure, is presented as a function of Peclet number, local volume fraction and time, in fully-developed and reversed flows. Suspensions of various pH values and electrolyte concentrations at flow cessation are also investigated out of an interest on the competition between hydrodynamic and electrostatic forces. These results capture the evolution of suspension microstructure as a consequence of changing shear field and of relaxation due to electrostatic repulsion upon flow cessation. Explanation for this evolution and its implication on suspension rheology is discussed.

Tuesday 2:20 Sweeney A SC22

Plastic to brittle transition in bubble rafts

Chin-Chang Kuo and Michael Dennin
Physics and Astronomy, University of California, Irvine, Irvine, CA 92697-4575, United States

One of the main characteristics of foam is the fact that it exhibits a range of mechanical response, from flow to elastic response, depending on the nature of the applied stress. For applied shear stress or rate of strain, a foam is solid-like for small stresses or rates of strain and flows for large applied stresses or rates of strain. In contrast to shear flow, we consider the response of a model two-dimensional foam, a bubble raft, to deformations induced by pulling the system apart. In this case, we observe a transition of plastic-like pinch-off of the material to brittle fracture as a function of the pulling speed and the system size. For high rates of pulling or large systems, the material fails through brittle fracture. For small systems or slow rates of pulling, we observe pinch-off behavior characteristic of plastic deformation. In this talk, we will present comparisons between the pure bubble raft system and systems of plastic beads in order to elucidate the role of attractive interactions in this transition.

Tuesday 2:45 Sweeney A SC23

Transient shear-induced microstructure and rheology of dilute colloidal gels

Bharath Rajaram and Ali Mohraz
Department of Chemical Engineering & Materials Science, University of California, Irvine, Irvine, CA, United States

Understanding the microstructural evolution and rheology of colloidal gels under transient large-strain deformations is of critical importance to a wide host of technologies that use these materials as feedstock, including the food processing, ceramic industries, and in emerging technologies such as direct write assembly. For these systems, the microstructural evolution and rheology are coupled by a complex interplay between the interparticle and hydrodynamic interactions at the micro- and nano-scale, and the macroscopically imposed stresses or strains, making their predictions from theoretical models difficult. In this study, we directly probe the shear-induced evolution of the microstructure and dynamics of dilute, depletion induced colloidal gels suspended in a refractive index- and density- matched solvent mixture. The real-time response of the gel network to shear flow is quantified using a fast scanning confocal microscope coupled with a custom-built cone-and-plate shear cell. Three distinct regimes with sharp transition points are observed when the gel network is anchored to the lower stationary plate: (1) an initial period in which the quiescent structure reconfigures to an anisotropic network, (2) an intermediate regime characterized by a predominantly immobilized microstucture, albeit with sporadic local rearrangements and, (3) a final regime consisting of disconnected clusters advecting along the shear flow direction with a plug-like flow profile. Further, the gel network's dynamics exhibit transient, yet prominent, heterogeneities in the intermediate regime. The implications of these results on the non-linear rheology of colloidal gels are discussed.

Tuesday 3:35 Sweeney A SC24

Hydrating cement pastes: Novel rheological measurement techniques of the acceleration of gelation

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

We study the rheology associated with gelation of hydrating cements used in oil well cementing operations and the use of accelerators to advance rates of setting. Cement pastes made of API Grade H oilwell cement with water/cement mass ratios of 0.25 - 0.40 are studied. Setting times are accelerated from 7 hours to 1 hour by the addition of 5% wt/wt calcium chloride/cement. Complex viscosity follows an exponential time dependence and the shape of the gelation curve is essentially unaffected by the calcium addition levels. This leads to a "time-concentration" shifting law for the effect of the accelerator. A novel parallel plate geometry is introduced that eliminates slip and enables dynamic oscillatory measurements in the linear viscoelastic regime during setting. Another instrument based on the penetration of a sphere through the setting cement at rates of 1 µm/s is presented. This instrument would enable high throughput evaluation of cement additives. The differences between small strain oscillatory measurements that measure a complex viscosity and continuous deformation measurements such as the penetrometer are discussed.

Tuesday 4:00 Sweeney A SC25

Viscoelasticity and shear-induced aggregation in solutions of single walled carbon nanotubes with tunable interaction potential

Colin C. Young, Anson W. Ma, and Matteo Pasquali
Chemical and Biomolecular Engineering, Rice University, Houston, TX 77030, United States

Single walled carbon nanotubes (SWNTs) can be dispersed in strong acids via the reversible mechanism of sidewall protonation, creating an electrostatic repulsion which counterbalances van der Waals attraction. Acids of different protonating strengths, created by mixing chlorosulfonic and sulfuric acids in different proportions, have been used to create solutions with a tunable inter-SWNT potential. We report how the microstructure and viscoelastic properties of such solutions vary with this potential. In addition, steady shear flow at a low shear rate and low frequency oscillatory shear have been observed to induce aggregation in SWNT-acid solutions; this effect can be reversed by flow at higher shear rate. The rheology of SWNT-superacid systems thus strongly depends on the inter-SWNT potential, the phase in which the nanotubes are dispersed (isotropic, liquid crystalline, or biphasic), and the shear history of the sample; the interdependence of these effects will be elucidated in this presentation.

Tuesday 4:25 Sweeney A SC26

Extensional rheology of carbon nanotubes in chlorosulfonic acid

Dmitri E. Tsentalovich, Anson W. Ma, Natnael Behabtu, Colin C. Young, and Matteo Pasquali
Chemical and Biomolecular Engineering, Rice University, Houston, TX 77251, United States

Carbon nanotubes (CNTs) are macromolecules that have extraordinary mechanical and electrical properties. They have great potential in industrial and defense applications that require high strength, lightweight materials. Dispersing them in superacids (e.g. chlorosulfonic acid) has proved to be an effective and scalable way to process these otherwise insoluble materials into macroscopic articles such as fibers and films. At high enough concentrations, CNTs form a liquid crystalline (LC) phase. The phase behavior of CNTs in chlorosulfonic acid matches theoretical predictions for rigid rods in an athermal solvent. In this presentation, we report the extensional rheology of biphasic CNT-chlorosulfonic acid solutions that are measured using a capillary thinning rheometer. This is the first time that extensional measurements have been performed on solutions of CNTs that are able to form liquid crystals. In addition, the extensional rheology of biphasic solutions is of particular interest because there is little information on such systems in the literature. The presence of an LC phase made up of rigid rods gives the CNT solutions unique extensional properties. It is found that during self-thinning of a thread of CNT solution, the extensional viscosity initially increases probably as a

result of nanotubes getting aligned. However, at high enough strain the extensional viscosity decreases and we postulate that this is because CNTs slip past each other and the LC domains are broken apart. This type of behavior seems to be unique to biphasic CNT-superacid solutions and has not been reported for any other systems of CNTs or rod-like polymers. Moreover, the current finding has important implications on identifying appropriate processing conditions and controlling the degree of CNT alignment in the fiber spinning process.

Tuesday 4:50 Sweeney A SC27

Effects of polyethyene glycol modification on the magnetorheological behavior of Fe_3O_4 nanopaticle magnetic fluids

Xiuying Qiao[1], Mingwen Bai[1], Ke Tao[1], Xinglong Gong[2], Rui Gu[2], Hiroshi Watanabe[3], Kang Sun[1], Jingyuan Wu[1], and Xiaoyu Kang[1]
[1]State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China; [2]Department of Modern Mechanics, University of Science and Technology of China, Hefei, Anhui 230027, China; [3]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Polyethyene glycol (PEG)-coated Fe_3O_4 ferrofluids were prepared by suspending the PEG-coated Fe_3O_4 nanoparticles in an oligomeric PEG-400 carrier liquid, and their magnetorheological steady flow behavior was investigated. The PEG modification did not change the crystalline structure of Fe_3O_4, and the PEG-coated Fe_3O_4 nanoparticles were of nearly spherical shape and had a narrow size distribution. These nanoparticles exhibited no significant aggregation in the absence of the magnetic field. Under the magnetic field, the nanoparticles aggregated into string-like clusters oriented in the direction of the field. Correspondingly, the ferrofluids behaved essentially as the Newtonian fluids in the absence of the magnetic field but exhibited, under the magnetic field, a magnetorheological effect, i.e., the increase of the shear stress/viscosity associated with a pseudo-plastic and thinning character with no real yield stress. This lack of the real yield stress, possibly reflecting the absence of huge clusters connecting the measuring parts (plates) in the rheometer, suggested that the magnetorheological effect of the ferrofluids were related to deformation/disruption of the magnetically formed clusters of finite sizes under the shear. Interestingly, this effect was most significant for the Fe_3O_4 nanoparticles having an intermediate amount of PEG coating. This result suggested a possibility that the relaxation of PEG chains in the coating layers of nanoparticles in the clusters contributed to the magnetorheological effect.

Symposium MS
Polymer Rheology: Melts, Solutions and Blends

Organizers: Shi-Qing Wang and Marie-Claude Heuzey

Tuesday 1:30 Sweeney B MS15

Reptation dynamics of single-walled carbon nanotubes in a network

Nikta Fakhri[1], Fred MacKintosh[2], Laurent Cognet[3], Brahim Lounis[3], and Matteo Pasquali[1]
[1]Chemical and Biomolecular Engineering, Rice University, Houston, TX 77251, United States; [2]Physics & Astronomy, Vrije Universiteit, Amsterdam, The Netherlands; [3]centre de Physique Moleculaire Optique et Hertzienne, universite de Bordeaux and CNRS, Talence cedex, France

Single-walled carbon nanotubes (SWNTs) are an ideal system of stiff filaments with tunable bending stiffness. We have studied the reptation motion of individual SWNTs in agarose gel and have elucidated the effect of finite flexibility on rotational and translational motion. By using NIR fluorescence microscopy, we have directly imaged the reptation motion of SWNTs in a network and quantified the dependence of mobility on physical parameters such as SWNTs stiffness and length as well as network pore sizes. Our results show conclusively that the finite flexibility of stiff filaments enhances rotational diffusion in agreement with Odijk's theory and inconsistent with Doi's scaling of rotational diffusion of a rigid rod. Our observations provide insight into reptation dynamics of stiff filaments as well as a framework to tailor SWNTs mobility in confined environments.

Tuesday 1:55 Sweeney B MS16

Effect of entanglement elasticity on the equilibrium primitive path length distribution in polymer melts

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Analytic expressions for the first and second moment of the equilibrium primitive path length distribution of entangled polymer chains and, based on these moments, an accurate approximation of this distribution were derived from the slip-link model by Khaliullin and Schieber [1]. The original slip-link model describes entanglements as rigid objects, moving affinely with flow. Recently, however, it has been extended to allow for elastic entanglements, which are connected to an affinely deforming background by virtual springs [2]. The objective of this work is to investigate the effect of entanglement elasticity on the equilibrium primitive path length distribution.

For the elastic slip-link model, the free energy is expressed in terms of the vectors connecting the anchor points of the virtual springs [2]. Because these vectors are all correlated, in contrast to the rigid slip-link model, no analytic expressions for the equilibrium primitive path length distribution or its moments have been found. However, these results can be obtained numerically by generating an ensemble of chains with statistics prescribed by the elastic slip-link model. We investigate the dependence of the distribution and its first four moments, obtained from such simulations, on the three parameters of the model: the number of Kuhn steps per chain, the average number of entangled strands per chain, and the elasticity of the virtual springs. Fortunately, rather simple dependencies are found. We discuss comparisons of these results with those obtained from atomistic simulations.

[1] R.N. Khaliullin and J.D. Schieber, Phys. Rev. Lett. 100, 188302 (2008). [2] J.D. Schieber and K. Horio, J. Chem. Phys. 132, 074905 (2010).

Tuesday 2:20 Sweeney B MS17

Microscopic definition of entanglement

Alexei E. Likhtman, M. Ponmurugan, and Jing Cao
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We propose to define polymer entanglements as long-lived contacts between the mean paths. The mean path is defined as a path connecting average positions of every monomer over characteristic time of entanglement tau_e. We performed molecular dynamics simulations on variety of bead-spring models in equilibrium and under shear and investigated properties of entanglements defined in such way. A new algorithm for identification of entanglements allows tracing evolution of individual entanglements and quantifying such mechanisms as constraint release and convective constraint release.

Tuesday 2:45 Sweeney B MS18

Constitutive equations for the flow behaviour of entangled polymer systems

Wim J. Briels
Science and Technology, Twente University, Enschede, The Netherlands

A semi-microscopic derivation is presented of equations of motion for the density and the flow velocity of concentrated systems of star polymers. The essential ingredient in the derivation of the constitutive equation is the transient force that results from perturbations of overlapping stars due to flow. A Smoluchowski equation is derived that includes these transient forces. From this, an equation of motion for the polymer number density is obtained, in which body forces couple the evolution of the polymer density to the local velocity field. Using a semi-microscopic Ansatz for the dynamics of the number of entanglements between overlapping stars, and for the perturbations of the pair-correlation function due to flow, body forces are calculated for inhomogeneous systems, where the density as well as the shear rate vary with position. Explicit expressions are derived for the shear viscosity and normal forces, as well as for non-local contributions to the body force, such as the shear-curvature viscosity. A contribution to the equation of motion for the density is found that describes mass transport due to spatial variation of the shear rate.

Tuesday 3:35 Sweeney B MS19

Probing state of chain entanglement during and after shear deformation

Xin Li, Yangyang Wang, and Shi-Qing Wang
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Based on entangled polybutadiene solutions that only undergo homogeneous shear, we probe the states of chain entanglement during startup shear, step strain relaxation and stress relaxation after shear cessation from steady state. We perform switch-rate experiments where a second startup shear at a higher rate is applied either when steady state has been established during the first startup shear at a lower rate or after shear cessation from steady state for different amounts of time or after a step shear. The magnitude of stress overshoot associated with the second startup shear yields information about how the state of entanglement is different from that of the equilibrium state.

Tuesday 4:00 Sweeney B MS20

Lack of unique state in steady state shear of entangled polymer solutions

Shiwang Cheng[1], Shi-Qing Wang[2], Sham Ravindranath[1], Pouyan E. Boukany[3], and L. J. Lee[3]
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In this work we reveal a dramatic feature of nonlinear rheology of well entangled polymer solutions. Instead of performing a sudden startup shear at a high Weissenberg number in a well entangled polymer solution that exhibits shear banding even after prolonged shear, i.e., after hundreds of strain units, we very gradually increases the speed of the shear surface toward the same final value as that involved in the startup shear. Specifically, this rate rampup is permitted to take place over an hour, allowing the entanglement network to respond evenly to the external deformation. We found with particle-tracking velocimetry that the solution no longer undergoes shear banding. For the same final external condition, different states of flow were attained. This finding not only questions whether shear banding is a steady-state property but also places constraints on how to formulate constitutive description of steady-state nonlinear rheological behavior of well entangled polymers.

Tuesday 4:25 Sweeney B MS21

Homogeneous shear, wall slip and shear banding of entangled polymeric liquids in simple-shear rheometry: A roadmap of nonlinear rheology

Shi-Qing Wang[1], Pouyan E. Boukany[2], and Sham Ravindranath[3]
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A host of PTV studies have recently been carried out to demonstrate that well entangled polymers tend to exhibit inhomogeneous cohesive failure upon large deformations in rheometric apparatuses. These extensive PTV investigations since 2006 have explored many parameters and external conditions and have produced a coherent unified picture concerning shear inhomogeneity. Armed with new data on the transition from wall slip to shear banding as a function of apparent rate that involve a low gap distance of 50 micron, we are finally ready to describe a “phase diagram” as a roadmap for nonlinear rheological phenomenology of entangled polymeric liquids (solutions and melts). All available data fall onto this phase diagram including the two special cases carried out by two other groups (Hu et al., J. Rheol. 2007, 51, 275; Hayes et al., Phys. Rev. Lett. 2008, 101, 218301). The presentation will close by enumerating a great number of unresolved questions and difficulties for future studies.

Tuesday 4:50 Sweeney B MS22

Nanoparticles as interface modifiers for controlling coalescence and break-up in immiscible polymer blends

Steven Vandebril, Jan Vermant, and Paula Moldenaers
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To stabilize the morphology of polymer blends, block co-polymers can be added which should be located at the interface, their role being similar to that of surfactants used for the stabilization of water/oil emulsions. An alternative consists in adding colloidal particles that locate at the polymer/polymer interface, resulting in “Pickering blends”. The aim of this study is to investigate the effect of the nanoparticles on the morphological processes during blending, i.e. coalescence and break-up. Polydimethylsiloxane (PDMS) and polyisobutylene (PIB) are chosen as model blend components, with a 70/30 volume ratio, resulting in a droplet-matrix morphology. Silica nanoparticles of different sizes and shape (anisotropy) with a silanized surface are used as interface modifiers. Their specific location at the interface is confirmed by Cryo-SEM images. Rheological measurements are used to show that the particles slow down coalescence, in particular when PDMS is the matrix phase. Moreover, break-up of the dispersed phase is suppressed, resulting in a fixation of the blend microstructure. For small particles both coalescence and break-up can be controlled in a positive way by increasing the particle concentration and anisotropy. On the other hand, large particles have a negative effect. Interfacial rheological measurements have been performed on planar interfaces using a newly designed double-wall ring. They demonstrate that the nanoparticles at the interface form a gel-like structure and act as interfacial mobility modifiers rather than classical compatibilizers.

Symposium SI
Surface and Interfacial Rheology

Organizers: Ophelia Tsui and Lenore L. Dai

Tuesday 1:30 Coronado/DeVargas SI20

Fracture in aqueous foam

Sascha Hilgenfeldt[1], Shehla Arif[2], and Jih-Chiang Tsai[3]
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Quasi two-dimensional aqueous foam has served as a model system for many processes in atomic lattices, such as defect propagation and plasticity. We use a layer of dry foam in a Hele-Shaw cell to study the microscopic aspects of material failure, i.e., crack propagation. As in atomic crystalline matter, two failure modes are observed: a ductile mode representing a fingering phenomenon in the viscoelastic foam involving neighbor changes of adjacent bubbles, and a much faster brittle mode of elastic cleavage involving film rupture. The two phenomena illustrate liquid/plastic and solid/elastic behavior, respectively, and both can be studied in detail with the microstructure (bubbles) of the material directly observable. The selected mode of crack propagation is governed by the time scales of the elementary processes of bubble deformation and film rupture. These can be derived from simple fluid mechanical force balances and explain the existence of both an upper speed limit for the ductile mode and a lower speed limit of the brittle mode. The predicted velocity gap is in good agreement with the experimental data and reveals that brittle crack propagation in this system occurs above the shear wave speed.

Tuesday 1:55 Coronado/DeVargas SI21

The impact of polyelectrolyte-surfactant aggregate composition on elasticity and mechanical properties of air-liquid interfaces

Matthew D. Reichert[1], Carlton F. Brooks[2], Anne M. Grillet[2], Lisa A. Mondy[2], and Lynn M. Walker[1]
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Polyelectrolyte-surfactant (PES) aggregates provide a useful means of altering rheological properties of fluid-fluid interfaces. Due to widespread use of such systems in commercial and industrial applications, the mechanical properties of interfaces with adsorbed layers of such aggregates are an area of active interest. Previous studies have shown that the interfacial elasticity and foaming capability of oppositely charged PES systems are very dependent on the molar ratio of surfactant to polyelectrolyte monomer[1], with a 1:1 ratio yielding more elastic, stable foams in cases that are not dominated by surfactant. This is shown in part through surface dilatational rheology (SDR) measurements, where a drop of solution is formed on the end of a needle, and area changes are applied while surface tension measurements are performed. The current study seeks to further characterize this interfacial phenomenon on a different PES system, poly cetyltrimethylammonium vinyl benzoate (pC16TVB). These PES aggregates have well-characterized bulk properties and a well defined monomer-surfactant ratio due to the polymerization method used to make them. Using SDR, we are able to apply a sinusoidal oscillation to the drop volume, and using axisymmetric drop shape analysis (ASDA) and the Laplace-Young equation, we calculate surface area and tension changes over time for a range of frequencies and amplitudes. We are able to demonstrate a peak in the Gibbs dilatational interfacial modulus, E, at a 1:1 ratio of polyelectrolyte monomer to surfactant, and we correlate this modulus to foam stability using a modified Ross-Miles test. Additionally, we show that at concentrations near and below the critical aggregation concentration (cac), E reaches values over 100 mN/m and is entirely out of phase with the applied volume change (highly elastic).

[1] Monteux, C, et al., J. Phys. Chem. B, 41, (2004)

Tuesday 2:20 Coronado/DeVargas SI22

Modeling the boundary conditions for liquid flow at solid surfaces

Shihai Feng, Alan Graham, and Antonio Redondo
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In this research, we used large-scale molecular simulations to study the no-slip boundary condition assumptions of continuum hydrodynamic theory. In these simulations, liquid atoms are subjected to simple shear flow and pressure-driven flow. Temporal and spatial averaging is used to calculate both the momentum transport and the boundary conditions. It is generally believed that liquid slips at the molecularly smooth wall surfaces if the interaction between the wall atoms and the liquid atoms are repulsive. With appropriate averaging, we found that the no-slip continuum assumptions are valid even when the solid-liquid interactions are purely repulsive. Furthermore we studied the effects of densities and curvatures of the cylindrical walls on slip length, which is commonly used as a measurement of the degree of velocity slip.

Tuesday 2:45 Coronado/DeVargas SI23

A computational study of the influence of viscoelasticity on the interfacial dynamics of dip coating flows

Arash Abedijaberi[1], Eric S. Shaqfeh[2], and Bamin Khomami[3]
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We examine the effect of viscoelasticity on the interfacial dynamics of air displacing a viscoelastic fluid under the presence of gravity, i.e., the dip coating flow. A stabilized finite element method coupled with a pseudo-solid domain mapping technique is used for completing the computations. The fluid is modeled by the Finitely Extensible Non-linear Elastic-Peterlin (FENE-P) constitutive equation. For all values of Capillary number, Ca and Bond number, Bo the flow is characterized by recirculation near the interface. Increasing Bo, at a fixed Ca, results in film thinning and an increase in the strain rates near the interface. We also observe that the film thickness, as a function of the Weissenberg number Wi, scaled with the capillary length at low Ca and high Bo collapses onto a single curve. As the value of Ca is increased, again the film thickness scaled with the capillary length collapses onto a single curve, but at increasingly higher values of Bo. We show that the interfacial dynamics in the dip coating flow are qualitatively similar to those observed in the Hele-Shaw type of flow. At low Wi, there is film thinning and as the value of Wi is increased, we observe the formation of normal elastic stress boundary layers in the capillary transition region. This is accompanied by a sharp increase in the film thickness and a compression of the bubble in the capillary transition region.

Symposium NP
Complex Fluids: Nanocomposites and Phase Separated Systems

Organizers: Erik K. Hobbie and Simon Cox

Tuesday 3:35 Coronado/DeVargas NP1

X-ray scattering measurements of particle orientation in sheared polymer nanocomposites

Wesley R. Burghardt and Saswati Pujari
Department of Chemical & Biological Engineering, Northwestern University, Evanston, IL 60208, United States

This talk will survey recent efforts to quantify flow-induced orientation in several classes of nanoparticle/polymer dispersions, using in situ synchrotron x-ray scattering during shear. The materials studied include: a model intercalated nanocomposite of organically modified clay dispersed in a low molecular weight polybutene (PB) matrix; dispersions of multiwalled carbon nanotubes (MWNTs) in viscous, uncured epoxy; and dispersion of functionalized graphene sheets in polystyrene. All three samples exhibit similarities in their rheological properties, including (i) solid-like behavior manifested in enhancements to low-frequency storage modulus; (ii) progressive suppression of this solid-like character by shear flow with increasing shear flow rate; (iii) shear-thinning steady shear viscosity; and (iv) structural relaxation following flow cessation, manifested by an increase in elastic character over time. However, the samples' particle orientation dynamics under flow are significantly different. In the clay/PB dispersion, rotational Brownian motion leads to a shear rate dependent orientation state, and partial relaxation of particle orientation upon flow cessation. The orientation dynamics upon flow cessation are closely correlated with evolution of dynamic modulus. Conversely, in the graphene/PS nanocomposites, the orientation state is only weakly dependent on flow conditions, and shows no appreciable relaxation upon flow cessation. Both observations are consistent with expectations with the non-Brownian behavior expected owing to the higher matrix viscosity in these samples. The MWNT/expoxy dispersions are also expected to be non-Brownian. In these samples, however, particle orientation is a strong function of shear rate, and a rapid, partial relaxation of flow-induced orientation is found upon flow cessation. We attribute these observations to elastic deformation of MWNTs within entangled clusters.

Tuesday 4:00 Coronado/DeVargas NP2

Effect of molecular weight on rheological properties of PDMS-grafted alumina in PDMS melts

Rose S. Ndong and William B. Russel
Chemical Engineering, Princeton University, Princeton, NJ 08544, United States

To enhance their properties, melt processed polymers are commonly filled with colloidal particles. Dispersing particles homogeneously in a melt is generally difficult, particularly with dense inorganic oxide particles that generate strong van der Waals attractions. These attractive forces can be modulated by introducing repulsive forces through surface modifications such as polymer grafting. Indeed, the relative viscosity of 430 nm alumina particles stabilized by end-tethered poly(dimethylsiloxane) (PDMS) in PDMS melts decreased with increasing graft density and molecular weight (50kg/mol or 31.4 kg/mol) as expected, but also with increasing molecular weight of the melt in the range of 4.7-41.1 kg/mol. This is surprising as well established theory predicts the grafted layer to be more swollen and, therefore, a better stabilizer in lower molecular weight melts. The answer is found in other studies showing that PDMS melts adsorb on the alumina surface, providing a steric barrier that increases with melt molecular weight.

A simple two-parameter correlation fits the shear-rate dependent viscosities with a value for the relative high shear viscosity (η_∞/μ) and a structural relaxation time (τ) that captures the effect of the interparticle interactions. The measured structural time can be correlated reasonably well with a characteristic relaxation time, τ_0 , estimated by balancing the viscous forces ($-6\tau\mu aU$) corrected for lubrication stresses in the gap (a/L) equal to the van der Waals forces ($A_H a/12L^2$), where μ is the melt viscosity, a the particle radius, A_H the Hamaker constant, and L a characteristic separation reflecting the thickness of the combined adsorbed and grafted layer.

Tuesday 4:25 Coronado/DeVargas NP3

Rheology and structure of dispersed nanoparticles in polymer melts

Joseph Moll[1], Shushan Gong[2], Sanat K. Kumar[1], and Ralph H. Colby[2]
[1]Chemical Engineering, Columbia University, New York, NY 10027, United States; [2]Materials Science and Engineering, Penn State University, University Park, PA 16802, United States

We focus on two systems of truly dispersed nanoparticles. The first dispersed system has polystyrene (PS) chains grafted to 14 nm silica particles (NP), in a PS matrix. PS has repulsive interaction with the silica surface but the grafting is sufficiently dense to inhibit particle-particle contact and the NP-g-PS acts like a surfactant micelle. Depending on the graft chain length, graft density and matrix chain length, the particles spontaneously form chains of NPs, sheets of NPs, etc. with profound consequences for rheology. The second system also uses silica nanoparticles but the poly(2-vinyl pyridine) matrix has a very strong attractive interaction with the NP surface. In this second system the NP and the polymer are mixed in solution, allowing some of the polymer chains to strongly adsorb to the NPs and then the solvent is removed. We discuss the similarities in the two systems, such as particle bridging by matrix chains and 'gelation' as a function of NP concentration, and the differences resulting from the very different interactions between polymer and particle. Structure is probed by SAXS and TEM, segmental motion (glass transition) is probed by dielectric relaxation spectroscopy and mechanical reinforcement is probed by rheological methods: Oscillatory shear (the low frequency storage modulus) determines the equilibrium plateau modulus of the network formed from the NPs connected by bridging chains and the peak shear stress in the start-up of steady shear determines the effective yield stress.

Tuesday 4:50 Coronado/DeVargas NP4

Rheological properties of ethylene-vinyl acetate and nano-crystalline cellulose composites

Denis Rodrigue, Hojjat Mahi, and Eddy Twite-Kabamba

Chemical Engineering, Laval University, Quebec, Quebec G1V0A6, Canada

In this work, Ethylene-Vinyl Acetate (EVA) copolymer with 25% VA content was melt blended with different amounts of nano-crystalline cellulose (NCC) between 2.5 and 15%. From the compounds, shear and extensional rheology was investigated. The results show that the complex shear moduli (both loss and storage), as well as shear viscosity increased with NCC content. However, the extent of viscosity enhancement was not as important as reported in the literature for other types of nano-particles. This indicates that the nano-composites have an intercalated structure and the nano-particles are not exfoliated. Also, it was found that the time-temperature superposition (TTS) principle is valid for these nano-composites in the range of parameters studied. This again shows a polymer dominated behaviour. Extensional rheological tests showed an increase in extensional viscosity with NCC addition. However, strain hardening (especially at higher rates) is reduced for the nano-composites in comparison to the neat polymer. This can be attributed to filler agglomeration in uniaxial elongation and creation of weak points at the interfaces.

Symposium GM
Rheology and Flow of Glass-like Materials

Organizers: Grigori Medvedev and Leon Govaert

Tuesday 1:30 Peralta/Lamy GM11

The effect of molecular size on glassy dynamics

Ryan J. Larsen and Charles F. Zukoski

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

The glass transition a general phenomenon that occurs in a wide variety of materials. However, the search for understanding the universal features of the glass transition has been complicated by the fact that the glass transition depends sensitively on various effects, such as attractions between particles and crowding effects. The respective roles of these effects can be elucidated by comparing various routes by which the glass transition is approached. Here we investigate both the concentration and temperature dependence of the viscosity and self-diffusivity of a molecular mixture (citric acid and ethanol). Both dependencies are captured by a simple free volume model. We compare our results to mode-coupling theory and a two-component equation of state for hard spheres. Our analysis suggests that the dramatic concentration-induced transition from liquid to glass exhibited by this system is dominated primarily by an increase in the average size of the molecules in the mixture. These results underscore how entropic effects associated with variations in molecular size can have a dramatic effect on the glassy dynamics of molecular systems.

Tuesday 1:55 Peralta/Lamy GM12

On the viscoelastic Poisson's ratio in amorphous polymers

Luigi Grassa[1], Alberto D'Amore[1], and Sindee L. Simon[2]

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The Poisson's ratio is defined as the ratio of the lateral contraction to the elongation in the infinitesimal uniaxial extension of a homogeneous isotropic body. In a viscoelastic material, the Poisson's ratio is a function of time (or frequency). In this paper the time-dependence of the Poisson's ratio is analytically evaluated from the bulk and shear response using the relations between the viscoelastic functions in the Laplace domain. It has been found that, in the region of a-relaxation, the Poisson's ratio may be a non monotonic function of time, with a weak minimum at short times, when the shear response is broader than bulk response such that the ratio t_G/t_K is much larger than 1, or a monotonically increasing function of time if the shear and bulk responses share similar timescales and relaxation time distributions. The latter case is verified using experimental data from the literature for a crosslinked polymer, whereas the former case is verified for two linear polymers.

Tuesday 2:20 Peralta/Lamy GM13

A stochastic constitutive model of glassy materials explains post-yield softening

Grigori A. Medvedev and James M. Caruthers

Purdue University, West Lafayette, IN, United States

Post-yield stress softening observed during constant strain rate deformation both in tension and compression is a generic feature of amorphous polymeric materials below the glass transition. A significant factor affecting the yield stress and, hence, the magnitude of post-yield softening is the annealing (aging) time prior to deformation. Predicting the post-yield softening, as opposed to just adding it as a separate phenomenological mechanism, has proven a challenge for constitutive models. For instance, a non-linear viscoelastic constitutive theory of Caruthers, et al. captures with a single parameter set a wide variety of phenomena, including yield, stress/ volume/ enthalpy relaxation, and physical aging, but fails to predict the post-yield stress softening. In this communication we report on the stochastic constitutive model for glassy material being

developed in our group and show that this model captures the post-yield softening phenomenon. An appealing feature of the proposed explanation is that it does not require additional assumptions for various stages of the deformation, i.e. the material at the post-yield strains is described by the same equations as the undeformed one. The stochastic description attempts to incorporate in the constitutive model the spatial dynamic heterogeneity of glassy materials, which is well established experimentally. We postulate that the mobility at a nanometer scale level is controlled by instantaneous values of local thermodynamic parameters, specifically entropy and stress, where the fluctuations in these parameters are significant. In this stochastic model the relaxation time spectrum emerges naturally as a result of an averaging over an ensemble of local responses, the stochastic model is naturally thermorheologically complex. We will demonstrate how this evolution of the relaxation spectrum in the course of deformation is responsible for the post-yield softening effect.

Tuesday 2:45 Peralta/Lamy GM14

Mean-field behavior and viscoplastic theory of glassy-polymeric strain hardening

Robert S. Hoy[1], Corey S. O'Hern[1], and Mark O. Robbins[2]
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Massive strain hardening is a mechanical property unique to polymeric materials containing 'long' chains. Glassy strain hardening (GSH) has traditionally been attributed to the presence of entanglements. However, entropic-elasticity-based theories, which assume the hardening modulus G_R is proportional to the entanglement density, fail to accurately predict the GSH of bidisperse mixtures of short and long chains. Using MD simulations, we show that instead, hardening is controlled by the large-scale (nonaffine) stretch of chains coupled to a glassy medium, and is amenable to a "mean-field" description. We then develop a simple Maxwell-model-like theory relating time-dependent chain orientation and GSH (in monodisperse systems) to coherently relaxing chain contours. In this picture, under active deformation, nonaffine relaxation is strain-activated and arises from the requirement that the chain contour length remain constant (because of stiff covalent bonds). The stress is predicted by assuming it is controlled by the same microscopic plastic events that control plastic flow. We predict a continuous crossover from perfect-plastic flow in the limit of short chains to 'classical' GSH at large strains in the limit of long chains, without invoking entanglements. Our predictions are consistent with recent experiments that have shown that segment-scale relaxation times decrease sharply under active deformation and then increase sharply when deformation is ceased. Finally, we discuss how our predictions may be tested using available experimental techniques.

Tuesday 3:35 Peralta/Lamy GM15

Molecular dynamics simulations of deformation-induced accelerated dynamics in glassy polymers

Mya R. Warren[1] and Joerg Rottler[2]
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A molecular level analysis of segmental trajectories obtained from molecular dynamics simulations is used to obtain the full relaxation time spectrum in aging polymer glasses subject to three different deformation protocols. As in experiments, dynamics can be accelerated by several orders of magnitude, and a narrowing of the distribution of relaxation times during creep is directly observed. Additionally, the acceleration factor describing the transformation of the relaxation time distributions was computed and found to obey a universal dependence on the global strain, independent of age and deformation protocol.

Tuesday 4:00 Peralta/Lamy GM16

Experimental observation and viscoelastic model prediction of non-linear mechanical behavior of PMMA in the glass transition region

Eun-Woong Lee, Grigori A. Medvedev, and James M. Caruthers
Purdue University, West Lafayette, IN, United States

Predicting the non-linear mechanical behavior of glassy polymers manifested in such experiments as constant strain rate loading up to and past yield and large deformation creep and recovery from creep remains a major challenge. A successful constitutive model should be able to describe all the above experiments using a single set of parameters independently determined from the linear data for a given material. One of the problems hampering the development and validation of constitutive models in the field has been the lack of a comprehensive data set obtained for a single well characterized material that includes both diverse linear and non-linear data. This communication attempts to fill that gap. We report on an extremely diverse data set obtained for lightly cross-linked PMMA produced via bulk free radical polymerization. This set comprises the PVT data, the heat capacity data, and the linear relaxation data in addition to the non-linear mechanical data in uniaxial tension and compression, including stress relaxation. A broad range of thermal histories, including varying aging times, has been explored. An evaluation of the performance of the reduced time models of which the thermo- viscoelastic constitutive model of Caruthers, et al. is one example will be presented, where capturing aging time effect on creep and post-yield softening in constant strain rate deformation is particularly challenging.

Tuesday 4:25 Peralta/Lamy GM17

Viscoelastic durometry

Adam W. Mix[1], Carl N. Anderson[2], and A. Jeffrey Giacomin[1]
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Durometry uses indentation with a standardized indentor size and shape, spring stiffness and preload, and initial protrusion. Durometry then assigns a standardized scale reading, called *hardness* and normally between 0 and 100, to the indentor penetration. For a linear elastic material, durometry yields a solitary penetration from which Young's modulus can be deduced. However, for polymeric solids, we often observe a descent of the scale reading, *s(t)*, from its initial to final hardnesses. This descent in measured hardness reflects the time dependent descent in Young's modulus, *E(t)*, from its initial to its final moduli. This descent is caused by material viscoelasticity. We have developed software for a digital durometer to capture *s(t)*, from which we then deduce *E(t)*. In this way, a durometer can be used as a handheld, nondestructive viscoelastometer for solids.

Tuesday 4:50 Peralta/Lamy GM18

Physical aging and structural recovery of epoxy film subjected to carbon dioxide jump

Shankar Kollengodu Subramanian and Gregory B. McKenna
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Physical aging and structural recovery of glassy polymers subjected to temperature jumps have been very well documented in the literature [1]. However, there are only limited sources available in the understanding of the same in plasticizer jump condition. Plasticizers in general are known to causes a depression in the glass transition of polymers. Hence it is important to understand their impact on the physical properties of polymers. Our group has previously studied the structural recovery of glassy polymers subjected to concentration jumps using a strong polar molecule (H_2O) [2]. In this work, we explore the plasticization effects of the weak polar molecule carbon dioxide, on the structural recovery and physical aging of epoxy films and also compare these with the results of temperature jump experiments to the same final conditions of the carbon dioxide pressure and temperature.

References: [1] A.J.Kovacs, Forschr. Hochpolym.-Forch., 3, 394-507 (1963). [2] Y.Zheng, G.B.McKenna, Macromolecules, 36(7), 2387-2396 (2003).

Symposium SA
Self-Assembling, Associative, and Gel-like Systems

Organizers: Ferenc Horkay and Matthew W. Liberatore

Tuesday 1:30 O'Keeffe/Milagro SA6

Flow of colloidal gels in uniform and constricted microchannels

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Flows of colloidal suspensions within confined geometries appear in both biological and technological settings, ranging from blood flow through vascular networks to materials assembly methods, such as ink-jet printing and direct-write assembly. For attractive suspensions, the competition between interparticle and hydrodynamic forces during flow leads to structural rearrangement. In addition, effects due to confinement, such as wall slip and transient jamming, may induce further restructuring. To elucidate the effects of geometry and confinement on the structure of attractive suspensions, we image the flow of colloidal gels *in situ* in straight microchannels using confocal microscopy. Silica particles are first coated with a cationic polyelectrolyte and then flocculated by the addition of an anionic polyelectrolyte. In the quiescent state, the suspension is an isotropic and homogeneous gel. Under shear flow, the suspension contains dense clusters that yield at intercluster boundaries, resulting in network breakup at high shear rates. These structural changes coincide with a transition from pluglike flow at low pressures to fluidlike flow at high pressures. To model the flow of colloidal inks through nozzles for rapid prototyping processes, we also investigate the structure of colloidal gels flowing through constrictions. As the gel traverses the constricted region, both the average velocity and particle density increase downstream. While the average flow profile is smoothly varying, stagnation zones develop at the constriction entry leading to markedly non-uniform local flow profiles. Dense clusters again undergo shear-induced yielding at intercluster boundaries, which enhances the structural heterogeneity of the suspension at the constriction outlet.

Tuesday 1:55 O'Keeffe/Milagro SA7

An experimental design approach to understand rheology of HEUR systems

Suraj S. Deshmukh[1], Flor Castillo[2], Bob Hefner Jr.[2], Valeriy Ginzburg[2], Raymond Jones[2], Debashis Chakraborty[2], Jean P. Chauvel Jr.[2], Alfredo Larre[2], and Chris Christenson[2]

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Telechelic HEUR systems have been reported to show a diverse set of rheological behavior ranging from simple Newtonian to shear-thinning to gel-like and shear-thickening behavior. These systems have been extensively studied in the past decade due to their use as thickeners in a wide variety of application areas such as personal care formulations, coatings, adhesives etc. We have used an experimental design approach to efficiently explore the large experimental parameter space for these systems that includes synthesis and other experimental variables. This approach has helped us understand and model the wide range of observed behavior and also provided us guidance in synthesizing new telechelic HEUR systems with a broader range of molecular weight and chain lengths of the hydrophobic end groups. In particular, we used the modified Transient Network (TN) framework of Tanaka and Edwards (1992) to qualitatively describe the steady-shear rheology of HEUR solutions in both shear-thinning and shear-thickening regimes. Furthermore, statistical models have been generated to complement the existing structure-property relationships and to capture the sensitivity of the rheological behavior to different experimental conditions such as a wide range of concentration, temperature and salt conditions.

Tuesday 2:20 O'Keeffe/Milagro SA8

Structural and rheological evolution of particulate gels

Xiujuan Cao[1], Herman Cummins[2], and Jeff Morris[1]

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The gelation dynamics of a sol of colloidal silica of approximately 10 nm particles is studied using a combination of light scattering and rheometry. By changing the ionic strength (addition of a salt solution resulting different ultimate molarities) of the mixture, a stable sol can be destabilized, leading to aggregation and later gelation. The gel time t_{gel} can be varied from hours up weeks, indicating a reaction-limited aggregation process. Static light scattering is used to extract the fractal dimension D_f of the aggregates, which is found to be approximately 2. The evolution of cluster size is probed by dynamic light scattering, which follows an exponential growth. A simple aggregation kinetic model is present, showing that the aggregation rate depends on the salt concentration. The critical cluster size at the gelation point can be estimated from the model. Rheometry is used to assess the gelation time and further development of the network strength after gelation. It was observed that the gel time (after salt solution addition) depends on both the particle volume fraction and salt concentration, showing a divergence at low volume fraction or low salt concentration. For a single solid fraction, data for the cluster hydrodynamic radius, normalized by the single particle radius, from experiments with wide range of gel times can be collapsed onto a single master curve when actual time after the salt addition, t, is scaled as t/t_{gel}; a similar collapse of the linear viscoelastic data after can be obtained using the same scaling of time. This indicates there is a universal behavior in the aggregation and gelation process that the salt concentration affects the gel time but not the strength of the gel network.

Tuesday 2:45 O'Keeffe/Milagro SA9

Multi-functional soft polymer composites

Joseph L. Lenhart, Randy Mrozek, Jan Andzelm, and Mark VanLandingham

Weapons and Materials Research Directorate, US Army Research Laboratory, Aberdeen Proving Gro, MD 21005, United States

A polymer gel is a physically or chemically cross-linked polymer that is highly swollen by solvent. The gel properties can be tuned by varying the polymer chemistry, solvent type, polymer-solvent architecture and molecular weight, and solvent loading. In addition, small molecule additives and fillers can be incorporated into the gel formulation to enhance the properties further. This tunability offers the potential for gel implementation in an array of Army related technologies ranging from combat casualty care and tissue surrogates, to robotics and electronics devices. While potentially versatile materials, several obstacles hinder widespread deployment of gel-based technologies including: 1) limited operational temperature windows and material lifetimes; 2) poor toughness and durability; 3) unstable performance in other harsh environmental conditions (ie. extreme mechanical, electrical, chemical, and radiation environments); and 4) limited multi-functional capability. Past research has focused on expanding operational temperature windows and materials lifetimes by designing non-aqueous gel materials from commercial precursors. More recent work is focused on continuing to broaden the applicability of polymer gels for Army technologies by a) improving gel toughness, b) developing computational tools and measurement approaches to facilitate materials design, and c) incorporating fillers/additives into the gel formulation to impart multi-functional properties. This talk will summarize our progress in these areas, and demonstrate how multifunctional soft polymer composites can be realized through the judicious selection of materials and processing approaches. The research is currently focused on the materials physics and structure-property relationships, rather than specific applications. However, the relevance of these materials will be discussed as a broad platform for various technologies including robotics, smart clothing, armor, sensors, energy storage, battlefield medicine, etc.

Tuesday 3:35 O'Keeffe/Milagro SA10

Characterization of gels by LAOS

Jason E. Maxey
Baroid Development Group, Halliburton, Houston, TX 77032, United States

Drilling muds have long been known to develop weak bonds between particles and emulsion droplets in suspension, forming a microstructure that is required to provide (among other things) viscosity, solids suspension, and hole cleaning ability. The usual measurement for this performed with a transient flow start-up test at ~5 s^{-1} on a standard oilfield viscometer, with the "gel strength" recorded as the peak in this transient test. This has been a useful test but is limited in several ways, including the sensitivity of the equipment and limitations in the test itself. Hidden behind these limitations are basic differences in the formation of microstructures in differing mud systems, where changes in the surfactants, base oils, and use of organophilic clays and polymer viscosifiers affect the development of structure within the fluid. Two points of particular interest in the performance of these differing microstructures are 1) how they affect settling of weighting materials in the fluid (i.e., barite sag); and 2) the comparative ease with which the microstructure can be dissociated after low- or no-flow periods and the rate at which fluid return to flow conditions. A comparison of some traditional techniques for analysis of gels and newer approaches using large amplitude oscillatory shear are compared. Multiple invert emulsion drilling fluids sampled from field operations are tested, comparing multiple parameters suspected to influence microstructure. In addition, field mud samples are treated by addition of simulated drilled solids, organophilic-modified bentonite, polymeric viscosifiers, and other common additives and their effects on microstructure in the drilling fluid is observed.

Tuesday 4:00 O'Keeffe/Milagro SA11

Rheology and photocrosslinking of alginate hydrogels

Christopher A. Bonino[1], Julia E. Samorezov[2], Oju Jeon[2], Eben Alsberg[2], and Saad A. Khan[1]
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Alginate which can be photocrosslinked into hydrogels and biodegrade in vivo is a promising material for biomedical applications such as tissue engineering and drug delivery. Alginate can be chemically modified with methacrylate groups, which crosslink via ultraviolet (UV) light exposure in the presence of a photoinitiator. The mechanical stability and rate of degradation, which are crucial properties of biomaterials for regenerative medicine, can be manipulated by altering the degree of methacrylation and resultant crosslinking of alginate. In this work, we use dynamic rheology to study the evolution of the crosslinking reaction for methacrylated alginates in situ with a UV photocuring bottom plate fixture with a light emitting diode (LED) radiation source. The Winter-Chambon criteria is applied to determine the gel point and relaxation exponent. We also report an alternative approach for detecting the gel point from the change in sample strain with a controlled stress. In addition, we investigate the effects of changing the degree of alginate methacrylation and UV intensity on the crosslinking reaction. We find that the methacrylation and UV intensity affect the rate of gelation, as well as the gel modulus, which can be used to tailor the properties of the hydrogel scaffolds.

Tuesday 4:25 O'Keeffe/Milagro SA12

Amphiphilic derivatives of alginate: Rheology and controlled release

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

Alginate-based solutions and gels are widely used in tissue engineering and drug delivery applications. Typically, gels are formed through ionic crosslinking of the alginate chains with calcium or barium ions. We have explored a mechanism to create alginate gels with both ionic and physically associating crosslinks through hydrophobic modification. We have successfully synthesized hydrophobically-modified-alginate (HMA) by chemically attaching alkyl groups onto an alginate backbone. The resulting amphiphilic polymers are expected to form micelle-like structures in aqueous media with the alkyl chains clustered into hydrophobic cores. Solubility of several model hydrophobic drugs in dilute HMA solutions were found to be increased by more than an order of magnitude, probably due to preferential migration of the drug into the hydrophobic core. We prepared HMA-based gels through crosslinking the alginate chains with calcium ions. These crosslinked HMA gels were found to exhibit excellent mechanical properties ($G' \sim 100$ kPa) as indicated by rheological studies. We were also able to extend the release rate of drug from a day to 5 days using our system. The mechanism of drug release was found to be diffusion controlled for most part of the release profile. Finally, we explored the influence of calcium crosslinker density and degree-of-substitution on the mechanical and release characteristics.

Tuesday 4:50 O'Keeffe/Milagro SA13

Effect of thermodynamics, chemical kinetics, and chemical heterogeneity on thermoreversible polymer networks

Robert S. Hoy[1] and Glenn H. Fredrickson[2]
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We use hybrid MD/MC simulations to examine the static and dynamic properties of dense, thermoreversibly associating polymer networks. Static properties, e. g. percolation and microstructure, are significantly affected by the placement of sticky monomers (SM) along parent chains. Although gels are formed most efficiently when this placement is uniform and maximizes 'chemical' intrachain SM separation, SM placement

strongly affects dynamics and mechanical properties, and chemically heterogenous SM placement is advantageous for certain applications [1]. More generally, sticky bond (SB) recombination is nontrivially affected by the fact that the SBs are embedded in polymer chains, and by polymer-melt dynamics. The "interplay" of chemical kinetics, SB thermodynamics, SM placement, and the underlying (non-associative) polymer-melt dynamics is quite rich [2]; understanding it may provide a framework for the design of "smart" reversible networks and elastomers with finely tunable rheological properties.

[1] K. E. Feldman et. al, Macromolecules **42**, 9072 (2009). [2] RSH and GHF, J. Chem. Phys. **131**, 224902 (2009).

Symposium CR
Computational Rheology: Behavior 'in Silico'

Organizers: Rajesh Khare and Daniel J. Lacks

Tuesday 1:30 Kearney CR20

Numerical solution of the second order fluid constitutive equation for 3D free surface flows

Murilo F. Tomé and Igor F. Revoredo
Matemática Aplicada e Estatística, Universidade de São Paulo, São Carlos, São Paulo 13560 970, Brazil

This work is concerned with a numerical method for solving the Second Order Fluid constitutive equation for three-dimensional incompressible free surface flows. The governing equations are solved by finite differences on a 3D-staggered grid. The free surface of the fluid is modeled by a Marker-and-Cell type and the full free surface stress conditions are employed. The numerical method developed in this work is validated by comparing the numerical predictions obtained for the flow in a tube with the corresponding analytic solution for Second Order Fluids. By using mesh refinement, the convergence of the numerical technique is verified. Results fo the simulation of the time-dependent extrudate swell for various values of Reynolds and Deborah numbers are presented.

Tuesday 1:55 Kearney CR21

Analytical rheology: Identifying and resolving degenerate structures

Sachin Shanbhag
Scientific Computing, Florida State University, Tallahassee, FL 32306, United States

Recently, a computational algorithm based on Bayesian data analysis was presented to invert the linear rheology of branched polymers (Shanbhag, S., Rheol. Acta., \textbf{49}, 411--422, 2010). When rheological data of an unknown polymer mixture is supplied, the algorithm produces an exhaustive distribution of structures and compositions, consistent with the rheology. Frequently, it identifies multiple or degenerate structures. A resolution of the degeneracy is sought by appealing to the concept of combinatorial rheology (Larson, R.G., Macromolecules, \textbf{34}(13), 4556--4571, 2001), where the unknown sample is strategically blended with a well-characterized fraction. Experimental load is alleviated by identifying the optimal type, molecular weight, and composition of the polymer fraction to blend with the unknown sample, to discriminate between the degenerate structures, most conclusively. Two methods are proposed, and tested on a particular mixture that is characterized by severe degeneracy.

Tuesday 2:20 Kearney CR22

Numerical analysis of double concentric cylinder rheometer with slotted rotor

Weixiong Wang[1], Damir B. Khismatullin[2], Huaning Zhu[3], and Daniel De Kee[1]
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The apparent wall slip phenomenon is inevitably encountered in the standard rheological measurement for concentrated suspensions. It may significantly underestimate the apparent viscosity in the experiments. Previously we have proposed a slotted rotor design to reduce such effects. The objective of this study is to validate this design by conducting 3-D computational fluid dynamics (CFD) simulation and analyzing the velocity and shear stress fields in the double concentric cylinder rheometer with and without slotted rotor and the vane rheometer. Both shear thinning and yield stress fluids, modeled by a continuous viscosity constitutive equation, are considered in the simulations. The wall slip effects are taken into account using the wall slip length method. The results indicate that the double concentric cylinder rheometer equipped with a slotted rotor can measure the fluid properties with enhanced accuracy and less sensitivity to the wall slip velocity than a rheometer with a non-slotted rotor. The wall slip effects can be further reduced by either increasing the slot ratio or adding more slots to the rotor. Although the vane rheometer can reduce the wall slip effects too, it is only suitable for high shear thinning or high yield stress fluids due to the large end effects. As a conclusion, the use of a slotted rotor in the double concentric cylinder rheometer may significantly reduce both wall slip and end effects, making this design an excellent choice for rheological measurements.

Tuesday 2:45 Kearney CR23

Mathematical modeling to enforce a bounded magnitude for the eigenvalues of the conformation tensor, for stable simulation of viscoelastic fluids

Azadeh Jafari, Nicolas Fietier, and Michel O. Deville

Laboratory of Computational Engineering, Institute of Mechan, EPFL University, Lausanne, Switzerland

The fundamental principles associated with the development of mathematical models for efficient annd stable simulation of viscoelastic fluids are described. The main distinct constraints for simulation of viscoelastic fluids, without any exception for any kind of constitutive models is satisfaction of the symmetric positive definiteness (SPD) of the conformation tensor. This means that eigenvalues should remain positive for all steps during the simulation. Negative igenvalues causes the unbounded growth of instabilities in the flow.

Regarding the transformation, matrix logarithm formulation, suggested in Fattal et. al. J. non-Newtonian fluid mechanics 123 (2004), SPD of the conformation tensor is preserved during the simulation , but the problem that can easily appear is overflow and underflow numerical errors during the simulation. This problem happens when the classical conformation is reconstructed from exponential formulation with either infinite positive eigenvalues or infinite negative eigenvalues using the logarithm formulation. The aim of this work is development of mathematical model to preserve both SPD of the conformation tensor and bound the magnitude of eigenvalues when reconstructing the classical formulation. A possible mathematical formulation that enforces this condition is to use an enhanced format of hyperbolic tangent of the conformation tensor. The capability of this formulation for the FENE-P model in the context of spectral element method is compared with the one obtained with the classical logarithm formulation.

Tuesday 3:35 Kearney CR24

Accelerated boundary integral method in non-periodic geometries

Amit Kumar and Michael D. Graham

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706-1691, United States

We present a fast O(NlogN) method for solving the Stokes flow boundary integral equation in an arbitrary geometry. The acceleration in the method is achieved by employing the General Geometry Ewald Like Method (GGEM) for computing the Green’s function in the geometry of interest. Based on this Green’s function, an efficient methodology is developed for computing the single and the double layer integrals in the boundary integral equation. Other details of the method including boundary discretization, integration techniques, and iterative solution procedure will also be presented. A comparison with other accelerated boundary integral techniques for Stokes flow will be made. The efficacy of the method will be demonstrated by the solution of several large scale test problems involving the flow of red blood cells and vesicles in a slit geometry.

Tuesday 4:00 Kearney CR25

Reptate: A free software for analysing rheology of entangled polymers

Alexei E. Likhtman[1] and Jorge Ramirez[2]

[1]Department of Mathematics, University of Reading, Reading RG6 6AX, United Kingdom; [2]Departamento de Ing. Química, U. Politécnica Madrid, Madrid 28006, Spain

Reptate is a software package for viewing, exchanging and analysing rheological data. Several of the classical and latest theories of polymer dynamics are included in Reptate, so they can be tested and fitted to the experimental data. This software is one of the results of large “Multiscale Polymer Processing” project undertaken in the UK during 1999-2009. It is versatile, user-friendly and free. Reptate can be installed on the computer connected to a rheometer and will assists in accessing quality of data as well as fit them to variety of theories. In the talk we will demonstrate several typical examples where reptate can be useful and save time in everyday research.

Tuesday 4:25 Kearney CR26

Constitutive modeling of highly ordered solutions of main-chain liquid crystalline polymers containing hairpins

Oleg I. Matveichuk and Johan J. Slot

Department of Mathematics and Computer Science, Eindhoven University of Technology, Eindhoven, The Netherlands

A microscopic model to describe the dynamics of solutions of main-chain liquid crystalline polymers (LCPs) is presented. The model is formulated in terms of a set of Langevin equations in which the semi-flexibility of the polymer chains, mean-field nematic interactions and the presence of hairpins is incorporated. For sufficiently long semi-flexible chains it is known that the loss of entropy in highly-ordered nematic states is partly recovered by the formation of hairpins or kinks. The presence of hairpins has been conjectured to have an influence on the flow behavior of these systems. The main focus is therefore to study the influence of hairpins on the rheological properties of such LCP solutions. Detailed results are presented for both shear and elongational flow. The model is quantitative and contains only those parameters which can be measured directly or extracted from independent rheological measurements.

Tuesday 4:50 Kearney CR27

Simulations of morphology and mechanical properties of block-copolymer gels

Jan Andzelm, Yelena Sliozberg, Tanya Chantawansri, Kenneth E. Strawhecker, Joseph L. Lenhart, and Mark VanLandingham
Weapons and Materials Research Directorate, US Army Research Laboratory, Aberdeen Proving Gro, MD 21005, United States

Polymer gels based on self-assembled, amphiphilic copolymers form stable, spatially extended networks with controllable morphology and tunable viscoelastic behavior. The polymer network consists of physical cross-links comprised of solvent-incompatible endblocks (micelles) connected by the midblocks (bridges). Polymer gels are useful in numerous applications ranging from biomedical materials to coatings and flexible robotics. We have used a field-theoretic (FT) method and also dissipative particle dynamics (DPD) to study the morphology and mechanical properties of copolymer microphase-separated structures. We will discuss the structure of triblock copolymer gels as a function of the solvent specific mid-block or the end-blocks as well as the effect of confinement or interaction with environment. We will show that the microstructure and viscoelastic properties of these gels depend on several factors such as copolymer concentration, block architecture, and relative size of the hydrophobic and hydrophilic blocks. We will also consider size and chemistry of solvent as well as effect of other polymers and copolymers. Results of simulations will be compared with experimental data where available.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Sweeney F PL3

Molecular aspects of flow-induced crystallization of polymers

Julia A. Kornfield
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

The dramatic acceleration of polymer crystallization that is induced by flow enables economical production of fibers, films, extruded products and molded parts. In this presentation, I will focus on the effects of shear on crystallization from a subcooled melt, particularly the transition from isotropic (spherullitic crystallization) to highly oriented crystallization. This morphological transition is of particular significance because it results in drastic changes in material properties (e.g., rigidity, toughness, permeability). The essential--and elusive--physics is the formation of thread-like precursors during flow. These oriented precursors (“shish”) template the subsequent growth of crystallites (“kebabs”), which can continue long after flow has ceased. A combination of rheo-optical and rheo-synchrotron measurements were applied to model polymers and their binary blends to reveal the molecular basis of “shish” formation. The dynamics of the longest chains in the melt were confirmed to be particularly important. Enhancement of shish formation by addition of “long chains” was greatly enhanced by long-chain/long-chain overlap, suggesting that they act cooperatively. Increasing the molar mass of the long chains increased their potency: e.g., adding < 1% wt of 3,500,000 g/mol isotactic polypropylene, iPP, to a 180,000 g/mol iPP dramatically reduced the threshold stress required to trigger highly oriented crystallization. Despite the central role of long chains in shish formation, shish proved not to be composed of long chains: small-angle neutron-scattering measurements on a series of selectively-deuteriated samples showed that the long chains are no more concentrated in the oriented precursors than in the melt as a whole. A conceptual model will be presented that accords with these diverse observations and its implications for resin design, predictive models and future experimental research will be discussed.

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Wednesday 9:55 Sweeney A SC28

Microstructure measurements of shearing concentrated, near hard sphere colloidal dispersions via 1-2 plane flow-SANS

Norman J. Wagner, Dennis Kalman, and Lionel Porcar
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Concentrated colloidal suspensions of hard, spherical particles exhibit shear thinning, shear thickening, and normal stress differences due to flow-induced microstructural rearrangements. This presentation presents the first direct measurements of these microstructural rearrangements measured in the plane of flow (1-2 plane). We develop a new experimental flow-SANS cell suitable for Small Angle Neutron Scattering Measurements (SANS) in the plane of flow (1-2 plane) and combine that with rheo-SANS in the radial direction (1,3 plane) to elucidate the connection between the microstructure and the measured shear rheology. Significant anisotropic structural rearrangements under shear are evident in the 1-2 plane. These microstructure changes are compared to the rheological behavior via stress-SANS laws that separate the thermodynamic and hydrodynamic components of the stress that drive shear thinning, shear thickening, and first normal stress differences. The experimental results are compared against predictions of Stokesian Dynamics simulations and theory.

Wednesday 10:20 Sweeney A SC29

Characterization of stiff and flexible anisotropic nanoparticles using rheo-optics

Naveen K. Reddy[1], Jan Vermant[1], Jan Dhont[2], Jorge Perez-Juste[3], Isabel Santos[3], Luis Liz-Marzan[3], Peter Lang[2], and Robert K. Prud’homme[4]
[1]Department of Chemical Engineering, K.U. Leuven, Leuven 3001, Belgium; [2]Institute for Festkorperforschung Forschungszentrum, Juelich, Germany; [3]Universidada de Vigo, Vigo, Spain; [4]Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, United States

Particle shape anisotropy plays an important role in controlling optical, magnetic and mechanical properties of nanoparticle suspensions and nanocomposites. However, characterizing nanoparticle size, shape anisotropy and the associated polydispersity is not straightforward. For stiff oblate and prolate gold particles we determine the hydrodynamic aspect ratios using rheo-optics and compare the results with that obtained from depolarized dynamic light scattering and transmission electron microscopy. We show that rheo-optics is a better method to determine the

hydrodynamic aspect ratio for small anisotropic particles. In the case of flexible graphene sheets the average sheet dimension measured using rheo-optics is in excellent agreement with AFM results. Preliminary data on flexibility of graphene sheets using rheo-optics by studying the response in oscillatory and flow reversal experiments are presented.

Wednesday 10:45 Sweeney A SC30

Laser microrheology for soft materials

Christelle Tisserand[1] and Yoann Lefeuvre[2]

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This work present a new technique of the passive microrheology for the study of the microstructure properties of soft materials like emulsions, polymer suspensions, colloids, gels, foams... Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between 104 and 10-1 seconds. Also when the particles move thanks to the Brownian motion, the Generalised Stokes Einstein Relation given by Mason and Weitz can be applied to calculate the visco-elastic moduli G' and G" over a large frequency range. We offer also different easier calculations like a fluidity index, an elasticity factor, a viscosity factor...This technique allows to follow the evolution of the microstructure to analyse for instance gelation, restructuration after shearing, stability, variation of the viscoelastic properties versus temperature, pH, stability of emulsion, suspension... This sensitive and robust method is easy to use thanks to the new instrument Rheolaser Lab. Rheolaser Lab offers an unique solution for microRheology measurement over frequencies range rarely obtain : 101Hz- 10-4Hz. This work will also focus show example on real life sample and the advantages of using a non intrusive method. - Rheology characterisation of salad dressing, with Mean Square Displacement comparison as well as G' and G" over frequencies - Gelation process of food products in order to measure the speed of the gelation and the final strength of the network - Recovery of Fabric softeners and the influence of the pre-shear regarding the recovery (pump shearing or pouring shearing), - Stability of paints... Finally, the work will show some data in order to establish the good correlation between MicroRheology and mechanical Rheology.

Wednesday 11:10 Sweeney A SC31

Rheology of suspensions of cube shaped particles

Rajesh K. Mallavajula, Donald L. Koch, and Lynden A. Archer

Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

The rheological properties of suspensions of Brownian cube shaped particles are interesting because of the greater increase in the translational freedom caused by layering relative to suspensions of Brownian spheres. We studied the theoretical (multipole and finite element) solutions of simple shear flow around an isolated cube and used this solution to obtain the stresslet on the cube and the intrinsic viscosity.The stress-strain-rate relationship is anisotropic with different particle stresslets when the extensional axis is parallel to an axis or a diagonal of the cube. This anisotropic relationship will be used as the hydrodynamic stress in Brownian dynamics simulations for suspensions of hard cubes in shear flow. Simulations are performed over a wide range of volume fractions and Peclet numbers. Using order parameters and radial distribution functions, the structure and the phase behavior of the suspensions will be analyzed. We will also study the bulk rheological properties of the suspension including hydrodynamic and collisional shear and normal stresses. To study the rheology of cubic suspensions experimentally, we have synthesized cube shaped Fe_3O_4 super-paramagnetic nanoparticles and Ag nanocubes.Their rheological properties are characterized at shear rates in shear thinning and shear thickening regime for dilute, moderate and high volume fractions. These observations will be correlated to the theory and simulations.

Wednesday 11:35 Sweeney A SC32

Heterogeneity in the simple shear flow of concentrated suspensions

Kyung Hyun Ahn

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

Simple shear flow such as Couette and capillary flow is the most fundamental flow type and stands at the start line of any research due to its simplicity. Any real flow can be regarded as a combination of both shear and extensional flow, and the simple shear flow is the most basic component of the flow. However in real situations, it is not as simple as the name implies. For most complex fluids, the simple shear flow, or more precisely the Couette or capillary flow is often complicated and non-uniform unlike kinematic description in the textbook. Shear banding or jamming is an example, and has been studied intensively for the last decade. Though the non-uniform nature of such behavior has been observed and reported, it has rarely been studied on its microstructural origin - the heterogeneous nature of the microstructural evolution in particular. For this purpose, we modified a conventional capillary rheometer to measure the viscosity of concentrated suspensions at high shear rate and to visualize the fluid flow at the same time. The suspension showed complex behavior even in the capillary flow field such as yielding, shear-banding and flow instability (sudden jamming and immediate relaxation). Flow was visualized using high speed camera and 2D Fast Fourier transform was used for more precise characterization of particle structure. Pressure fluctuation was measured, analyzed, and directly related with the microstructural evolution. Based on these results, I will talk about the heterogeneous nature of the flow of concentrated suspensions.

Symposium MS
Polymer Rheology: Melts, Solutions and Blends

Organizers: Shi-Qing Wang and Marie-Claude Heuzey

Wednesday 9:55 Sweeney B MS23

Effect of reactive compatibilization on coalescence and rheological properties of thermoplastic olefin blends

Amirhossein Maani, Marie-Claude Heuzey, and Pierre J. Carreau
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Due to the higher toughening contribution and better processability than other traditional ethylene copolymers, metallocene catalyzed ethylene a-olefin copolymers are increasingly used as impact modifiers in thermoplastic olefin (TPO) compounding. The aim of this study was to understand the role of pre-made and in-situ formed copolymers on the suppression of shear induced coalescence in polypropylene/ethylene octene thermoplastic olefin blends. Various types of ethylene propylene and ethylene octene copolymers of different compositions were used as the pre-made copolymers. However, it was found that reactive (in-situ) compatibilization was the most promising way to control the extent of coalescence. A maleated polypropylene was grafted to a maleated ethylene octene copolymer using a linking agent during reactive blending in an internal mixer. Using the Palierne model (1990) the formation of a polypropylene grafted ethylene octene copolymer did not significantly change the interfacial tension between the blend components. However, the transient rheological response and the morphological evolution of the compatibilized and non-compatibilized blends under shearing were quite different. A significant coalescence inhabitation for the compatibilized blend was observed, believed to be due to repulsive steric interactions of the grafted copolymer chains at the interface. The capability of the Lee-Park (LP) (Lee and Park 1994) and Lacroix-Grmela-Carreau (LGC) (Lacroix et al. 1999) model in predicting the transient viscosity and droplet size evolution of the blends was also evaluated. While both models predicted well the rheological data, only the LGC model was found to be capable of predicting the morphological changes.

Wednesday 10:20 Sweeney B MS24

Interfacial relaxation phenomena in immiscible blends of polypropylene/polystyrene

Vahid Shaayegan[1], Paula Wood-Adams[1], and Nicole Raymonde Demarquette[2]
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Interface relaxation processes of immiscible blends of polypropylene (PP) with dispersed droplets of polystyrene (PS) were studied by means of small-amplitude oscillatory shear (SAOS) and creep experiments. The effects of composition as well as compatibilizer on the shape of the spectrum and on the form relaxation peak were elucidated. Since form and interface relaxation mechanisms usually occur at time scales which are not accessible with SAOS experiments only, and in addition, interfacial tension calculations with viscoelastic models are more meaningful at frequencies around the relaxation peaks, creep experiments were used to extend the experimental window and observe the long-time relaxation mechanisms. An experimental creep protocol was developed and employed to obtain linear viscoelastic (LVE) creep compliance data in the absence of changes in morphology. It was found that a compatibilized blend with a lower concentration of compatibilizer shows the presence of a long-time relaxation peak attributed to the relaxation of the Marangoni stress (interface relaxation). The simple and generalized Palierne emulsion models and the viscoelastic Bousmina model were then fit to the extended LVE data and combined with microscopic determinations of droplet size to infer the interfacial tension. It was found that while the simple Palierne model failed to predict the behaviour of compatibilized blends, Bousmina's model predicts both compatibilized and uncompatibilzed blends well.

Wednesday 10:45 Sweeney B MS25

Droplet dynamics in eccentric annular flow

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The design of novel polymers by chemical synthesis is an expensive and time-consuming process. An alternative approach to obtaining novel polymer systems with specific properties is to blend two or more commercially available polymers. Since the constituents and the blending operation itself are relatively cheap, this alternative approach is preferred. However, this method too has some drawbacks. For one, specifically tailoring the properties of a polymer blend is a process of trial and error. Moreover, it is not easy to predict how the designed blend will behave when subjected to industrial processing. One way of obtaining more information about the properties of the resulting blend is to simulate them under industrially appropriate conditions. In this work, we simulated the droplet dynamics of an immiscible polymer blend in the annular gap between eccentric cylinders. The inner cylinder was rotated at a constant angular velocity, whereas the outer one was kept stationary. A cylinder system with a large eccentricity ratio was chosen to allow flow recirculation to occur. A polymer blend model that can predict a non-constant droplet number density and matrix viscoelasticity was adopted. The flow problem was discretized by a collocation method and then solved by a multilevel preconditioned Newton-Krylov method. The influence of the large eccentricity ratio and matrix viscoelasticity on the droplet dynamics was investigated. It was found that significant droplet breakup and extension were restricted to the region of main flow around the inner cylinder. Because of the large eccentricity ratio, droplet breakup and extension were most pronounced near the stationary outer cylinder in the small gap region. The memory of the matrix phase increased droplet breakup and reduced droplet extension. The shear-thinning behavior of the matrix phase had the opposite effect. This study gives information about how the properties of droplets of polymer blends can be tailored by modifying the rheology of the polymer blend matrix.

Wednesday 11:10 Sweeney B MS26

Droplet coalescence in shear flow: From bulk to confined conditions

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Coalescence of liquid droplets dispersed in an immiscible liquid matrix plays an important role in many industrial processes such as liquid-liquid extraction, emulsification and polymer blending. Nowadays, microfluidic devices are becoming common practice in industry. When emulsions or polymer blends are processed in such devices, the effects of the walls on the morphology development cannot always be neglected. For confined shear flow, the deformation and breakup of droplets have extensively been studied, as reviewed by Van Puyvelde et al.(1). The presence of strings and ribbons in concentrated, confined blends suggests that confinement stimulates droplet coalescence. However, a systematic study of the coalescence of isolated droplet pairs is needed to verify this hypothesis and to provide a physical explanation for the observations. In the present work, the coalescence of two Newtonian droplets in a Newtonian matrix has been investigated microscopically(2). For that purpose, a home-built counter rotating parallel plate shear flow cell has been used. Collision and coalescence have been studied for a range of droplet sizes, both in bulk conditions and for gap spacings that are comparable to the droplet size. From our observations it is clear that geometrical confinement promotes droplet coalescence. All other conditions being equal, confined droplets rotate less than unbounded droplets before coalescence occurs. For droplets with a diameter of about 20% of the gap height the critical Ca-number for coalescence is significantly increased as compared to bulk conditions. In order to obtain a better understanding of the forces and fluid dynamics that govern this process, the droplet trajectories, the time-dependent orientation angles of the droplet doublet and the droplet deformation during the interaction process have systematically been studied.

(1) Van Puyvelde et al. Polymer, 49, 5363-5372 (2008). (2) Chen et al. Langmuir, 25, 12885-12893 (2009).

Wednesday 11:35 Sweeney B MS27

Dispensing of complicated fluids – the influence of the rheological properties

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The dispensing of fluids in the industrial environment is an important problem as accurate dosing is linked to items such as product quality or accurate filling of liquids products. While dispensing a desired volume or mass of a Newtonian liquid through an orifice is generally not problematic, the dispensing of non-Newtonian liquids might lead to surprising results when viscoelasticity and non-linear behaviour are not taken into account. The traditional way to circumvent these problems is to first calibrate a dispenser for each individual fluid at all required flow rates or pressures and desired dispensing volumes. While this is a safe method to assure an accurate dispension of this fluid, it requires time and does not allow to predict a priori if a fluid can be dispensed with the required accuracy. A much more convenient way would be to classify a fluid by its rheological properties and to use these material properties in order to predict the behaviour in the dispensing orifice. In this paper we are therefore going to demonstrate for several extreme classes of non-Newtonian liquids their behaviour under two possible operating modes of flow induction in a dispenser: a volumetric controlled dispensing at a defined flow rate, and a pressure driven dispensing by applying a controlled pressure profile. For the volumetric controlled dispensing the focus is mainly on the time scales and the breaking dynamics of the fluid after exciting the orifice. In the pressure driven case the dispensing the flow rate itselve will become for certain fluid classes also a function of time even for a constant applied pressure. Our aim is to give in this paper an outline of a ‘map of misery’ that explores for all relevant non-Newtonian fluid classes the boundaries for dispensing these fluids and that allows to predict within these boundaries the dispensing behaviour depending on the material properties of the fluid classes.

Symposium NM
Nano- and Micro-Rheology: Indentation and Beyond

Organizers: Mark VanLandingham and Hongbing Lu

Wednesday 9:55 Coronado/DeVargas NM1

Modeling instrumented indentation in visco-elastic and visco-plastic materials

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Instrumented indentation is widely used for the characterization of small-scale mechanical behavior of “soft” materials, such as polymers, composites, and biomaterials that exhibit time-dependent behavior. Modeling instrumented indentation in viscoelastic and viscoplastic solids has been important in improving and developing methods for analyzing indentation measurements in soft materials. In this presentation, we will discuss our recent results on modeling instrumented indentation in viscoelastic and viscoplastic solids. We first examine the relationships between initial unloading slope, contact depth, and viscoelastic properties for various loading conditions, including load- or displacement-control. We then discuss the “hold-at-peak-load” and “hold-at-the-maximum-depth” techniques, as well as the constant indentation strain-rate method. We will also evaluate methods for obtaining storage and loss modulus using oscillatory indentation. Finally, we will discuss several methods for measuring shear relaxation modulus and creep compliance from indentation loading curves.

Wednesday 10:20 Coronado/DeVargas NM2

Contact mechanics in glassy polymers

Lambert van Breemen, Leon Govaert, and Han Meijer
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Polymers can display excellent tribological properties, but the correlation between friction and wear properties and the polymer's intrinsic mechanical properties is generally blurred by measurements with too many variables. As a result a large scatter in literature data on the response of polymers to indentation and single-asperity scratching is found, in particular the dependence on scratch load, temperature, tip geometry, and sliding velocity.

Generally it is understood that the measured friction force is an additive composition of an adhesion- and a deformation-related component, suggesting that components operate and contribute independently. In an experimental set-up a decomposition of these components is impossible. However by combining experiments with numerical (FEM) simulations, a decoupled analysis is made possible. Simulations with no adhesive interaction between tip and polymer show almost no influence of sliding velocity on friction force, whereas our experiments show a significant influence. In case of an additive decomposition, this would imply a time-dependency of the adhesive component, which however is very unlikely. By inclusion of the velocity (time) independent Amontons-Coulomb friction law (1781), creating an interaction between tip and polymer, it is demonstrated that an increase of the adhesive component strongly influences the contribution of the deformation related component, by the formation of a bow wave in front of the sliding tip. This implies that the suggested additive decomposition is not applicable and the large macroscopic deformation response proves to be the result of small changes in local processes.

As a result, relations between intrinsic mechanical properties and frictional properties are established which could lead to new tools that help understanding and improving the friction and wear properties of polymers.

Wednesday 10:45 Coronado/DeVargas NM3

Extension of the beam theory for the polymer bio-transducers with low aspect ratios and viscoelastic characteristics

Ping Du[1], I-Kuan Lin[1], Hongbing Lu[2], and Xin Zhang[1]
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Polydimethylsiloxane (PDMS) based micropillars (or microcantilevers) have been widely used as bio-transducers for measurement of cellular forces on the order of pN to μN. The accuracy depends on appropriate modeling to convert the micropillar deformations into corresponding reaction forces. The traditional approach is based on Euler beam theory with the consideration of a linear elastic slender beam. However, the low aspect ratio of PDMS micropillars does not satisfy the slender beam requirement. Consequently, Timoshenko beam theory, appropriate for a beam with low aspect ratio, should be used. In addition, the inherently time-dependent behavior in PDMS has to be considered for accurate force conversion. In this work, the Timoshenko beam theory, along with the consideration of viscoelastic behavior of PDMS, was used to model the mechanical response of micropillars. The viscoelastic behavior of PDMS was characterized by the stress relaxation nanoindentation, and the relaxation function was extracted and described by a generalized Maxwell model. The bending of rectangular micropillars was performed by a wedge indenter. The viscoelastic Timoshenko beam formula was used to calculate the mechanical response of the micropillar, and the results were compared with measurement data. The calculated reaction forces agreed well with the experimental data at three different loading rates. Parametric study was conducted to evaluate the accuracy of the viscoelastic Timoshenko beam model by comparing the reaction forces calculated from the elastic Euler beam, elastic Timoshenko beam, and viscoelastic Euler beam model at various aspect ratios and loading rates. The extension of modeling from elastic Euler beam theory to viscoelastic Timoshenko beam theory has improved the accuracy for the conversion of the PDMS micropillar deformations to forces, which will benefit the polymer-based micro bio-transducer applications.

Wednesday 11:10 Coronado/DeVargas NM4

Characterization of new surface shape memory phenomena in soft and rigid shape memory polymers

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Shape memory polymers are those polymeric systems capable of fixing one or more temporary, nonequilibrium, shapes and to be later triggered to return to an equilibrium shape by a stimulus. Examples of shape memory polymers include glassy networks, semicrystalline networks, physically crosslinked blends, and a variety of block copolymers. Commonly, such shape memory phenomena have been studied using bulk tensile deformations using traditional tensile testing or dynamic mechanical analysis apparatus. Here, we will reveal methods and results associated with surface shape memory of a variety of shape memory polymers developed in our lab, with special attention given to soft liquid crystalline elastomers and much stiffer glassy covalent networks. These systems were studied for the degree of fixing and recovery when deformed using an indentation method designed to utilize a commercial rheometer. In particular, a stylus-type indenter was used to locally deform each sample at the 1-100 micron scale at a variety of temperatures to a controlled depth, following which each sample was cooled to a temperature below that required for significant strain-fixing. Then, the recovery achieved during heating was observed in-situ or externally using profilometry. The shape memory characteristics of strain fixing, strain recovery, and recovery sharpness were compared between materials systems and with bulk tensile shape memory cycles, revealing good correlation between the two. Application of the observed surface shape memory to reversible embossing was demonstrated and applications thereof will be discussed.

Wednesday 11:35 Coronado/DeVargas NM5

Analysis of hydrated biological tissues and tissue surrogate gels under concentrated impact loading

Z. Ilke Kalcioglu[1], Meng Qu[1], Kenneth E. Strawhecker[2], Mark VanLandingham[2], James F. Smith[3], and Krystyn J. Van Vliet[1]
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The mechanical behavior of tissues under dynamic loading conditions consistent with “impact events” such as industrial accidents, ballistic injuries, and blast effects is an emerging area of rheological study. Quantification of such dynamic energy dissipation can also enable the design of tissue surrogate materials that can serve as mechanical mimics of hydrated tissues, and can be examined in ambient conditions under controlled laboratory testing. Here, we examine the quasistatic and impact indentation responses of both hydrated tissues and candidate tissue surrogate materials via pendulum-based microscale impact, in order to identify design principles by which synthetic, air-stable polymers can recapitulate soft tissue responses. More specifically, we studied soft tissues of two organs (liver and heart), and compared them with a commercially available tissue surrogate gel (Perma-GelTM), and styrenic triblock/diblock copolymers at different vol% triblock concentrations. While quasistatic instrumented indentation indicated the opportunity to modulate dissipation as a function of composition in the block copolymers, through impact indentation we were able to quantify resistance to penetration and energy dissipative constants for each material under the rates and energy densities of interest for tissue surrogate applications. We found that the energy dissipation capacity under dynamic impact increased with increasing vol% diblock in these styrenic gels, and were thus able to design an environmentally stable material that well matched the energy dissipation capacity of fully hydrated soft tissues for the impact velocities employed herein (1 μm/s to 20 mm/s, corresponding to approximate strain energy densities from 0.4 kJ/m^3 to 20 kJ/m^3). More generally, the methodologies detailed here facilitate further optimization of impact energy dissipation capacity of polymer-based tissue surrogate or flexible armor materials, either in air or in fluids.

Symposium GM
Rheology and Flow of Glass-like Materials

Organizers: Grigori Medvedev and Leon Govaert

Wednesday 9:55 Peralta/Lamy GM19

Crystallization kinetics of semi-crystalline polymers: From processing to properties

Tim van Erp, Leon Govaert, and Gerrit Peters
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Solidification in industrial processes, like injection moulding, involves flow fields, high thermal gradients and high pressures. Investigating polymer solidification under comparative processing conditions is a necessary step in order to predict the final polymer properties. Clear, key issue is accurate control during processing. Therefore, in this study a custom designed dilatometer has been used to obtain samples at different cooling rates and elevated pressures under quiescent conditions for a commercial iPP homopolymer. These samples are used to investigate the complex relation of processing induced morphologies towards mechanical properties.

The influence of pressure and cooling rate on mechanical properties, i.e. yield stress, and on the morphology, expressed in terms of crystallinity, phase-content and lamellar thickness, is presented. Interestingly, results on the PVT samples display no noticeable change in yield stress for low cooling rate with different applied pressures. However, for high cooling rate the yield stress decreases with increased applied pressure.

Polymer crystallization, in quiescent conditions, consists of two parts: (1) nucleation and (2) spherulitic growth. Both processes are influenced by pressure; enhanced nucleation and suppressed growth rate. These results provides a solid basis for the identification of a crystallization model suitable to describe solidification in polymer-processing operations, based on the Kolmogoroff-Avrami-Evans non-isothermal approach. In here, three parallel, noninteracting kinetic processes are introduced for the different phases. A deconvolution technique applied to the iPP WAXD patterns allowed evaluation of the final phase content. The distribution of three observed phases, i.e. alpha, gamma and meso, depends clearly on cooling rate and applied pressure. This model is capable of predicting the distribution of phase content and based on this non-isothermal kinetic approach the resulting mechanical properties are explained.

Wednesday 10:20 Peralta/Lamy GM20

Architectural effects on the viscoelastic bulk response in polystyrene

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

The pressure-volume-temperature (PVT) behavior and pressure relaxation response of a three-arm star polystyrene sample are measured using a custom-built pressurizable dilatometer. From the PVT behavior, the glass transition temperature (T_g) is calculated as a function of pressure, and dT_g/dP is found to be approximately 30% higher for the star relative to linear polystyrene samples. Pressure relaxation experiments for the star polymer are performed by making volume jumps in the vicinity of the pressure-dependent T_g. Master curves are built by time-temperature superposition, and the temperature dependence of the horizontal shift factors is found to be the same as those obtained from the viscoelastic shear response measured using a commercial rheometer. The bulk spectra are observed to have a similar slope as the shear spectra at short times,

but the magnitude is lower; this result is consistent with the results observed for linear polystyrene and the implications are discussed. Finally, the viscoelastic retardation spectrum derived from the bulk response is found to be narrower than that from the linear sample.

Wednesday 10:45 Peralta/Lamy GM21

Direct visualization of glassy dynamics in a model polyamide rod system

Abhishek M. Shetty[1], Patrick Spicer[2], and Michael J. Solomon[1]
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We study arrested dynamics in a model colloidal rod system comprised of polyamide rods by means of confocal microscopy. The aspect ratio of the rods varies from about 28 to 212 and the dimensions of the rods are such that they undergo Brownian motion. From acquired image series we show that arrested dynamics in these suspensions occurs at a critical volume fraction (f_g) that depends sensitively on the aspect ratio of the colloidal rods. This arrest volume fraction was identified by measuring the volume fraction dependence of an average correlation coefficient (R) between images of the confocal microscopy time series. We find that the arrest volume fractions, f_g, obtained for the different aspect ratios are slightly lower than the minimum percolation volume fraction for a random homogenous network of rods. We explain this result as a consequence of the presence of charge repulsion in our system. We also investigate the elasticity and yielding behavior of these rod suspensions above the critical volume fraction f_g by means of oscillatory shear experiments. We observe a power law scaling that we explain in terms of central force percolation.

Wednesday 11:10 Peralta/Lamy GM22

Irreversible aging dynamics and phase behavior of aqueous suspensions of Laponite

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In this work, we study the aging behavior of aqueous suspension of Laponite having 2.8 weight % concentration. In rheological experiments we observe inherent irreversibility in the aging dynamics which forces the system not to rejuvenate to the same state in the shear melting experiment carried out at a later date since preparation. The extensive rheological experiments carried out as a function of time elapsed since preparation and temperature demonstrate a self-similar trend in the aging behavior irrespective of the concentration of salt. We observe that an exploration of the low-energy states as a function of aging time is only kinetically affected by the presence of salt. We estimate that the energy barrier to attain the low-energy states decreases linearly with increase in the concentration of salt. The observed superposition of all the elapsed time and the salt-concentration-dependent data suggests that the aging that occurs in low salt concentration systems over a very long period is qualitatively similar to the aging behavior observed in systems with high salt concentration over a shorter period.

Wednesday 11:35 Peralta/Lamy GM23

Dynamics and structures of dilute magnetic colloidal suspensions confined in thin films and monolayers near the glass transitions

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A quasi two-dimensional model of magnetic colloidal chains is examined by extensive Brownian dynamics simulations on dilute magnetic colloidal monolayer and on dilute magnetic colloidal chains confined in thin films under an external magnetic field applied perpendicular to the films. The diffusivity of colloids and chains decreases with increasing an applied external magnetic field. We compare the simulation results on (1) monodisperse case, (2) polydisperse case, and (3) binary case. On monodisperse case, the crystallization occurs. On the other hands, diffusivity dramatically decreases near glass transition, when crystallization does not occur on polydisperse case and binary case. However, Universalities in the dynamics of chains and monolayer colloids on any systems are found based on the mean-field theory recently proposed by Tokuyama. These long-time self-diffusion coefficients collapse on a single master curve. It is also found that universalities are found to exist not only in the dynamics but also in the spatial distribution of colloidal chains confined in films with different chain lengths on monodisperse case [1]. On the other hand, the magnetic field dependences of the mean-square displacements are qualitatively similar to those of the monolayer colloids on polydisperse and binary case, even if the field dependence of spatial distributions is different from that of the monolayer colloids [2].

References: [1] Y. Terada and M. Tokuyama: J. Phys. Soc. Jpn. 78 (2009) 084803. [2] Y. Terada and M. Tokuyama: J. Phys. Soc. Jpn. 79 (2010) 034802.

Symposium SA
Self-Assembling, Associative, and Gel-like Systems

Organizers: Ferenc Horkay and Matthew W. Liberatore

Wednesday 9:55 O'Keeffe/Milagro SA14

Rapid exfoliation and physical gelation of a clay-polymer nanocomposite

H. Henning Winter[1], Katie Lania[1], Marco Dressler[1], Deepak Arora[2], and Xiaoliang Wang[3]
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A new exfoliation mechanism is proposed for organically modified clay (layered silicate) in a matrix of end-functionalized ("sticky") macromolecules. The evolving clay structure gives rise to physical gelation which can be monitored rheologically. When mixing the clay particles into the polymer, sticky macromolecules anchor on the outer clay surfaces and generate an entopic pulling force that peels clay sheets away from the stack. The molecular force is due to the restricted free energy in the presence of the solid surface. The assembly of anchored macromolecules (brush) on the outside of clay particles can overcome the internal cohesion since the organically modified clay sheets are only weakly connected with each other. The entropic force increases with temperature due to increased thermal motion, but then decreases again when macromolecules begin to detach at high temperature. The experimental protocol includes time-resolved rheometry (Rheol Acta 33:385-397, 1994) and rescaling of data (Rheol Acta 45:331-338, 2006). Surprisingly, the product of equilibrium modulus and longest relaxation time, $G_e(t_r) \cdot \lambda_{max}(t_r)$, was found to remain constant throughout the late stages of physical gelation. Parameter is the duration of the isothermal ripening process ("ripening time", t_r).

Acknowledgment: NSF support through CBET-0651888.

Wednesday 10:20 O'Keeffe/Milagro SA15

Injectable hyaluronan-based composite hydrogels for biomedical applications

Jules J. Magda[1], Madhuvanthi Kandadai[1], Mataz Alcoutlabi[1], Xiaojun Wang[2], Durairaj Baskaran[2], Jimmy Mays[2], Sarah Atzet[3], Thomas Zarembinski[3], and Ferenc Horkay[4]
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Native hyaluronan (HA) is a charged linear polysaccharide that is present throughout the human body and that serves a number of important physiological functions, such as a lubrication of articular joints and retention of water in connective tissues. However, because the lifetime of a given native HA molecule within the body is typically very short (less than 3 days), there is a biomedical need for HA-derived materials that can be injected into the body at low viscosity and that form longer-lasting gels in situ. In this presentation, I will compare the rheological properties of two different in situ gelling HA-based biomaterials. The first biomaterial is formed by mixing modified reactive HA chains with telechelic PEG chains designed to induce gelation after an induction period of about 5-10 minutes. This chemical gel is envisioned for tissue engineering applications. The second material is obtained by hydrophobic association of poly(leucine) branches chemically attached to HA backbones. This physical gel could be used to boost the viscosity of synovial fluid that has been degraded due to osteoarthritis of the knee.

Wednesday 10:45 O'Keeffe/Milagro SA16

Flow-induced irreversible gel formation in micellar solutions: Experiments and modeling

Neville Dubash, Joshua Cardiel, Perry Cheung, and Amy Shen
Mechanical Engineering, University of Washington, Seattle, WA 98195, United States

It has been known that solutions of wormlike micelles can form flow-induced gel-like structures. Flow-induced structures previously reported in the literature, which occurred under pure shear flow conditions, have all been temporary with the gels dissipating upon cessation of the flow. Recently, however, it has been shown that it is possible to produce a purely flow-induced irreversible transformation in certain micellar solutions. This irreversible gel formation is brought about via a mixed shearing/extensional flow in which the fluid experiences very high strain rates and total strains. Here we examine this gelation phenomenon and show that it results in a transition from a weakly viscoelastic solution to a highly viscoelastic gel where the relaxation time and the plateau modulus both increase by more than an order of magnitude. In addition, we present a simple model which is able to capture the irreversible rheological changes observed in our experimental system. The model is based on existing network scission models for micellar solutions, and incorporates new features to describe the irreversible gel formation.

Wednesday 11:10 O'Keeffe/Milagro SA17

Irreversible structural transition induced by mechanical shear in a novel peptide-amphiphile system

Katie A. Megley and Matthew Tirrell
Bioengineering, University of California, Berkeley, Berkeley, CA 94720, United States

Shear-induced self-assembly has been extensively studied using model surfactant systems, which form long extended micelles at a critical shear rate. These extended micelles are able to entangle, giving the system viscoelastic properties. Most of the work in this area, using conventional rheometry has resulted in the formation of reversible gel structures, once the shear force was removed, the solution reverted back to a Newtonian fluid state. Recent work has identified a method by which a stable, irreversible gel can be formed using microfluidics to apply extensional flow (Vasudevan, M. et. al., 2010). Here, we present rheological studies of a peptide amphiphile, a short peptide sequence attached to a fatty acid tail, which transforms into extended worm-like micelles. The particular peptide sequence is alanine (A) rich with interspersed lysine (K) residues, which gives it a strongly alpa helical secondary structure. When a lipid tail is added to the peptide creating a peptide amphiphile, spherical micelles initially form upon liquid mixing and then undergo a switch to form long cylindrical micelles which in turn entangle creating gel material with viscoelastic mechanical properties. The physical transition from spherical to worm-like micelle coincides with a secondary structure transition from alpha helix to beta sheet which is monitored using circular dichroism microscopy. As in the surfactant system, our peptide amphiphile solution initially behaves as a Newtonian fluid and then transitions to a shear thinning gel once a critical shear rate is surpassed. The resulting gel is self healing, and stable at 4°C on the order of weeks to months. The tunable nature of this system makes it an attractive material for use as an injectable tissue engineering matrix.

Wednesday 11:35 O'Keeffe/Milagro SA18

Rheological studies of irreversible gelation of wormlike micellar solution

Joshua Cardiel, Neville Dubash, Perry Cheung, and Amy Shen
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It is well known that wormlike micellar solutions under flow can form reversible gel-like materials with viscolestic behavior. Recently, it has been shown that it is possible to form irreversible gels by pumping a semi-dilute surfactant-salt precursor through a microfluidic device [1]. In this talk, we will present the rheological behavior of the precursor before and after the irreversible gelation occurs. By using a combination of macrorheology and microrheology techniques, we show that the wormlike micellar solution undergoes a transition from a weakly viscoelastic, shear thickening solution to a highly viscoelastic, shear thinning gel, where the relaxation time and the plateau modulus both increase by more than an order of magnitude. In addition, we also exam the effect of aging on the precursor rheology and present the relationship between the gelation process (both gelation time scale and gelation volume) and the aging effect of the precursor.

Symposium NP
Complex Fluids: Nanocomposites and Phase Separated Systems

Organizers: Erik K. Hobbie and Simon Cox

Wednesday 9:55 Kearney NP5

Microstructural properties and rheological modeling of nanocomposites

Marco Dressler and H. Henning Winter
Chemical Engineering, University of Massachusetts, Amherst, MA 01003, United States

Complex fluids of an organic polymer as a matrix phase and an organophilic layered silicate as a disperse phase can form a microcomposite or a nanocomposite. In Polymer Layered Silicate (PLS) nanocomposites, single clay sheets of atomic thickness (surface/height ratio up to one thousand) are dispersed, e.g., as intercalated or exfoliated hybrids. For the intercalated hybrid, a single polymer chain is embedded between adjacent clay sheets and the integrity of clay crystallites (stacks of clay sheets) is maintained. For the exfoliated morphology, the distance between clay sheets is so large that the clay crystallites are delaminated. Recently, a rheological equation of state has been proposed for an exfoliated PLS nanocomposite. This equation of state has been derived from a phenomenological free energy expression and it has been assumed that the free energy has contributions from the polymer, the clay, and the polymer/clay interaction. In our talk we analyze this rheological equation of state and we discuss which microstructural characteristics a more sophisticated equation of state should reflect. To this end, we consider free energy expressions for PLS dispersions which have been derived in the framework of statistical mechanics and we conjecture whether more realistic equations of state can be derived from these thermodynamic potentials. This allows us to take into account the energetic and the entropic interactions between clay, surfactant, and polymer in PLS dispersions and to describe the unmixed microcomposite, the intercalated hybrid, and the exfoliated morphology. Furthermore, we propose a constrained microstructural variable for clay sheet orientation and deformation which accounts for the area preservation of crystalline clay sheets under external deformation. The goal of this study is to obtain a rheological equation of state that allows to predict the microstructure-rheology relationships for exfoliated hybrids and to model melt compounding of PLS nanocomposites.

Wednesday 10:20 Kearney NP6

Polymer-nanoparticle blends and their unusual liquid and solid state properties

Jeong J. Wie, Jonathon Seppala, and Michael E. Mackay
University of Delaware, Newark, DE, United States

Materials from polymers have made significant technological impact, due to their ease of processing and low cost with recent advances promoted through the use of nanoparticles. It is expected the nanoparticles will impart new and novel properties as their size approaches the persistence length of the polymer by prohibiting dense packing of the segments. Here we show this effect provides a viscosity decrease in the melt, as we have shown before, in addition to making the melt and solid more compressible while simultaneously increasing the tensile modulus. These disparate effects are rationalized through the packing effect mentioned above or equivalently the nanoparticle induced density fluctuations.

Wednesday 10:45 Kearney NP7

In-situ synchrotron study on uniaxial deformation of SBS grafted with polyhedral oligomeric silsesquioxanes

Andre Lee
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Symmetric triblock polystyrene-butadiene-polystyrene (SBS) copolymers of different initial morphologies were grafted with polyhedral oligomeric silsesquioxane (POSS) molecules of different chemical substituents. The POSS octamers, R'R7Si8O12 were designed to contain a single silane functional group, R', which was used to graft onto the dangling 1,2 butadienes of the polybutadiene block and seven identical organic groups, R=isobutyl (iBu) or phenyl (Ph), exposed to the block copolymers. in-situ X-ray scattering during uniaxial tensile deformation of these POSS modified SBS were investigated. Microstructural alignment of SBS as influenced by grafted POSS at different draw ratio was quantified with the second-order Hermann’s orientation function. It was observed that when iBu-POSS was grafted to the butadiene segment, the long-range and local order of the morphology were preserved. The presence of these grafted iBu-POSS plays no significant role on the alignment of domains upon uniaxial deformation. However, for systems with Ph-POSS grafted to the butadiene segment, the morphology was disrupted due to the interaction between Ph-POSS and polystyrene endblocks. This restricted motion causes the polystyrene-rich cylinders to orient perpendicular to the stretch direction at the low strain limit.

Wednesday 11:10 Kearney NP8

Linear viscoelasticity of chiral liquid crystals

Zhenlu Cui
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We investigate the small amplitude oscillatory Poiseuille permeation flow of chiral liquid crystals (CLCs). We model the system by Stokes hydrodynamic equations coupled with orientational dynamics and study the frequency-locked solutions of the system by employing a coarse-grained approach. The response of CLCs has been calculated. Viscoelastic behavior is only observed at intermediate frequencies and the material is essentially viscous at low and high frequency regimes.

Wednesday 11:35 Kearney NP9

Simulating obstacle-foam interaction

Simon Cox and Tudur Davies
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When a foam flows, it does so through a series of neighbour switching T1 topological changes [1]. These are a local manifestation of a macroscopic plastic response. We present quasi-static bubble-scale simulations using the Surface Evolver [2] that probe their effect on the flow around obstacles embedded in the foam [3]. Applications include mould-filling and enhanced oil recovery.

The forces on an obstacle in a foam flow are mostly elastic: that is, they are due to the tension in the soap films and the pressures in the bubbles that touch it. Topological changes at the leading and trailing edges cause these forces to vary. We quantify how the drag depends on obstacle shape, and the extent to which the lift on an obstacle is determined by its asymmetry. We also show that the bunching of films behind a non-circular obstacle leads to a non-zero torque, an elastic effect that is modulated by the plasticity [4].

[1] D. Weaire and S. Hutzler (1999) The Physics of Foam. Clarendon Press, Oxford. [2] K. Brakke (1992) The Surface Evolver. Exp. Math. 1. 141. [3] S.J. Cox, B. Dollet and F. Graner (2006) Foam flow around an obstacle: simulations of obstacle-wall interaction. Rheol. Acta. 45, 403. [4] I.T. Davies and S.J. Cox (2010) Sedimentation of an elliptical object in a two-dimensional foam. J. Non-Newt. Fl. Mech. (in press).

Wednesday Afternoon

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Wednesday 1:30 Sweeney A SC33

Dynamic simulation of fiber suspensions

Prakorn Kittipoomwong[1], Ahmad Jabbarzadeh[2], and Howard See[1]

[1]School of Chemical and Biomolecular Engineering, University of Sydney, New South Wales 2006, Australia; [2]School of Aerospace, Mechanical and Mechatronic Engineering, University of Sydney, New South Wales 2006, Australia

Paricle-level simulation is employed to investigate the rheological behavior of fiber suspensions. Each fiber is modeled as a three-dimensional cluster of neutrally-buoyant spheres connected by harmonic springs. Rotne-Prager level description is employed to represent far-field hydrodynamic interactions. Rheological properties and the corresponding particle orientation distribution of straight and curved fiber suspensions are examined. Shear viscosity as a function of concentration is founded to be in a good agreement with comparable literature results. Semi-rigid fiber suspensions exhibit larger shear viscosity than that of equivalent stiff fiber suspensions.

Wednesday 1:55 Sweeney A SC34

Fiber orientation for suspensions of long fibers: Comparison of rigid and flexible models

Cong Zhang and David A. Jack

Mechanical Engineering, Baylor University, Waco, TX 76798, United States

The field of short-fiber dense suspensions has been extensively studied for several decades, but there has been little work until of late on the field of long-fiber suspensions. Existing short-fiber models are quite proficient at capturing the orientation effects due to processing conditions for rigid fibers, and it would be of industrial benefit to have similar models available for long-fiber systems. Of particular interest is understanding the limitations of classical rigid suspension models for flexible suspensions, and where the classical models can continue to be applied in long-fiber systems. Recent work in flexible fiber suspension kinematics has focused on a series of models which represent the motion of a single fiber as a series of connected beads or a series of rigid rods in series with torque transferring hinges between them. This work employs the rod-chain model of Wang et al. (2006) to study the motion of discrete flexible fibers. The present work validates the rod-chain model in the limiting case of a stiff fiber with that of the Jeffery model for a rigid fiber, and then studies the change in the expected period as a function of reduced fiber stiffness. Results are presented for both individual fibers and a stochastic distribution of fibers to study the variations in the transient effects between the rigid and the flexible fiber systems. Results demonstrate that the observed period increases as the fiber flexure increases, and provides insight into the modifications required for the orientation distribution function of flexible suspensions. To demonstrate the importance in studying the alterations in the transient effects on a processed part, a study of the cured composite stiffness is presented for the flexible fiber system using the micro-mechanical approach of Hsiao and Daniel (1996) and compared to that of the rigid fiber micromechanical approach discussed by Jack and Smith (2008).

Wednesday 2:20 Sweeney A SC35

Fiber orientation and stiffness predictions for thin geometries using the Fast Exact Closure

Babatunde Agboola and David A. Jack

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The Folgar-Tucker and the Phelps-Tucker diffusion models for predicting the orientation of short fibers in a polymer suspension has received considerable attention in recent years. Industrial implementations of these models suffer a significant setback due to the fact that the computationally efficient orientation tensor equations of change of the second-order moments requires the fourth-order moments. This has lead to extensive studies on closures for approximating the fourth-order tensor, and of particular note are the accurate orthotropic closures. These orthotropic closures require some form of curve fitting in the formation of the closure, with data coming from select orientation states or from flow simulations of the computationally inefficient full orientation distribution function. A novel approach was recently published by Montgomery et al. (2010) where the authors developed an analytic form to solve the equation for change of the second order orientation tensor called the Fast Exact Closure. This closure does not require the use of curve fitting techniques, and in the limiting case of no diffusion the method exactly solves the Jeffery's equation. In the present work, we demonstrate this new closure is exceptionally accurate in predicting the orientation state with results similar to that of the ORT closure obtained through a curve fitting approach. Industrial simulations are provided to present the resulting material stiffness expectation of thin parts, both locally and of the bulk part, from implementations with the new closure. Results are compared to those obtained from existing closures and from solutions obtained from the method of spherical harmonics, which are considered to be numerically accurate.

Wednesday 2:45 Sweeney A SC36

Rheology and flow characteristics of cellulose suspensions using magnetic resonance imaging

Emilio J. Tozzi[1], David M. Lavenson[1], Anna Sverdberg[2], Michael J. McCarthy[3], and Robert L. Powell[1]
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Efficient operation of biomass processes and pulp and paper applications require realistic data on the flow characteristics of cellulosic slurries in pipes. Cellulosic suspensions have a complex rheology that varies with flow rate, fiber properties and concentrations. Of particular interest is the determination of the viscosity - shear rate relation which can be found from simultaneous measurement of velocity profile and pressure drop. Such information is also useful in validating numerical or analytical models of fiber suspension flow. A previous study of velocity profiles in complex fiber suspensions measured with magnetic resonance imaging showed that profiles can be asymmetric at certain combinations of flow rates, concentrations and fiber lengths. In this work we use magnetic resonance imaging to measure velocity profiles of fiber suspensions across a range of concentrations and flow rates in which velocity profiles are symmetric, which facilitates characterization using rheological models, such as generalized Newtonian models. The intensity profile of MR signal, an indicator of velocity fluctuations, exhibited noticeable changes as flow transitioned from laminar to turbulent. Also measured was the influence of adding polymers to flowing fiber suspensions on velocity profiles, signal intensity, and pressure drop.

Wednesday 3:35 Sweeney A SC37

Orientation, microstructure and rheology in sheared suspensions of anisotropic dicolloidal particles

Amit Kumar[1] and Jonathan Higdon[2]
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The orientation, microstructure and rheology in non-Brownian shear flow was studied for suspensions of dicolloidal particles using a novel PME Stokesian Dynamics algorithm for anisotropic particles. Four different particle shapes were studied with dicolloids modelled as the union of two intersecting spheres. Dynamic simulations were conducted for periodic systems of 1000 particles for volume fractions $\phi = 0.05$ to 0.55. The suspension microstructure was disordered for all particle shapes at $0 < \phi < 0.5$, with some systems showing ordered microstructure at $\phi = 0.55$. The viscosity in the disordered state was similar for all particle shapes at equal volume fraction. Negative first and second normal stress differences were found for $\phi < 0.5$, but positive values were observed for certain ordered systems at $\phi = 0.55$. Complex orientation behavior was observed as a function of volume fraction and particle shape. All particles showed an orientation shift towards the vorticity axis for $\phi > 0.1$. Certain shapes showed a shift away from the vorticity axis for $\phi < 0.1$. The high ϕ orientation dynamics were consistent with predictions based on the mobility tensor $M^{\omega S}$ relating the angular velocity to particle stresslet. The orientation dynamics were dominated by the second normal stress differences. The shift away from the vorticity axis for small ϕ was induced by migration away from orientations with large orientation fluctuations.

Wednesday 4:00 Sweeney A SC38

Rheology and mass transport of biomass slurries by fiber-level simulation

Jianghui Wang and Daniel J. Klingenberg
Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, United States

Biomass has been considered as a promising alternative sustainable fuel source. To lower capital and operating costs and increase the economic viability of biofuels, the conversion processes need to be conducted at high solids concentration. However, high solids concentrations result in large yield stresses which create challenges for mixing, heating, and transporting the biomass.

Rheological and mass transport properties of biomass slurries at high fiber concentration were studied by fiber-level simulations. The specific viscosity of the suspensions increases with increasing fiber curvature, stiffness, friction between mechanical contacts, and solids concentration. The specific viscosity increases linearly with concentration in the dilute regime, increases with the cube of the concentration in the semi-dilute regime, and approaches a plateau at high concentrations. Concentrated fiber suspensions are highly viscous, and exhibit significant yield stresses. Yield stresses scale with volume concentration and fiber aspect ratio in the same way as that observed in experiments.

Shear-induced diffusion in simple shear flow for suspensions of both spheres and fibers was also studied. Two different models for the fibers were employed: one in which each fiber consisted of a flexible series of linked rigid cylinders, and another in which each fiber consisted of a rigid chain of hard spheres. The scaled diffusivity ($D/a^2\dot{\gamma}$, where D is the diffusivity matrix, a is radius, and $\dot{\gamma}$ is shear rate) increases for both kinds of suspensions as particle concentration or friction is increased, and the scaled diffusivity ($D/n\dot{\gamma}\,l^5$, where n is number density and l is fiber half length) decreases as the fiber aspect ratio is increased. The rheological properties and shear-induced diffusion in fiber suspensions are controlled by mechanical contacts between fibers, and thus depend on the suspension microstructure.

Wednesday 4:25 Sweeney A SC39

Dissipative particle dynamics modeling of blood suspensions with multiscale and low-dimensional models of red blood cells

Bruce Caswell[1], Wenxiao Pan[2], Dmitry Fedosov[2], and George E. Karniadakis[2]
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We have employed Dissipative Particle Dynamics (DPD) in a multiscale model (MS-RBC) of healthy and of malaria-infected red blood cells. This model captures the experimental mechanical behavior of single RBCs in a variety of static and dynamic tests. In a parallel development, a new low-dimensional model of the red blood cell (LD-RBC) has been tested against the MS-RBC model. The MS-RBC model represents the cell membrane with hundreds or even thousands of DPD-particles connected by springs into a triangular network in combination with out-of-plane elastic bending resistance. In contrast, the low-dimensional model (LD-RBC) is constructed as a closed torus-like ring of only 10 large hard DPD-particles previously employed to represent colloidal particles. These are connected by worm-like chain springs combined with bending resistance. The LD-RBC model can represent the force-extension data of real RBCs over the entire range of measured cell deformations for healthy and for malaria infected RBCs. Except for channel sizes comparable to RBC diameters, suspensions of LD-RBCs also capture the essential hydrodynamics of blood flow in tubes as faithfully as do suspensions of MS-RBCs. In particular, the LD-RBC suspensions are shown to properly capture the experimental data for the apparent viscosity of blood and its cell-free layer in tube flow. Hence simulations with LD-RBC suspensions allow low cost exploration of blood flows over a wide range of hematocrits. This cost advantage relative to MS-RBCs derives form the small number of colloidal particles needed to represent a cell, and from their hardness which obviates checking for cell-cell or cell-solvent penetration. The incorporation of weak-attractive inter-cellular forces in the LD-RBC gives rise to the ‘rouleaux’ structures often observed in blood, and which will be shown to account quantitatively for the high viscosity of blood at low shear rates.

Wednesday 4:50 Sweeney A SC40

Numerical simulations of concentrated, non-colloidal suspensions in Poiseuille flows

Kyongmin Yeo and Martin R. Maxey
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Fully three-dimensional numerical simulations of non-colloidal suspensions in pressure-driven flows between parallel planar walls are performed using the force-coupling method. The numerical simulations are performed for the volume fractions of 30% and 40%. The channel height is varied from 18*a* to 40*a*, where *a* is the particle radius, representative of micro-channel devices. It is shown that the particle concentration profiles, with peak values near the centerline, agree well with the previous experimental results except very near the wall where a monolayer of trapped particles may form. The particle stresses and the suspension micro-structures are investigated as functions of the distance from the wall.

Symposium MS
Polymer Rheology: Melts, Solutions and Blends

Organizers: Shi-Qing Wang and Marie-Claude Heuzey

Wednesday 1:30 Sweeney B MS28

Compliance issues with rheometers*

Wei Zheng, Gregory B. McKenna, and Sindee L. Simon
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Instrument compliance is known to be an important issue in experimental rheological measurements. Without minimizing the instrument compliance or correcting it afterwards, the obtained moduli as well as their frequency or temperature dependence can be inaccurate. Anton Paar claims to have corrected the instrument compliance for their dynamic data. However, based on the outputs, we cannot reproduce their results. We found problems in their data correction. The problem with Anton Paar’s compliance correction is described in detail. Here we report results from measurements of the dynamic shear moduli of poly(alpha-methyl styrene) and its oligomer and show how to correct the data from the Anton Paar instrument using a method built upon previous studies [1,2]. Additionally, recommendations for a proper measurement procedure with this instrument are also suggested.

1. Schröter K., S. A. Hutcheson, X. Shi, A. Mandanici, and G. B. McKenna, “Dynamic shear modulus of glycerol: Corrections due to instrument compliance,” J. Chem. Phys. 125, 214507-1- 214507-4 (2006). 2. Hutcheson S. A., and G. B. McKenna, “The measurement of mechanical properties of glycerol, m-toluidine, and sucrose benzoate under consideration of corrected rheometer compliance: An in-depth study and review,” J. Chem. Phys. 129, 074502-1-072402-14 (2008).

* The title of this submission has been modified to remove the name of a commercial product or company to bring the title into compliance with SOR policy.

Wednesday 1:55 Sweeney B MS29

Assumed periodicity and dynamic shear stress transduction in rheometry

Chanyut Kolitawong[1], A. Jeffrey Giacomin[2], and Leann M. Johnson[3]
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In viscoelastic property measurements, material is subjected to time unsteady deformations using a rheometer. In step shear strain experiments, for example, the shear strain suddenly jumps to a steady value. In this paper, we develop a method to study the dynamic response of a shear stress transducer in a sliding plate rheometer for any time unsteady rheological test. This general method is developed by first considering a special case of step shear strain for a fluid sample with material ingress in the annular transducer gap. Both the fluid sample and its ingress obey the generalized Maxwell model. Our main mathematical trick is assumed periodicity where a single step in shear strain is treated as the first step in a reciprocating square wave. After solving the problem in the frequency domain, we recover our single step by taking the limit as the period goes to infinity. The transducer eccentricity following step shear is then determined analytically by solving the force balance on the transducer active face using bipolar cylindrical coordinates. Dimensionless graphs are provided for estimating transducer dynamic response in step shear strain. Finally, a worked example illustrates the application of these results.

Wednesday 2:20 Sweeney B MS30

Rod climbing revisited

John M. Dealy and Phuong Vu
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The tendency of the surface of a pool of viscoelastic liquids to rise up near a rotating rod (often called the "Weissenberg effect") is often used to demonstrate the presence of normal stress differences in such materials. These demonstrations, and nearly all published reports of this phenomenon, involve polymer solutions at room temperature. In high-viscosity molten polymers, there is a very long starting transient, and in some cases no steady state is reached. Sequences of photos reveal this curious behavior as exhibited by several molten polyethylenes.

Wednesday 2:45 Sweeney B MS31

Polymer solutions in co-rotating Taylor-Couette flow without vorticity

Christian Wagner and Andreas Zell
Technische Physik, Saarland University, Saarbrücken, Saarland, Germany

We present experimental results of the flow of dilute and semi-dilute polymer solutions in co-rotating Taylor-Couette cylinders. The experimental setup consists of a modified Mars II rheometer (Thermo Scientific) with two drive units that are mounted opposite of each other. The rotational velocities of the inner and outer cylinder are chosen in a way such that the flow is free of vorticity. This flow is similar to a so called elongational flow. Typically, polymer solutions are strongly affected by elongational flow in which elastic stresses build up that can be orders of magnitudes larger than shear stresses in shear flow. In our setup, the direction of elongation is not constant but rotates with the flow. This is in contrast to plane shear flow which consists of both an elongational and a rotational part, with the direction of elongation being constant. Our PIV (particle imaging velocimetry) measurements show that for polymer solutions without shear thinning the flow is indeed free of vorticity and is equal to a stagnation point flow at a given position and a given instant in time. On the contrary, torque measurements reveal that the stresses are identical to the stresses that are present in a plane shear flow. Thus, we find that for polymer solutions a flow with vorticity and a constant direction of elongation is equal to a flow without vorticity in which the direction of elongation is rotating. Finally, we show that for shear thinning solutions the flow velocity becomes non-monotonous over the gap and reminds of a plug like profile which is known from the Poiseuille flow.

Acknowldegment: We thank J. Nijman, Thermo Scientific

Wednesday 3:35 Sweeney B MS32

Comparison of stress-controlled rheometer and strain-controlled rheometer for large amplitude oscillatory shear

Mirin Lee[1], Jung-Eun Bae[1], Hoon Cheol Jeon[1], Kwang Soo Cho[1], and Ki-Won Song[2]
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We tested LAOS of PEO solutions with sufficient entanglements by use of two kinds of rotational rheometer: stress-controlled and strain-controlled. The LAOS data from both rheometers can be analyzed by stress decomposition for strain-controlled rheometer and strain decomposition for stress controlled one. Strain decomposition is to decompose the strain measured from stress-controlled rheometer into elastic and viscous parts which is based on the same concept of stress decomposition. Although LAOS data from strain-controlled rheometer satisfy strain-frequency superposition by , those from stress-controlled rheometer show different behavior. We defined nonlinear version of dynamic compliances and compared them with nonlinear version of dynamic moduli.

Wednesday 4:00 Sweeney B MS33

Secondary loops in Large Amplitude Oscillatory Shear (LAOS) - a general physical interpretation

Randy H. Ewoldt[1] and Gareth H. McKinley[2]

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When the shear stress response to Large Amplitude Oscillatory Shear (LAOS) deformation is represented as a two-dimensional Lissajous-Bowditch curve, the corresponding trajectory can appear to self-intersect and form secondary loops. These secondary loops are a visually-prominent feature that quickly draws questions from the rheological observer. The interpretation of secondary loops has, to date, been limited to the study of specific material examples, being related to different microstructural features such as non-affine deformation and the absence of long-chain branching in polymer melts. However, secondary loops are more general than these explanations because the phenomenon has been observed for a variety of nonlinear constitutive models and material systems including micellar solutions, a polystyrene solution, several molten polymers, star-polymer networks, xanthan gum solutions, and an invert-emulsion drilling fluid. Owing to the variety of systems which show secondary loops in LAOS, we seek to provide a more general interpretation of this distinct rheological signature. We derive the mathematical criteria for the formation of secondary loops and furthermore suggest a qualitative physical understanding for the associated nonlinear material behavior. We show that when secondary loops appear in the viscous projection of the stress response (the 2-D plot of stress vs. strain-rate) they are best interpreted by understanding the corresponding elastic response (the 2-D projection of stress vs. strain). The analysis shows clearly that sufficiently strong elastic nonlinearity is required to observe secondary loops on the conjugate viscous projection. Such a strong elastic nonlinearity physically corresponds to a nonlinear viscoelastic shear stress overshoot in which existing stress is unloaded more quickly than new deformation is accumulated. This can be achieved by a variety of molecular- and micro-structures, such as polymer solutions, polymer melts, soft glassy materials and other structured fluids.

Wednesday 4:25 Sweeney B MS34

A mean-field anisotropic diffusion model for unentangled polymeric liquids and semi-dilute solutions

Jun M. Kim[1], Brian J. Edwards[1], Bamin Khomami[1], and Pavlos Stephanou[2]

[1]Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, United States; [2]Chemical Engineering, University of Patras, Patras, Greece

A mesoscopic model is proposed and compared with nonequilibrium molecular dynamics atomistic simulations of short-chain polyethylene liquids and experiments of semi-dilute DNA solutions under shear. Rheological and microstructural properties were examined to test the validity of the model. In addition, this model was further coarse-grained to the continuum level through pre-averaging, and was also compared with the simulation and experimental data to examine the relationships between different levels of description. Neighboring chains are modeled as a mean field in terms of an anisotropic diffusion matrix, which represents enhanced diffusion along the chain background once a significant degree of molecular extension and orientation has developed in response to an applied flow field. Brownian dynamics (BD) simulations of this coarse-grained model displayed remarkable quantitative agreement with NEMD simulations of dense liquids and experiments of semi-dilute DNA solutions for system properties with a single adjustable parameter representing the magnitude of diffusive enhancement along the chain backbone. The BD simulations revealed the dependence of system response on the chain stretching at low values of Weissenberg number (Wi) and on the rotational motion of individual chains induced by shear flow at high values of Wi, similarly to the NEMD simulation data. The continuum model matched the mesoscopic model at low shear rates, but greatly diverged at high values of Wi where tumbling dynamics of the individual chains dominated the system response. This provides direct evidence that the onset of rotational motion under shear in these liquids is directly responsible for the well-known breakdown in pre-averaged constitutive equations at the continuum level of description. Furthermore, a possible explanation of the shear stress plateau at intermediate ranges of shear rate is offered for experimental data of semi-dilute solutions, wherein this phenomenon occurs with the onset of chain rotation within these fluids.

Wednesday 4:50 Sweeney B MS35

Direct observation of flexible polymer chain relaxation and dynamics using ssDNA

Christopher Brockman, Sun Ju Kim, Folarin Latinwo, and Charles M. Schroeder

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In this work, we introduce a new experimental system for single molecule investigation of flexible polymer chains based on single stranded DNA (ssDNA). Traditional experimental techniques including “bulk” viscometry and light scattering measurements have revealed a wealth of information regarding polymer dynamics. Single molecule tools allow for the direct observation of polymer backbone dynamics, thereby enabling characterization of real-time dynamic information and distributions in molecular behavior, including “molecular individualism”. However, the vast majority of single molecule polymer studies has focused on double stranded DNA (dsDNA), a semi-flexible polymer. Here, we present a generalized platform for biochemical synthesis of long ssDNA of arbitrary sequence with concomitant labeling of the polymer backbone with a fluorescent dye, which serves as a new model system for molecular studies of flexible polymer chains. The bare persistence length of ssDNA ($l \approx 0.6$ nm) is similar to synthetic flexible polymer molecules such as polystyrene ($l \approx 0.7$ nm), whereas dsDNA exhibits a large persistence length ($l \approx 53$ nm) due to the structural rigidity of the double helix. Using the new experimental system for ssDNA, we present results from an initial set of dynamical studies, including polymer chain relaxation from high stretch. In addition to fluorescence measurements of polymer chain dynamics, we are currently measuring the force-extension relation of single polymer chains using magnetic tweezers and bifocal imaging with an inverted microscope. Finally, we present Brownian dynamics simulations to model ssDNA dynamics in order to predict

dynamic behaviors, such as polymer relaxation, under varying solvent conditions. Using computational and experimental tools, we seek to elucidate the fundamental dynamical differences between "real" and "ideal" polymer chains and explore the impact of enhanced chain flexibility on dynamical phenomena.

Symposium NM
Nano- and Micro-Rheology: Indentation and Beyond

Organizers: Mark VanLandingham and Hongbing Lu

Wednesday 1:30 Coronado/DeVargas NM6

Nano adhesion and indentation

Kenneth M. Liechti

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Adhesion and friction at small scales have become increasingly important with the advent of MEMS and NEMS devices. The characterization of surface adhesion is particularly challenging because of potential interactions between the measuring device and the quantity being measured. In classical tension testing, such interactions are well understood and avoided by conducting the experiments in displacement control. The situation is more complex when measuring adhesive interactions because there are situations where even displacement control will not always be able to avoid instabilities or snaps. That said, there are surprisingly few nano indentation devices that are capable of running even in displacement control. One such device is the interfacial force microscope (IFM) invented by Houston at Sandia National Laboratories in the early 1990's. This paper will review some of the interactions that have been examined with the IFM. Many of the early experiments were qualitative in the sense that interaction forces were compared and ranked. The remainder of the paper will focus on combining IFM data with molecular and continuum analyses to extract the mechanical and adhesive behavior of self-assembled monolayers on silicon and monolayers of ice-like water on mica.

Wednesday 1:55 Coronado/DeVargas NM7

Geometrically-controlled mechanomutability

Lin Han[1], Lifeng Wang[2], Khek-Khiang Chia[3], Robert E. Cohen[3], Michael F. Rubner[1], Mary C. Boyce[2], and Christine Ortiz[1]

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In recent decades, there has been extensive work carried out on stimulus-responsive materials that undergo actuation, swelling, variable wettability, etc. However, the design of "mechanomutable" materials, which undergo on-demand changes in mechanical behavior and properties, is still in the early stage. In this study, geometrically-anisotropic microstructures were fabricated from mechanomutable polyelectrolyte multilayers (PEMs) and new emergent mechanical phenomena were explored due to the coupling between "inherent" responsive material properties and morphometry (shape). The model material chosen was a PEM of poly(allyamine hydrochloride) (PAH) and poly(acrylic acid) (PAA), which undergoes reversible pH-responsive transition from a condensed, ionically crosslinked state (pH 5.5) to a swollen, ionized state (pH 2.0). End-attached PAA/PAH planar films and "tube forests" were prepared using layer-by-layer assembly in conjunction with a templating approach. AFM-based nanomechanical experiments and microstructurally-based finite element analysis (FEA) demonstrated mechanomutability of both the planar films and tube forests in indentation over a range of indentation depth rates (0.1 - 10 µm/s), in force relaxation, in nanoscale dynamic oscillatory loading, and in shear. The tube forests exhibited an order-of-magnitude increase in effective indentation stiffness with pH due to a transition from multiaxial compression (pH 2.0, E*~ 60 kPa) to the addition of bending/buckling deformation modes (pH 5.5, E*~ 2 MPa). Parametric FEA studies of the tube forest geometry (dimensions and inter-tube spacing) revealed that mechanomutability could be tuned over 3-4 orders of magnitude.

Wednesday 2:20 Coronado/DeVargas NM8

Characterizing rheological response of soft matter at small length scales

Mark VanLandingham[1], Kenneth E. Strawhecker[1], Z. Ilke Kalcioglu[2], Meng Qu[2], Krystyn J. Van Vliet[2], Quinn McAllister[3], and John W. Gillespie[3]

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Contact mechanics based techniques continue to find applications and to grow in interest within the polymeric and biological materials communities. For example, for both highly mineralized (stiff) and highly compliant biological materials, nanoindentation techniques (instrumented indentation and AFM) have been used to explore local mechanical properties and behavior associated with the complex structures. In the medical field, contact probe techniques are relatively easy to implement to study both stiff and compliant tissue, including in vitro and in vivo measurements. In other cases, application-relevant conditions involve contact between asperities or particles and a polymer surface, which can be modeled using instrumented indenters and/or AFM probes. Examples include protective polymer coatings and next-generation ballistic fabrics. In this research, instrumented nanoindentation and AFM-based indentation techniques are being used to study a variety of polymer materials, including polymer gels, glassy amorphous polymers, and polymer fibers, as well as soft tissues. Techniques currently being evaluated include analogues to traditional solid rheological methods, such as stress relaxation, creep, and dynamic mechanical measurements, as well as indentation impact, contact resonance and band excitation methods. Topics to be discussed include abilities of these techniques for probing linear and non-linear viscoelastic behavior in a quantitative fashion (effects of tip shape, tip-sample adhesion, etc.) and for studying energy dissipation at small length scales.

Wednesday 2:45 Coronado/DeVargas NM9

Monitoring of glass transition at a polymer surface by localized surface plasmon resonance

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The present work investigates glass transition on a polymer surface by Teichroeb and Forrest's (2003) technique of embedding gold nanoparticles (AuNP). However, instead of atomic force microscopy, localized surface plasmon resonance (LSPR) of the AuNP is exploited as the probe. The impregnation of AuNP into the polymer causes a spectral shift in the LSPR due to the changing dielectric environment surrounding nanoparticles. LSPR is sensitive to the close vicinity of the nanoparticles within a few nm from the nanoparticle surface. Therefore, the diffraction limit of light can be beaten by orders of magnitude and impregnation of AuNP into the polymer can be monitored to a spatial resolution down to a nm. AuNP, at an average size of 8 nm, were synthesized on poly isobutyl methacrylate (PiBMA) films on glass by physical vapor deposition. Subsequently, time series LSPR spectra of AuNP on PiBMA were acquired in transmission mode in a temperature controlled optical cell using a CCD spectrophotometer. The forced convective heating of the sample by Ar gas through the optical cell enables rapid stabilization of the temperature in few seconds. The temperature was measured at the sample surface by a K-type thermocouple. The effective dielectric constant surrounding the AuNP was calculated from LSPR optical extinction peak. Depth and velocity of penetration of AuNP were derived from the measured dielectric constant on the basis of dielectric mixing. Two types of measurements were conducted. First, the temperature was gradually increased from 25 to 70 C at 5 C increments maintaining the sample at each temperature for 10 min. The onset of AuNP penetration was found to be at 45 C, which is 10 C below the reported glass transition of PiBMA. Second, time series spectra were recorded at temperatures of 45, 55, 60, and 65 C until saturation of the LSPR signal (i.e., end of penetration of AuNP). The penetration velocity was found to be fairly constant in time while temperature activated at an energy of 0.05 eV.

Wednesday 3:35 Coronado/DeVargas NM10

Rheology of ultrathin polymer films

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A nano-bubble inflation technique developed in our lab[1], has been used to determine the absolute creep compliance of nanometer thin polymer films. Previous results have shown two distinct effects of the reduction in thickness. For polystyrene, there is a reduction in the glass transition temperature as the thickness is reduced below approximately 80nm with the T_g of the thinnest film (~11nm) being ~50°C below the bulk. Interestingly, poly (vinyl acetate) shows no such reduction down to ~23nm. However, both materials show a dramatic stiffening of the rubbery plateau creep compliance, with the compliance scaling as approximately the square of the film thickness. We present here new results on the behavior of polycarbonate at the nanoscale. As with the previous materials, the stiffness increases with a reduction in thickness and scales again as approximately the square of the thickness. The T_g reductions in polycarbonate are considerably larger than those seen in the polystyrene at a comparable thickness. For the polycarbonate we have performed experiments on films as thin as 3nm, for which the T_g reduction is greater than 100°C. We also show data suggesting the polycarbonate reaches the terminal flow regime. This occurs at room temperature for the 3nm film and at ~T_g+20°C for a 9.1nm film.

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

Wednesday 4:00 Coronado/DeVargas NM11

Quantifying microstructure heterogeneity with particle tracking

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Whether you are manufacturing multi-ingredient suspensions on the industrial scale or designing model biological systems in the laboratory, controlling the scale and uniformity of the sample's rheology is necessary. In order to enable predictive and inferential assessments of a complex fluid's mechanical properties, the underlying structure has to be quantified. Multi-Particle Tracking Microrheology (MPTM) has emerged as uniquely capable for quantifying the local mechanical properties within heterogeneous microstructures; because of this, it has been extensively used to provide measures of rheological heterogeneity of diverse mixtures from idealized biological cells, microgel dispersions and sol-gels, to foodstuffs. However, current metrics of heterogeneity only quantify how non-Brownian the tracers are diffusing, not how closely particle diffusion matches an expected model for any inhomogeneous colloidal state; and there is a focus on particle mobility without regard to the spatial distribution of microstructure imparted or triggered during sample making (formulation, mixing). This talk reviews methods to quantify rheological heterogeneity from MPTM data. We then promote shifting the focus of heterogeneous measures toward being relative to specific

colloidal states rather than Brownian motion. To spur this change, we draw from Single Particle Tracking (SPT) literature to identify probability distributions that characterize cage-jumping reflective of jamming transitions, and we overview chemical engineering and stereological measures that can be reapplied to quantify mixing homogeneity.

Wednesday 4:25 Coronado/DeVargas NM12

MEMS parallel-plate rheometer for oscillatory shear micro-rheology measurements

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There is a growing need to understand the effects of confinement on a variety of complex fluids ranging from novel laboratory formulations to biomaterials. These materials are often found in applications with flow in confined geometries including microfluidics, thin film coatings, cellular cytoskeletons, or blood vessels. Confinement will deform the micro structure of these complex materials, possibly altering their rheology and limiting their functionality. There is especially a need to study the rheology of biomaterials at physiologically relevant confinement to better understand their physiological function. Furthermore, characterization of these materials is often difficult due to the small sample volumes available, which has led to the development of “micro rheology” techniques. A current gap in micro-rheology techniques is the ability to examine the effects of confinement on micro-structure while evaluating both elastic and viscous properties.

We present a MEMS parallel plate rheometer for micro-rheology that confines viscoelastic materials to length scales on the O(1) um while probing the entire material response to dynamic oscillatory shear. The MEMS Parallel Plate rheometer uses a 1mm square nano positioner stage to apply a controlled sinusoidal strain. Storage and loss moduli ranging from 50 Pa to 20,000 Pa can be measured at frequencies ranging from 1 to 1000 Hz. Samples are confined by attaching a transparent cover plate to micro posts fabricated on the device. Because the strain is applied to the entire fluid body, this device examines the effects of confinement on the entire micro structure. Using this device, we present results from viscous and viscoelastic standard reference materials to confirm its accuracy. Based on analysis of device dynamics and results from standard materials, the MEMS rheometer is ideally suited for characterizing the rheology of confined biomaterials.

Wednesday 4:50 Coronado/DeVargas NM13

Characterization of temporal and spatial gradients in the viscosity of liquid applied coatings

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The viscosity of liquid-applied coatings changes during drying or curing, eventually forming a solid layer on a substrate. Additionally spatial gradients, particularly through the coating thickness, can develop during the solidification process. These temporal and spatial variations in the coating viscosity may lead to coating defects, such as surface texture, dripping defects and wrinkles. If the viscosity increase with time is too fast then the coating may not level well, resulting in surface texture; however, too slow an increase in coatings on vertical surfaces can cause ‘sag’ or drips. Further, locally high rates of evaporation of solvent or chemical reaction at the coating surface can lead to a high viscosity ‘skin’. Skinning has been linked to defects such as surface textures and wrinkles as well as inefficient drying processes. Magnetic microrheometry is used to characterize the local viscosity of coatings (through the coating thickness) since it is nondestructive, and can quantify viscosity change during solidification process. The coating viscosity is determined by tracking magnetic probe particle trajectories as a function of solidification time and position within coatings. The time-viscosity profiles of poly(vinyl alcohol) coatings are characterized at different drying temperatures (27~90^{o}C), and then the profiles are used to understand the interplay between sagging and leveling on the final coating surfaces. The spatial gradients of viscosity during drying and curing coatings are also investigated and the data used to develop relationships between the process conditions, coating chemistry and skin thickness. The effect of particle position relative to the coating substrate or free surface on the velocity is also studied; correction factors are used and conditions necessary to avoid the surface effects defined. The results are used to develop ‘process windows’ for controlling those surface irregularities of coatings.

Symposium GM
Rheology and Flow of Glass-like Materials

Organizers: Grigori Medvedev and Leon Govaert

Wednesday 1:30 Peralta/Lamy GM24

Dynamics of a colloidal glass during stress-mediated structural arrest

Ajay S. Negi and Chinedum O. Osuji
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Aging at rest in sufficiently dense colloidal suspensions following the cessation of shear flow leads to the formation of a solid-like material (G' > G") from an initially fluid state. Here, we use parallel superposition rheology to study the dynamic rheological properties of a glassy colloidal system during this structural arrest transition, as a function of the stress imposed on the system. A small oscillatory probe stress, σ_p is superposed on a time-invariant background or mean-field stress, σ_m and is used to sample the linear properties of the system in the presence of background stresses of varying magnitudes. Over a range of intermediate σ_m, time evolution of G' and G" show that the loss modulus exceeds the storage modulus at short times and exhibits a crossover at longer times as the system ages. The crossover is concurrent with a peak in G" and occurs at a characteristic timescale, the arrest time, which displays a VFT-like dependence on σ_m. Strikingly, the width of the peak in the time evolution of the loss modulus is strongly dependent on the background stress, exhibiting significant narrowing with increasing stress. These observations demonstrate the thermalizing effect of shear stress in glassy suspensions, here in the context of vitrification, rather than relaxation. Further, they show that structural arrest in these systems occurs with a unique dynamical display.

Wednesday 1:55 Peralta/Lamy GM25

Rheological fingerprinting of an aging soft colloidal glass

Brian M. Erwin[1], Dimitris Vlassopoulos[2], and Michel Cloitre[3]
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Highly concentrated solutions of multiarm star polymers exhibit unique history-dependent phenomena that are not observed in other colloidal or polymeric glasses but appear to be generic in hairy particle suspensions. Aging proceeds according to a unique scenario where the rejuvenated material solidifies after an inception time during which it remains a viscoelastic liquid [1]. The aged material separates at low shear rates into a solid and a shear-thinned band which coexist [2]. We investigate this complex flow behavior using linear and nonlinear rheology, and dynamic light scattering. The results are integrated into a generic state diagram which specifies the states of the glass for different initial conditions and mechanical histories: viscoelastic liquid and solid, homogeneous shear-thinned solution, and shear-banded material [3]. Aging can be interpreted as kinetic pathways through the state diagram. Shear-banding appears to be an intrinsic mechanical instability which occurs when the solid state of the glass is shear-melted. This approach provides a straightforward methodology to fingerprint the material behavior of soft glassy materials undergoing rheological transitions which can be used as predictive tool to design systems with a desired rheological response.

[1] C. Christopoulou, G. Petekidis, B. M. Erwin, M. Cloitre & D. Vlassopoulos, Phil. Trans. Royal Soc. London A, 367 5051-5071, 2009. [2] S. A. Rogers, D. Vlassopoulos, P. T. Callaghan, Phys. Rev. Lett. 100, 128304 (2008). [3] B. M. Erwin, D. Vlassopoulos & M. Cloitre, J. Rheol (2010).

Wednesday 2:20 Peralta/Lamy GM26

Time resolved viscoelastic properties during structural arrest and aging of a colloidal glass

Chinedum O. Osuji and Ajay S. Negi
Department of Chemical Engineering, Yale University, New Haven, CT 06511, United States

Evolution of the energy landscape during physical aging of glassy materials can be understood from the frequency and strain dependence of the shear modulus but the non-stationary nature of these systems frustrates investigation of their instantaneous underlying properties. Using a series of time dependent measurements we systematically reconstruct the frequency and strain dependence as a function of age for a repulsive colloidal glass undergoing structural arrest and subsequent aging. In this manner, we are able to unambiguously observe the structural relaxation time, which increases exponentially with sample age at short times. The yield stress varies logarithmically with time in the arrested state, consistent with recent simulation results, whereas the yield strain is nearly constant in this regime. Enhanced viscous dissipation during yielding is featured only in the arrested state, with the magnitude of dissipation increasing linearly with sample age. Strikingly, the frequency dependence at fixed times can be rescaled onto a master curve, implying a simple connection between the aging of the system and the change in the frequency dependent modulus.

Wednesday 2:45 Peralta/Lamy GM27

Anomalous aging in a family of ionic liquids near the glass transition temperature

Nabila Shamim and Gregory B. McKenna
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The present work reports the results of a systematic rheological study of the dynamic moduli of 1-butyl 3-methylimidazolium tetrafluoroborate [Bmim][BF_4], 1-butyl 3- methylimidazolium hexafluorophosphate [Bmim][PF_6], and 1-ethyl 3-methylimidazolium ethylsulfate ([Emim][$EtSO_4$]) in the vicinity of their respective glass transition temperatures. The results show an anomalous aging in that the dynamic and the low shear rate viscosities decrease with time at temperatures near to, but above, the glass transition temperature and this is described in detail in the conference. The samples that are aged into equilibrium obey the time temperature superposition principle and the shift factors and the viscosities follow classic super-Arrhenius behaviors with intermediate fragility values as the glass transition is approached. The data also show that these ionic liquids do not follow the Cox-Merz[1] relationship between the steady shear viscosity and the dynamic viscosity. Finally, we note that the use of the van Gurp[2] analysis provides an excellent representation of the time-temperature superposition of the systems and provides a ready means to illustrate the differences in glassy moduli of the three ionic liquids studied.

Reference: [1] Cox, W.P.;Merz, E.H., Correlation of dynamic and steady flow viscosities, J. Polym. Sci. 1958, 28, 619-622. [2] van Gurp, M.;Palmen, J. Time temperature superposition for polymeric blends, Rheol Bull 1998, 67, 5-8.

Symposium GR
General Rheology

Organizers: Jacinta C. Conrad and Jian Wang

Wednesday 3:35 Peralta/Lamy GR1

Double Cross model - a novel way of modeling viscosity curves

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Conventional viscosity models such as the Cross model and the Carreau-Yasuda model do not fit viscosity-shear rate curves very well if the polymer has long chain branching (LCB) or has a bimodal molecular weight distribution. This is because the relaxation behavior of these polymers is more complex than for linear polymers. These polymers often have a fast relaxation mode that is caused by the relaxation of the chain end of a LCB polymer or from the low molecular weight component of a bimodal polymer. In addition, they have a distinctly longer relaxation mode caused by the presence of LCB or a high molecular weight component in the polymer. It was found through this study that a double Cross model, which is simply the summation of two Cross models, not only fits the entire viscosity-shear rate curves of these polymers very well, but it also predicts the zero-shear rate viscosity in agreement with the actual measured value from a creep test. In addition, the ratio of the two characteristic relaxation times can provide insight into how different the two relaxation modes are in the polymer.

Wednesday 4:00 Peralta/Lamy GR2

Investigations on the molecular origin of anisotropic thermal conduction in polymers

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

Wednesday 4:25 Peralta/Lamy GR3

Solubility study via rheological characterization for pharmaceutical materials

Herman Suwardie
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Hot-melt extrusion (HME) becomes increasingly popular as an important method in drug manufacturing, especially for generic drug category. Rheological characterization will be indispensable prior to hot-melt extrusion process, especially to study about the viscoelasticity of the drug-polymers system. The information of the viscosity as a function of shear rates is very crucial in the scaling-up process. Rheological characterization can also easily determine the solubility of the drug in the polymer system at a certain temperature and drug concentration. Poly(ethylene) oxide is chosen as the polymer or excipient and acetaminophen (APAP) is chosen as the drug or API (Active Pharmaceutical Ingredient). Both dynamic time sweep and dynamic frequency sweep are performed using oscillatory rheometer to measure the dynamic viscosity of the mixture at various temperatures. Dynamic viscosity ratio is defined as the ratio of the dynamic viscosity of mixture of PEO and APAP at certain concentration with the dynamic viscosity of PEO at similar temperature. The dynamic viscosity ratio is plotted against % APAP at various temperatures. PEO-APAP system exhibits a unique trend. PEO-APAP system displays the decreasing trend and then increasing one. The minimum value at a constant temperature is defined as the maximum solubility at that temperature. The prior knowledge of the maximum concentration at a certain processing temperature for HME is paramount to optimize the success in final drug manufacturing. The steady viscosity of selected concentrations before maximum and after maximum solubility at various temperatures is performed employing both oscillatory and capillary rheometer.

Wednesday 4:50 Peralta/Lamy GR4

Linear and nonlinear viscoelastic behavior of $(SIS)_p$ multiblock copolymer solution

Yumi Matsumiya and Hiroshi Watanabe
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A series of symmetric styrene (S) - isoprene (I) - styrene (S) multiblock copolymers of $(SIS)_p$-type (p = 0.5, 1, 2, 3, and 5 corresponds to di-, tri-, penta-, hepta-, and undecablock) was synthesized and their rheological behavior was examined in n-tetradecane (C14), a solvent dissolving the I block and precipitating the S block. The molecular weights of the constituent blocks were almost identical for these copolymers. At 20C, the

$(SIS)_p$/C14 systems with copolymer concentration of 20wt% and 30wt% formed a bcc lattice of glassy, spherical S domains and exhibited the gel-like elasticity. This elasticity was sustained mainly by the bridge-type I blocks connecting the S domains and partly by the loop-type I blocks. The $(SIS)_5$ undecablock system was extensible up to $\lambda = 55$. Origin of this extensibility will be discussed in relation to the structure of the material.

Symposium SA
Self-Assembling, Associative, and Gel-like Systems

Organizers: Ferenc Horkay and Matthew W. Liberatore

Wednesday 1:30 O'Keeffe/Milagro SA19

Exploiting molecular self-assembly to design photorheological fluids

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Complex fluids whose rheological properties can be tuned by external electric or magnetic fields are well-known and widely studied. In comparison, fluids whose rheology can be tuned by light, i.e., photorheological or PR fluids, have only attracted mild attention in the literature. Most studies on this topic have come from chemists who have devised a variety of novel photoresponsive molecules that could serve as the basis for PR fluids. However, for PR fluids to move into the mainstream, it will be necessary to find low-cost routes to making them using simple, commercially available ingredients. This will encourage engineers and physical scientists to study such fluids and devise applications for them, such as to construct valves or sensors within microfluidic devices. In searching for low-cost approaches to PR fluids, our lab has developed a number of new concepts, all using simple molecules or colloidal nanoparticles. This talk will present several recent examples of our work. These include light-induced assembly of surfactants or lipids into long, cylindrical micelles in water or reverse micelles in oil. Another example involves the light-activated assembly of nanoparticles into a physical gel network. The last example involves our recent work demonstrating the light-activated gelling of a biopolymer solution.

Wednesday 1:55 O'Keeffe/Milagro SA20

Mechanical and structural transitions in block copolymer micelle solutions

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Concentrated solutions of a water-soluble block copolymer , $(PEO)_{20}$-$(PPO)_{70}$-$(PEO)_{20}$, exhibits an order-order transition (OOT) between a crystal phase of cubically-packed spherical micelles and a crystal phase of hexagonally-packed cylindrical micelles. This OOT displays a hysteresis dependent on temperature ramp that is observed at both the macroscale through rheology and nanoscale through small angle neutron scattering (SANS). The hysteresis is caused by the persistence of superheated spheres from the cubically-packed spherical micelle phase into a hexagonally-packed cylindrical micelle phase. This appears to be due to the hindered realignment of the spherical micelles during the thermally-induced transformation to cylindrical micelles. The ramifications of this hysteresis on templating particles in these block copolymer solutions will be discussed.

Wednesday 2:20 O'Keeffe/Milagro SA21

Direct observation of flow-concentration coupling in a shear banding fluid

Matthew E. Helgeson[1], Lionel Porcar[2], Carlos Lopez-Barron[2], and Norman J. Wagner[2]
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We present the first direct evidence of flow-concentration coupling in a shear banding fluid using the first measurements of scanning narrow aperture flow ultra-small angle neutron scattering (SNAFUSANS). Transmission measurements in the flow-gradient shear plane determine the spatial concentration profile of the material. Shear banding in a model fluid comprised of wormlike micelles (WLM) near an equilibrium isotropic-nematic transition is shown to exhibit shear-induced demixing, providing new insight into the non-equilibrium phase behavior of WLMs. The new experimental approach and analysis apply generally to any fluid, and will enable more rigorous testing of theories for shear banding and shear-induced phase separation.

Wednesday 2:45 O'Keeffe/Milagro SA22

Diffusive and geometric effects on pressure-driven flow of wormlike micellar solutions: Boundary layers and stability

Michael Cromer[1], Pamela Cook[1], and Gareth H. McKinley[2]
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Under appropriate conditions wormlike micellar solutions exhibit a shear-banded structure in wall-driven flows such as circular Taylor-Couette flow. We investigate the predictions of the VCM constitutive model (Vasquez, McKinley and Cook (2007)) in pressure-driven flow through a straight channel, and related geometric effects (e.g. micro devices, converging channels), and we compare our predictions with experimental results. The VCM model is a two species, microstructural network model, which incorporates the breakage and reforming of two species of micellar chains (a long chain ‘A’ and a shorter chain ‘B’), developed to describe entangled solutions of wormlike micelles.

The pressure-driven flow velocity profile deviates from the parabolic profile expected for a Newtonian fluid, exhibiting a complex spatial structure, which includes a wall slip layer as well as, above a critical pressure drop, an interior layer connecting shear bands. At this critical pressure drop the flow transitions to a shear-banded flow, and volumetric ‘spurt’ is observed. The interior layer, which connects the shear bands, forms near the walls and evolves in time towards the center of the channel (the width of this layer is governed by the characteristic length scale $(D\lambda)^{1/2}$ where D is the diffusion and λ is the relaxation time). These layers are challenging to resolve numerically, thus an adaptive domain spatial decomposition spectral method is formulated to capture the fine structure of the layers and their temporal evolution. Through asymptotic analysis and numerical simulation the role of diffusion in the model in pressure-driven microchannel flow is investigated. The stability of the solutions to perturbations in the flow direction is examined and contrasted with previous stability results on single species models.

Wednesday 3:35 O’Keeffe/Milagro SA23

Irreversible flow-induced structure transitions in cylindrical micelle solutions

Radhakrishna Sureshkumar[1], Mukund Vasudevan[2], Eric Buse[3], Donglai Lu[4], Amy Shen[4], and Bamin Khomami[5]
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It is well known that certain cylindrical micelle solutions can undergo shear thickening structure transitions when subjected to flow. The flow deformation rate required to impart such transitions is greater than the inverse time scale of the rotational diffusion of the cylinders. However, such transitions are reversible, i.e., upon flow stoppage, the structures disintegrate. We report permanent flow-induced structure transitions in translucent cylindrical micelle solutions. Specifically, when a cylindrical micelle solution (e.g. CTAB, SDS) is strained through a porous medium in a microfluidic channel, spontaneous self-assembly results in the formation of a nanostructured gel phase that persists months after flow stoppage (Vasudevan et al. Nature Materials, 9, 436-441 (2010)). The details of this novel phenomenon and plausible mechanisms will be discussed.

Wednesday 4:00 O’Keeffe/Milagro SA24

Surfactant effect on the rheology and gelation of a model insoluble drug in aqueous HPMC solutions

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In recent years, inclusion of solid particles into a gel matrix is an industrially relevant area for the development of novel drug and nutrient delivery systems. In many of these systems the use of surfactants to stabilize and disperse the solid particles is unavoidable. In our current research efforts, the effect of surfactant net charge and concentration on the gelation temperature and the steady-state rheology of aqueous hydroxypropyl methylcellulose (HPMC) solutions with and without griesofulvin, a model water insoluble drug, have been studied. The evaluated surfactants were the non-ionic lecithin, anionic sodium dodecyl sulfate (SDS), and cationic cetylpyridinium chloride (CPC), all of them below their critical micelle concentration (CMC). Gelation temperature (T_{gel}) was extracted from the crossover of the dynamic moduli measured during a heating ramp from 25 to 75 °C at 0.5 °C/min, a strain of 0.01, and frequency of 1 Hz in a Reologica StressTech HR rheometer with an external temperature controller in a double-gap Couette cell. Steady-state viscosity was measured in a shear rate range from 0.1 to 100 s^{-1} at 25 °C. The viscosity curves of HPMC/SDS solutions show a Newtonian plateau at low shear rates followed by a shear-thinning regime. The viscosity at constant shear rate decreases upon addition of surfactant. Nevertheless at concentrations above ~ 0.6CMC it increases above that for HPMC without surfactant. Gelation temperature above 5mM of SDS increases. However, it drops in the presence of griseofulvin. The viscosity of the solutions with CPC and lecithin with and without griseofulvin also showed a Newtonian plateau followed by shear-thinning. However, the magnitude of the viscosity increases with surfactant concentration. For both of these surfactants, T_{gel} shifts towards higher temperatures. These results will be discussed in terms of molecular interactions between HPMC and surfactants, and adsorption and replacement mechanisms on the surface of griseofulvin.

Wednesday 4:25 O’Keeffe/Milagro SA25

Complex fluid microstructure design, beyond rheological modification

Marco Caggioni, Seth E. Lindberg, and Patrick Spicer
Corporate Engineering Microstructures, Procter and Gamble, West Chester, OH 45069, United States

Mechanical properties of soft materials play a key role in enabling functions of complex biological systems such as cells. Year after year, the investigation of the cell cytoskeleton’s complex rheological properties is unveiling how the combination of different colloidal structures provides a tailored microstructure able to fulfill a variety of requirements over the cell life. The concept of combining the effect of different rheology modifiers to meet specific mechanical requirement is certainly very attractive when developing new complex fluids and also in formulating the new generation of consumer products such as shampoo or liquid detergents. Starting from simple microstructure building blocks such as microgel suspensions, worm like micellar structures, colloidal gels and shear thickening suspensions we show how their combination allow designing fluids with a variety of rheological properties. The fluid’s viscoelastic and flow properties can be described in a microstructure space for which the microstructure building blocks represent part of an “orthogonal” base.

Wednesday 4:50 O'Keeffe/Milagro SA26

Stiffening, fracture, and friction of physically associating solutions

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Physically associating solutions, which display temperature-dependent relaxation, are useful to explore elastic to viscous behavior and the onset of a wide range of mechanical instabilities. Our aim is to employ shear rheometry as a tool to simultaneously study the mechanical strength, toughness, and frictional properties of a physically associating acrylic triblock copolymer solution, utilized here as a model system. At elevated temperatures these solutions are viscoelastic liquids with near Maxwellian relaxation. The relaxation time increases dramatically as temperature is reduced, such that at room temperature the solutions effectively become viscoelastic networks. When deformed over a range of shear rates, these solutions demonstrate elastically driven behavior that can be quantified via shear rheometry. During fast deformation (i.e.,Weissenberg number, Wi, greater than unity), strain stiffening followed by softening is observed, reminiscent of fluid fracture. At decreased rates (Wi less than unity), evidence of viscoelastic- and liquid-like instabilities is observed. Additionally, post-fracture stress plateaus are related to the frictional stress at the sliding fracture-like interface. Compared to previous studies of extreme nonlinearity, the work performed here benefits from studying solutions with well-defined molecular structures, tailorable chain architectures, and a wide range of accessible relaxation times. Connections can also be established between the shear geometry used here and conventional mechanical analysis in tension and compression.

Symposium NP
Complex Fluids: Nanocomposites and Phase Separated Systems

Organizers: Erik K. Hobbie and Simon Cox

Wednesday 1:30 Kearney NP10

Method for measuring the non-linear modulus filled elastomers after weathering

Christopher C. White[1], Donald Hunston[2], and Kar Tean Tan[2]
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Although filled elastomers represent a commercially important class of materials, there are challenges to effectively characterize their rheological properties after weathering. The elastomers after weathering quite often exhibit cracks and tearing. The tearing reduces the area of the over which the tensile force can be distributed, thus producing a lower modulus value. The affect of tearing then camouflages the molecular changes in the elastomer due to the exposure to weathering. Here a method based on comparison between the tensile and compressive modulus is employed to differentiate between the molecular changes in the elastomer due to weathering exposure and extent of cracking. The model has been validated with non-weathered samples and weathered samples with and without controlled cracking. This method allows time-dependant modulus characterization of the weathered elastomers in the presence of significant cracking.

Wednesday 1:55 Kearney NP11

Anomalous creep behaviour of aging polybutadiene clay nanocomposite

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In a shear melting process, clay platelets in polymer - clay nanocomposites are known to undergo alignment in a direction of flow. After cessation of shear melting, under quiescent conditions, disorientation dynamics of clay platelets is known to cause slow enhancement of elastic modulus and viscosity as a function of time, thereby demonstrating aging behavior. The microsturctural evolution and understanding the structure property relationship in such aging nanocomposite systems is a great challenge in industrial processing of these materials. This work investigates the aging dynamics of Polybutadiene - Cloisite 10 A based nanocomposites using under a deformation (stress) field. It is observed that under small stresses, lesser strain gets induced in the nanocomposite for the creep experiments carried out at later times after stopping shear melting. However, contrary to expected behavior, at intermediate and higher stresses a rapid increase in strain is observed for the experiments carried out at later times since cessation of shear melting. We discuss possible mechanisms that may lead to the observed anomalous behavior.

Wednesday 2:20 Kearney NP12

Sedimentation in foams

Tudur Davies and Simon Cox
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A foam is a complex fluid with a highly nonlinear response to applied stress [1]. We investigate its response to the sedimentation of solid objects with quasi-static simulations using the Surface Evolver [2]: circular and elliptical discs in two dimensions and a sphere in three dimensions. When two circular discs sediment sufficiently closely they interact: they move so that they are in a stable configuration where the line connecting their centres is vertical [3]. In the same way, an elliptical object aligns itself so that its major axis is parallel to gravity as it sediments through a foam [4]. This is the result of the interaction between the foam structure and the sedimenting objects. The bunching up of

films and the deformation of bubbles around an object contribute towards the drag, lift and torque exerted on it. Extending our simulations to three dimensions, we consider the sedimentation of a spherical object though an ordered foam packed within a cylindrical tube.

[1] D. Weaire and S. Hutzler (1999) The Physics of Foam. Clarendon Press, Oxford. [2] K. Brakke (1992) The Surface Evolver. Exp. Math. 1. 141. [3] I.T. Davies and S.J. Cox (2009) Sedimenting discs in a two-dimensional foam. Colloids and Surfaces A 334:8-14. [4] I.T. Davies and S.J. Cox (2009) Sedimentation of an elliptical object in a two-dimensional foam. J. Non-Newtonian Fl. Mech. (in press) doi:10.1016/j.jnnfm.2010.04.005.

Wednesday 2:45 Kearney NP13

Flow-induced evolution of the microstructure of MWCNT suspensions

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CNTs have been the subject of interest since their discovery and have been used to enhance different physical properties of polymer composites. An extensive work has been performed to establish a relationship between the microstructure and rheology of these suspensions under flow. In this work, the flow induced evolution of the microstructure of suspensions of multiwalled carbon nanotubes (MWCNT) in an epoxy was analyzed for various concentrations and temperatures. It was observed that upon cessation of shear flow the storage modulus increased with time; however, the increase depended on the flow history of the suspensions as well as the suspension concentration and temperature.

Wednesday 3:35 Kearney NP14

The rheology and microstructure of carbon black and carbon nanotube suspensions

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The rheology and microstrucure of carbon nanotube (CNT) and carbon black (CB) suspensions within a Newtonian epoxy resin has been compared. Linear viscoelastic (LVE) and steady shear experiments were performed on suspensions of varying CB or CNT content in a Newtonian epoxy matrix. Both systems showed an increase in base viscosity, shear thinning and storage modulus with increasing concentration; however, it was necessary to use roughly ten times more CB than CNTs to obtain a similar rheological response. Optical microscopy in conjunction with a optical shear cell, showed that both CB and CNTs formed large aggregates at low shear rates and these were broken up at high shear rates. This was supported by readings of electrical conductivity and linear viscoelasticity after steady shear. The origin of the LVE behaviour is complex and as yet not fully modelled, however, the similarity between CB and CNTs systems implies that the dominant rheological effectare due to interaction between CNTs and CBs rather than internal elasticity or orientation of the CB or CNT.

Wednesday 4:00 Kearney NP15

In-situ lubrication-dispersion of multi-walled carbon nanotube in polymer melt

Joung Sook Hong[1], In Kook Hong[2], Kyung Hyun Ahn[2], and Seung Jong Lee[2]
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Application of carbon nanotube demands the dispersion step of the entangled CNTs. In this study, CNT is dispersed in a polymer melt (polypropylene) by the dilution of master batch. A CNT master batch is the mixture of PDMS and CNT (4.5wt%CNT/PDMS) which was prepared by using a roll-milling. The CNT master phase in the polymer matrix is broken-up into small CNT drops by iterative morphology evolution. It turns the CNT master phase into small drops including CNT or the more condensed CNT phase. Because the drop including CNT is so small, CNT looks like lubricating out of entangled CNT. PDMS plays a role as a lubricant of CNT. This lubrication-dispersion method effectively reduces the dispersion time in the polymer melt and CNTs disperse homogeneously. At the initial stage of dispersing, the property of dispersion is depending on the mixing time. As the mixing time goes on (> 5min), the dispersion is saturated in the rheological and electrical point of view. In the case of 20/80 PDMS/PP with 0.7wt%CNT, the surface resistance reaches to 1E5 ohm/sq in the short dispersion time (< 7min). The dispersed CNT into the matrix increases the rheological property (Eta*, G') of composite significantly though PDMS (20wt%) has low property. Based on the rheological and electrical observation, the lubrication-dispersion method of CNT shows the percolation threshold at the CNT loading of approximately 0.5wt%.

Wednesday 4:25 Kearney NP16

Shear banding analogies between nematic polymers and wormlike micelles

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Shear banding in wormlike micellar liquids serves as an important model system for anisotropic soft matter fluids. Rheo-NMR techniques of Callaghan et al. revealed stationary 1D bands in the shear gap, while modeling of Olmsted & Fielding identified sufficient rheological pre-conditions for 1D shear banding with the diffusive Johnson-Segalman (dJ-S) model. Cook, McKinley et al. explored the role of microscopic dynamics of chain-size distributions in stationary 1D shear band structures. More recently, experiments by Lerouge et al. and dJ-S modeling by Fielding reveal a more complex picture, including unstable transitions to 2D stationary roll cells in the flow-gradient and vorticity plane. The

analogous experiments for nematic polymers (Kiss & Porter, Berry et al., Larson & Mead, Moldenaers et al., Burghardt et al., Lettinga et al.) reveal dynamic attractors in steady shear driving conditions, negative first normal stress differences, 2D stationary roll cells, and instabilities to unsteady 2D and 3D structures. For rigid-rod macromolecular dispersions, we have the benefit of kinetic mean-field hydrodynamic theories (Doi, Hess, Marrucci & Greco, Feng & Leal, Dhont & Briels, Wang). Model predictions are surveyed, including contributions of Larson & Ottinger and the teams of Hess, Leal, Rey, Maffettone, Dhont & Briels and our group. Analogies are drawn with dJ-S predictions of Olmsted & Fielding. E.g., nematic polymers exhibit 1D shear banding, but the flow-nematic structures are dynamic and irregular at relevant Ericksen numbers. 1D attractors are often but not always unstable to 2D perturbations, influenced strongly by wall orientational boundary conditions. Models capture stationary 2D roll cells with vorticity-aligned boundary conditions and low Deborah numbers, and transitions to unsteady 2D attractors. Unsteady 1D and 2D attractors generically possess dynamic, localized order-disorder domains (defects). We explore whether wormlike micellar models have analogous features.

Wednesday 4:50 Kearney NP17

Rheological properties of suspensions of multi walled carbon nanotubes in ionic liquids: Effects of solvents polarity and anion size

Yasmin Korth and Christian Friedrich
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The dispersion of carbon nanotubes (CNT, nm-thick and micrometer-long fibers) in matrices, without bundling or aggregation, is of crucial importance for the beneficial combination of fiber properties with those of matrix fluids. For fuel cells and battery applications ionic liquids serve as solvents . Therefore, we disperse one sort of multi-walled carbon nanotubes (MWCNT) in different ionic liquids, which are made up of hexyl-methyl-imidazolium cation and several anions ranging from small chloride over tetrafluoroborate to large bis(trifluoromethylsulfonyl)imidanion, respectively. The linear viscoelastic characterization of those suspensions yields the plateau modulus as a representative parameter. Finally, we discuss the observed changes in the plateau modulus in dependence of temperature and solvent quality. In addition the same sort of multiwalled carbon nanotubes dispersed in 1-Butyl-3-Methylimidazoliumtetrafluoroborat is characterised rheologically. Measuring the dynamic moduli of different dispersions in dependence of temperature and concentration we identify regions, in which network formation (gel like state of suspensions) is dominant for these systems. That is the reason why we are able to show that the effective aspect ratios and the flexural properties of the fibers determine the gelation and the network formation of the suspensions.

Thursday Morning

Symposium SC
Suspensions, Colloids and Emulsions

Organizers: Chinedum Osuji and Y. Elaine Zhu

Thursday 8:05 Sweeney A SC41

Stress relaxation in nonlinear microrheology: Startup and cessation

Roseanna N. Zia[1] and John F. Brady[2]
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In active microrheology, a probe particle is driven by an external force through a complex medium. Most work has focused on steady behavior and the relationship between microstructure, probe speed and viscosity. Transient behavior in the linear response regime has also been studied via low-amplitude oscillatory forcing and the complex modulus; for weak forcing, the microstructural response that drives viscosity is indistinguishable from equilibrium fluctuations. But important information about the basic physical aspects of structural development and relaxation are captured by startup and cessation in the nonlinear regime, where the structure is driven far from equilibrium. Here we study the transient behavior of probe motion and viscosity under nonlinear microrheological forcing of a colloidal dispersion. The strength with which the probe is forced compared to thermal forces governs the behavior and defines a Peclet number, $Pe=F^{ext}/(kT/b)$, where kT is the thermal energy and b is the bath particle size. For large Pe, a boundary layer forms on the timescale of the flow, a/U, where a is the probe size and U its speed. On the other hand, relaxation following cessation occurs over several timescales corresponding to distinct physical processes. For very short times, the timescale for relaxation is set by the boundary layer of thickness $\delta \sim b/Pe$, and so $t \sim \delta^2/D$, where D is the relative diffusivity between the probe and a bath particle. Nearly all velocity relaxation occurs during this process, owing to the dependence of probe hindrance on the contact value of the microstructure. At longer times the Brownian diffusion of bath particles closes the wake on a timescale set by how long it takes a bath particle to move its size: $t \sim b^2/D_b$. As isotropy is restored, the majority of the microstructural relaxation occurs with little change in probe speed. Theoretical results are compared with Brownian dynamics simulation and with analogous results for macrorheological flows.

Thursday 8:30 Sweeney A SC42

Microstructural theory for concentrated sheared colloidal suspensions

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This work describes a theory for predicting microstructure of colloidal suspension as a function of the dimensionless quantities: $Pe = 6\pi\eta\dot{\gamma}a^3/k_bT$ and particle volume fraction, ϕ, where $\dot{\gamma}$ is the shear rate, a is the particle radius, η is the viscosity of the fluid and k_bT is the thermal energy. This problem was pursued by conditionally averaging probability distribution function conservation equation (Smoluchowski equation) for two particles. Many-body effects in the averaged hydrodynamic and thermodynamic coefficients of the conservation equation were then formulated self-consistently through probabilistic third-particle integrals. The resulting differential-integral conservation equation was solved using an iterative method. Comparison between the theory predictions and simulation results show that the theory is able to predict the well-known near equilibrium ($Pe << 1$) and dilute suspensions results. In addition this theory accurately predicts the major features of microstructure at $Pe > 1$ concentrated ϕ, which differentiates it from the previous theoretical works in the field. The rheological quantities of shear stress, τ_{xy}, and first and second normal stress differences, N_1 and N_2 were calculated based on the computed microstructure and were compared with Stokesian Dynamics simulation results. The results of this work suggest that the proposed self-consistent approach is able to capture the many-body hydrodynamic interactions in colloidal suspensions.

Thursday 8:55 Sweeney A SC43

Mixing and segregation of particle suspensions in 2D chaotic flows

Bu Xu and James F. Gilchrist
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This work simulates segregation of non-colloidal particle suspensions in a two dimensional time-periodic flow. Two different mixing protocols having alternating moving boundaries in a cavity known to generate chaotic advection with the same energy input rate are applied to the suspension. A diffusive flux model is used to capture the essence of shear-induced migration. In this system, fluid deformation drives both mixing and segregation where the local rheology is a function of particle volume fraction. The impact of flow topology and shear migration are investigated. As a result of the complex interplay between these two aspects, the concentration profile ranges from that representing the underlying topology to that of steady flow in a lid-driven cavity, depending on the strength of mixing versus migration. In this system, increasing the size of chaotic regions does not result in enhanced mixing. These results challenge conventional wisdom in designing small-scale flows for mixing and separation in micro-scale applications.

Thursday 9:20 Sweeney A SC44

Stokesian dynamics simulations of single particle of different shapes immersed in a Newtonian fluid under shear

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Industrially, fillers are commonly mixed into polymer matrices to modify the processability and mechanical properties of the final products. Rheological properties of such systems depend on volume fraction, shape, orientation of dispersed phase as well as the properties of matrix and modeling is inevitable to understand such complex systems. One promising method to accomplish this is the direct simulation method, which was introduced by Yamamoto and Matsuoka [1], where fibers are modeled by connected beads, called particle simulation method(PSM). After the original work, several other models were proposed [2-3] and the current trend of fiber simulation is to increase coarse-grained level by using rod as a repeating unit, without considering hydrodynamic interaction. However, the effects of hydrodynamic interaction on the behavior of the fillers and on the subsequent rheological properties of the composites under flow are still now not clear. In this work we show, using a Stokesian Dynamics Simulation software based on PSM [4-5] that considers both near and far field hydrodynamic interaction, that these play an important role in the behavior of single particles immersed in a Newtonian fluid. In particular, we show this to be true for flexible fibers and ring-shaped particles.

[1] S. Yamamoto, T. Matsuoka, J. Chem. Phys. 98 (1993) 644. [2] C. F. Schmid, D. J. Klingenberg, Phys. Rev. Lett. 84 (2000) 290. [3] L. H. Switzer, D. J. Klingenberg, J. Rheol. 47 (2003) 759. [4] M. Yamanoi, J. M. Maia, J. Non-Newt. Fluid Mech., 2010a, in press. [5] M. Yamanoi, J. M. Maia, J. Non-Newt. Fluid Mech., 2010b, in press.

Thursday 10:20 Sweeney A SC45

A pairwise theory for the rheology of soft particle pastes

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Soft particle pastes (SPPs) are composed of densely packed, disordered suspensions of soft and deformable particles. Examples include polyelectrolyte microgels, compressed oil in water emulsions, vesicles gels and star polymers. A pairwise interaction theory is developed to calculate the equilibrium and non-equilibrium distribution functions of SPPs at rest and in shear, which depend on the elastic interactions between the particles and frictional contact between particles. The stationary model of the distribution function is used to predict the osmotic pressure and elastic moduli of quiescent SPPs. The dynamic model of the distribution function is used to predict the shear stress, yield stress and normal stress differences of SPPs. The theoretical predictions are favorably compared to experimental observations and computer simulations of SPPs including microgels, compressed emulsions and star polymers. The resulting models provide a useful design tool for the formulation of SPPs with desired rheological properties.

Thursday 10:45 Sweeney A SC46

The dynamics of a simple model for a yield stress fluid

Kara L. Maki[1] and Yuriko Renardy[2]
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A simple model for a yield stress fluid is obtained from Larson's partially extending convection (PEC) strand model by replacing the zero shear stress limit for large shear rates with a non-negative limit (PECR), and augmenting with a Newtonian solvent (PECR-N). The constitutive behavior of PECR-N exhibits the typical non-monotonic shear stress vs shear rate behavior which allows for yielding to occur above a critical value of applied stress. The experimental determination of yield stress can be complicated by extremely slow yielding which may occur for a range of applied stresses. We therefore focus on the case where the elastic time scale is large compared with the viscous time scale and study the evolution of the conformation tensor for parallel shear flow with prescribed shear stress. The resulting dynamical system is solved both numerically and with asymptotic methods to clarify the different types of solution behavior. We find that multiple time scales are responsible for the path to transition from a fast curve, landing on a slow manifold, and escaping to yielded states which are steady or time-periodic. Novel solution types will be discussed.

Thursday 11:10 Sweeney A SC47

Suspensions of non-interacting magnetic nanoparticles under alternating magnetic fields

Moshe Gottlieb
Chemical Engineering Department, Ben Gurion University, Beer Sheva 84105, Israel

Magnetic nanoparticle (MNP) suspensions are known to generate heat when subjected to an alternating external magnetic field. It has been recently demonstrated that these thermal effects may be used for treating cancer by overheating tumors. Two separate mechanisms are responsible for the generation of heat: Néel, which is internal to the particles, and Brown which is external to the particle and results from the viscous heating of the fluid around it when the particle turns to align with the alternating magnetic field [1]. We calculate Brownian heating by

determining the flow field generated by the particle's motion. The dynamics of MNPs in suspension under an alternating magnetic field were calculated by solving analytically the Navier-Stokes equation for a simplified non-interacting particle model. The non-interaction assumption is valid for concentrations typically employed for magnetic heating. The velocity field was then used to derive the heat generation of the MNP suspension through the viscous heating term of the energy equation. It was found that through this methodology it is possible to approximate the magnitude of Brownian heating within MNP suspensions under alternating magnetic fields.

[1] Schmidt A M Macromol. Rapid Commun. 27 1168 (2006).

Thursday 11:35 Sweeney A SC48

Deformation of a superparamagnetic hydrophobic ferrofluid droplet in a viscous medium under uniform magnetic fields

Yuriko Renardy[1], Shahriar Afkhami[2], Annette S. Tyler[3], Michael Renardy[1], Tim G. St Pierre[3], Robert C. Woodward[3], and Judy S. Riffle[4]

[1]Department of Mathematics, Virginia Tech, Blacksburg, VA, United States; [2]Mathematical Sciences, New Jersey Institute of Technology, Newark, NJ, United States; [3]Physics, University of Western Australia, Nedlands, Western Australia, Australia; [4]Chemistry, Virginia Tech, Blacksburg, VA, United States

The effect of applied magnetic fields on the deformation of a biocompatible hydrophobic ferrofluid drop suspended in a viscous medium is investigated numerically and compared with experimental data. A numerical formulation for the time-dependent simulation of magnetohydrodynamics of two immiscible non-conducting fluids is used with a volume-of-fluid scheme for fully deformable interfaces. Analytical formulas for ellipsoidal drops and near-spheroidal drops are reviewed and developed for code validation. At low magnetic fields, both the experimental and numerical results follow the asymptotic small deformation theory. The value of interfacial tension is deduced from an optimal fit of a numerically simulated shape with the experimentally obtained drop shape, and appears to be a constant for low applied magnetic fields. At high magnetic fields, on the other hand, experimental measurements deviate from numerical results if a constant interfacial tension is implemented. The difference can be represented as a dependence of apparent interfacial tension on the magnetic field. This idea is investigated computationally by varying the interfacial tension as a function of the applied magnetic field, and by comparing the drop shapes with experimental data until a perfect match is found. This estimation method provides a consistent correlation for the variation in interfacial tension at high magnetic fields. A conclusion section provides a discussion of physical effects which may influence the microstructure and contribute to the reported observations.

Symposium MS
Polymer Rheology: Melts, Solutions and Blends

Organizers: Shi-Qing Wang and Marie-Claude Heuzey

Thursday 8:05 Sweeney B MS36

Non-monotonic stretch of isolated polymer chains in ultra-fast shear flows

Indranil Saha Dalal, Nazish Hoda, and Ronald G. Larson

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Using Brownian dynamics simulations, we investigate the behavior of single polymer molecules in shear flow at ultra-high Weissenberg number, where the Peclet number (Pe) of a single Kuhn step of the chain can exceed unity. A bead-spring model with stiff Fraenkel springs (similar to rods) is used to represent a freely jointed polymer chain at a resolution of a single Kuhn step, and Underhill-Doyle springs [J. Rheol. 49(5), 963-987 (2005)] are used for coarse-grained versions of this chain. Here, we do not consider the effects of hydrodynamic interactions and excluded volume interactions. We observe that, for all chain lengths investigated, the average stretch in the shear flow direction increases monotonically with shear rate for Peclet numbers $Pe < 0.03$, as observed in previous work and in experiments with DNA chains. At rod Peclet numbers in excess of unity, the stretch begins to decrease with increasing shear rate, in accordance with the similar simulations of Sendner and Netz [Eur. Phys. J. E 30, 75-81 (2009)]. We find that the dependence of stretch in the flow direction is linked to the thickness of the coil in flow gradient direction by a Graetz-Leveque boundary layer analysis, both at shear rates near the maximum in stretch, and for $Pe > 0.03$, where the chain stretch decreases with increasing shear rate. The decrease in stretch is predicted by the Graetz-Leveque analysis, when individual springs are strongly oriented by the flow. We also show that coarse-grained Underhill-Doyle springs yield stretch comparable to that of fine-grained chains at comparable Weissenberg number when $Pe < 0.03$, but fails at $Pe > 0.03$.

Thursday 8:30 Sweeney B MS37

Structures in the melt: The influence of flow and pressure

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Solidification in industrial processes, like injection moulding, involves flow fields, high thermal gradients and high pressures. Investigating polymer solidification under comparative processing conditions is a necessary step in order to predict the final polymer properties. Clear, key issue is accurate control during processing. Well controlled near-processing conditions are achieved by means of a custom made Multi-Pass

Rheometer (MPR) equipped with a special flow cell developed in our group. Experiments are carried out with time resolved X-ray scattering in combination with a flow cell allowing shear rates and pressures up to 1000 reciprocal seconds and 1000 bar, resp.

Surprisingly, the application of strong flow fields leads to formation of structures even when the temperature is close to the nominal melting point of the material. These flow induced structures are bundles of stretched molecules with pre-crystalline order and density higher than the melt. Important, at this temperature, lamellar structures are absent in the early stages allowing quantitative study on the formation of high temperature structures.

Results show that, depending on processing conditions applied, i.e. weak or strong flow com- bined with pressure, the high temperature structures are stable or dissolve back to the melt. Consequently, these high temperature structures and their mechanism of formation have dramatic influence on the subsequent structural and morphological developments of the crystalline phase at lower temperature. Moreover, they largely influence the final properties of materials, such as enhanced stiffness, wear and permeability.

Thursday 8:55 Sweeney B MS38

A fast nucleation algorithm for the crystallisation of polymer melts

Kenny Jolley and Richard S. Graham

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The coarse-grained Kinetic Monte Carlo simulations presented by Graham and Olmsted [1, 2], have been shown to predict both enhanced nucleation and the formation of shish-like nuclei under shear flows. While this algorithm is highly efficient, it cannot access the very large barriers to nucleation which are typically seen in experiments [3]. This is especially problematic for the quiescent case.

We present a fast nucleation algorithm that works by simulating a reduced region around the peak of the barrier where the statistics are non-Boltzmann. The dynamics of the system at the base of the barrier obey the Boltzmann distribution, and are thus well understood. However, normal nucleation simulations spend a large proportion of the simulation time exploring the base of the barrier. Our algorithm is significantly faster as it only explores the region where the statistics are not known.

We will present the results of an exploration of the parameter space of the nucleation model [2], which were obtained using this algorithm. This includes large barriers with large sized nuclei for quiescent and slow/fast shear flows.

[1] Graham RS, Olmsted PD, Coarse-Grained Simulations of Flow-Induced Nucleation in Semicrystalline Polymers, Physical Review Letters (2009) 103 (11) 115702. [2] Graham RS, Olmsted PD, Kinetic Monte Carlo simulations of flow-induced nucleation in polymer melts, Faraday Discussions (2010) 144 71-92. [3] I. Coccorullo, R. Pantani, and G. Titomanlio, Spherulitic Nucleation and Growth Rates in an iPP under Continuous Shear Flow, Macromolecules 41, 9214 (2008).

Thursday 9:20 Sweeney B MS39

Flow induced crystallization of polylactide: Experiment and simulation

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Viscoelastic properties of polymer melts are highly sensitive to any structural changes, including molecular weight changes and the formation and growth of crystallites. We have made use of this sensitivity to study the flow induced crystallization of polylactide in shear. A simple empirical model is used to characterize the variation of complex viscosity due to thermal degradation and when combined with a statistical analysis of residuals, to determine the induction time of crystallization at low supercooling and various shear rates and strains. This technique is highly sensitive to the number of crystallites at the initial stages of crystallization and is therefore an accurate indirect measure of nucleation. This then allows for studying in detail the effect of flow on nucleation and for providing experimental tests of molecular theories. We have performed a series of experiments looking at the effect of shear rate at different temperatures and shearing time on the onset of crystallization. These data were then used to evaluate a flow induced crystallization theory. In this theory, changes in chain entropy upon stretching are used to compute the effect of flow on the crystal nucleation rate, which is then related to the experimentally determined induction time.

Thursday 10:20 Sweeney B MS40

Early stages in polymer crystallization: Mechanism of fluid-to-solid transition for isotactic poly-1-butene

Deepak Arora[1] and H. Henning Winter[2]

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Quiescent crystallization experiments on isotactic poly-1-butene under isothermal conditions help us establishing the mechanism of network formation in crystallizing polymers. Experiments include optical microscopy, DSC and rheology. Optical microscopy and DSC near the fluid-to-solid transition suggest that the transition, as determined by time-resolved mechanical spectroscopy, is not caused by packing/jamming of spherulites but by the formation of a percolating network structure. Impingement of pairs of spherulites starts to occur long before percolation. This makes it difficult to define spherulitic impingement for the whole sample. At percolation, the absolute crystallinity is about 7-8 vol%. The transition material can be understood as a soft physical gel with an out-of-equilibrium structure.

Thursday 10:45 Sweeney B MS41

Extensional flow induced crystallization of isotactic polypropylene using a filament stretching rheometer

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A filament stretching rheometer within a heated enclosure is used to impose homogeneous uniaxial flow on both linear and branched isotactic polypropylene. The Janeschitz-Kriegel protocol is followed and the samples are stretched and allowed to crystallize at a temperature of 140o C. Differential Scanning Calorimetry is used to measure the degree of crystallinity of the stretched samples. The flow induced crystallization of the polymer is then characterized as a function of both the total imposed strain and extension rate. Our work on polyisobutene has found that the degree of crystallinity increased from 45% to 62% with an increase in extension rate from $e=0.01s^{-1}$ to $e=0.5s^{-1}$ at a fixed strain. No significant change in crystallization was observed for varying imposed strain. The increase in crystallinity is likely due to the effective orientation and alignment of the polymer chains with increasing extension rate. In this talk, we will discuss whether similar relationships between extension rate and crystallinity are observed for isotactic polypropylene and investigate the role of branching on extensional flow induced crystallization of these systems.

Thursday 11:10 Sweeney B MS42

Criteria for shear-induced crystallization: Strain, Weissenberg Number and mechanical work

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The effect of strain, Weissenberg number (We) and specific mechanical work on rate of crystallization (nucleation followed by growth) and on growth of anisotropy was studied for shear-induced crystallization of isotactic poly-1-butene. Small angle light scattering (SALS), transmission intensity measurements and optical microscopy were the experimental techniques used. The samples were sheared for a finite strain at the beginning of the experiment and then crystallized without further flow (Janeschitz-Kriegl protocol). Shear conditions were varied as We = 0 to 12.5 and strains up to 200. Spherulitic growth was observed under quiescent conditions (We = 0) and at small strains and We. Strain requirements to attain steady state/ leveling off of the rate of crystallization were found to be much larger than the strain needed to achieve steady state of flow. Strain effects on nucleation density and so on the rate of crystallization were found to be tremendous even for few strain units, as far as shearing was performed with We >>1. For We~ 1, near the transition to shear thinning, even the large strains up to 180 could not enhance nucleation density significantly. The large strain and We >1 criteria were also observed for morphological transition from spherulitic growth to oriented growth. The strain requirements for oriented growth and the steady value of rate of crystallization became less and less for higher Weissenberg number indicating a criterion based on specific mechanical work. Weissenberg number can be interpreted as the memorized strain by the material.

Thursday 11:35 Sweeney B MS43

Coarse-grained simulations of polymer nucleation during strong flow

Richard S. Graham
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I present results from a recent highly coarse-grained simulation algorithm for crystal nucleation from polymers under strong flow [1,2]. The simulation predicts both enhanced nucleation and shish-kebab formation under flow and is sufficiently tractable to model low-undercooling. Comparisons with experimental data for nucleation under flow will be presented. I will also discuss connections between the simulations and models of both higher and lower degrees of coarse-graining. This will include some analytic results that connect the simulations to simpler differential models, commonly used in computational modelling of polymer processing, and a discussion of methods to connect to more detailed simulations.

[1] Graham RS, Olmsted PD, Coarse-Grained Simulations of Flow-Induced Nucleation in Semicrystalline Polymers, Physical Review Letters (2009) 103 (11) 115702. [2] Graham RS, Olmsted PD, Kinetic Monte Carlo simulations of flow-induced nucleation in polymer melts, Faraday Discussions (2010) 144 71-92.

Thursday 12:00 Sweeney B MS44

Power-series approximation of relaxation time spectrum

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It is easy to fit dynamic modulus by polynomial of logarithm of frequency without ill-posedness. Hence, dynamic modulus can be approximated by a polynomial of log frequency of finite order and relaxation spectrum is assumed as the polynomial of log relaxation time of the same order. Then the coefficients of the polynomial of spectrum can be determined from those of dynamic modulus by solving a system of linear equations which is free from ill-posedness. We tested the algorithm for various simulated data and experimental data. We compared the algorithm with nonlinear iterative regularization method.

Symposium NM
Nano- and Micro-Rheology: Indentation and Beyond

Organizers: Mark VanLandingham and Hongbing Lu

Thursday 8:05 Coronado/DeVargas NM14

Non-linear rheology at the micro-scale

Eric M. Furst
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Micro-scale rheological measurements provide several unique advantages in materials development and characterization, including the ability to measure the rheology of scarce materials, materials that are changing quickly with time, screen material rheology rapidly, or assess the degree and potential implications of rheological heterogeneity. However, because most micro-scale measurements are made with *passive* microrheology by tracking the thermal motion of micro-probe particles embedded in the material, they are limited to quantifying the material's linear rheology as a consequence of the fluctuation-dissipation theorem. An open question is whether micro-probe techniques can be adapted to measure non-linear rheology by actively driving the probe with an external force. In this talk, I will provide an overview of active microrheology with a focus on measurements of non-linear rheology in colloidal suspensions. Specifically, measurements of viscosity thinning made by laser tweezer microrheology will be compared with the bulk shear thinning behavior obtained from macro-rheology. The experimental results will be compared to existing theoretical frameworks with an emphasis on identifying the potential strengths, limitations and unresolved issues regarding active non-linear microrheology.

Thursday 8:30 Coronado/DeVargas NM15

Direct measurement of shear–induced cross correlation of Brownian motion

Andreas Schneider, Andreas Ziehl, and Christian Wagner
Saarland University, Saarbrücken, Saarland, Germany

Neutral particles in a fluid are moving relatively to each other and interact via the fluid. These hydrodynamic interaction effects decay with the particle distance. In shear flow, little is known about the dynamics of Brownian particle motion itself and the hydrodynamic interaction effects of several particles in spite of their fundamental relevance and importance in applications in microfluidics or in fluid mixing.

In shear flow, for orthogonal random particle-displacements, a cross-correlation is expected. Any random jump of a particle from one to a neighboring streamline of different velocity leads to a change of the particle's velocity itself along the streamlines. According to this qualitative picture, cross-correlations between orthogonal particle fluctuations are expected to be strongly asymmetric in time.

We investigate experimentally the fluctuations in a linear shear flow of a single particle in a harmonic potential as well as of two hydrodynamically interacting particles trapped to two neighboring potentials. In our experiment, we use a special shear flow-cell where one or two micron sized latex beads are held at its center by optical tweezers. Shear-induced cross-correlations were determined directly by measuring the particle's positions with a high speed camera of 15kHz and 4nm resolution. These correlations are strongly asymmetric in time. In addition the probability distribution of a single particle in a trap was measured, which can be also calculated in terms of a Langevin model, similar to the correlations. Both the probability distribution and the correlation can be fitted by using the same value of the shear rate, which altogether gives a consistent picture of not yet directly observed shear-induced cross-correlations of particle fluctuations. We think that our findings could be of great fundamental value for the understanding of colloidal or polymeric solutions in shear flow.

Reference: Phys. Rev. Lett. 103, 230602 (2009)

Thursday 8:55 Coronado/DeVargas NM16

Heterogeneous microstructure of biofilm probed by particle tracking microrheology

Heekyoung Kang, Soojin Shim, Jeyong Yoon, Kyung Hyun Ahn, and Seung Jong Lee
School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Republic of Korea

Biofilm is a complex aggregate of microorganisms surrounded by the slime they secrete. It is composed of bacteria, void and extracellular polymeric substances (EPS). Because biofilm prevents flow of material inside pipeline, or it can cause infection on the surface of the medical devices, it is highly desired to remove biofilm from the surface. To remove biofilm effectively, understanding the mechanism and characterizing the viscoelastic properties are essential. There have been studies on measuring mechanical properties of biofilm using conventional rheometer. However, in this case, the microstructure of biofilm could be destroyed. In addition with this kind of bulk rheology, the heterogeneity of biofilm structure cannot be characterized, nor can the developing process of biofilm be observed. In this study, particle tracking microrheology technique was applied to overcome these disadvantages. Biofilm was induced directly from bacteria which are attached to glass surface. During structure formation, fluorescence particles were added to biofilm and they were tracked on the microscope. The rheological properties of biofilm such as elasticity and modulus could be evaluated in-situ during structure formation by observing the movement of the probing particles. As a result, the order of modulus from particle tracking microrheology was less than that from conventional rheometer because local properties were considered with microrheological measurement in this case. The individual mean square displacements (MSD) of the dispersed particles inside biofilm were classified to different groups depending on whether they are in the void or in the EPS. The effect of shear on the heterogeneity of microstructure of biofilm was also considered using the skewness and MSD distribution function, which may well be discussed with regard to 3D images captured by confocal microscopy

Thursday 9:20 Coronado/DeVargas NM17

Microbead rheology of viscoelastic solids

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Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States

Viscoelastic properties of soft materials are often estimated by tracking a micron-sized bead embedded in the host medium. We derive equations that relate the dynamic modulus G^* of the medium with (i) the mean-square displacement (MSD) and (ii) the power spectral density (PSD) of a thermally fluctuating single probe bead in a viscoelastic solid. We show that it is important to separate a purely elastic part from the viscoelasticities of a solid. A purely elastic part is represented by the frequency matrix that typically appears in the generalized Langevin equation (GLE) from projection operators. The remaining viscoelastic liquid components are represented by the memory function that obeys the second fluctuation-dissipation theorem. In the frequency regime where effects of inertia are negligible, the derived equations reduce to the fluctuation-dissipation theorem for the frequency-dependent compliance first used by Schnurr *et al.* [Macromolecules **30**, 7781 (1997)]. If the memory function is spectrally decomposed, G^*, MSD and PSD are expressed by the same sets of viscoelastic parameters, suggesting that G^* can be efficiently estimated by using these parameters determined from MSD or PSD. We show that PSD is better to work with than MSD in the sense that the PSD is analytically expressed while MSD is not, in general.

Thursday 10:20 Coronado/DeVargas NM18

Understanding nanoparticle diffusion and exploring interfacial nanorheology using molecular dynamics simulations

Yanmei Song and Lenore L. Dai
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We have studied the dynamics of nanoparticles at polydimethylsiloxane (PDMS) oil-water interfaces using molecular dynamics (MD) simulations. The diffusion of nanoparticles in pure water and low viscosity PDMS oil are found to be reasonably consistent with the prediction by the Stokes-Einstein equation. In addition, we have calculated the shear moduli and viscosities of bulk oil and water as well as oil-water interfaces from single-nanoparticle tracking and demonstrated the potential of probing nanorheology from a MD simulation approach. Surprisingly, we found that the lateral diffusion of nanoparticles as well as apparent interfacial nanorheology at the PDMS oil (low viscosity)-water interface are independent of the position of the nanoparticle at the interface.

Thursday 10:45 Coronado/DeVargas NM19

Microrheological screening over a large material composition space

Kelly M. Schultz and Eric M. Furst
Department of Chemical Engineering, University of Delaware, Newark, DE 21209, United States

High-throughput microrheology combines the use of microfluidic devices and passive microrheology for facile characterization of rheological properties over a large composition space, while minimizing both the sample volume and sample preparation time. This enables materials discovery and characterization, specifically of scarce and rare materials. Within the microfluidic device, distinct samples with uniformly varying compositions are separated by an immiscible fluid. Rheological properties of each sample are collected using multiple particle tracking microrheology. We demonstrate the power of this approach using a covalently cross-linked hydrogel designed for therapeutic applications. Gelation state diagrams compiled from hundreds of microrheological samples yield the compositions in which gelation occurs as a function of total polymer concentration, number of active sites for cross-linking on the gelling molecule, and molecular weight of the cross-linking molecule. Using these state diagrams, specific hydrogel compositions selected for their weak gel properties are chosen to effectively process the hydrogel into nanofibers using electrospinning. This demonstrates the power of microrheological screening to identify material properties of engineering interest while minimizing the amount of material and time for rheological characterization.

Thursday 11:10 Coronado/DeVargas NM20

Electrohydrodynamic quenching in polymer melt electrospinning

Eduard Zhmayev, Daehwan Cho, and Yong L. Joo
School of Chemical & Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Polymer melt electrospinning (PME) is one of the prime contenders to meet the industrial demand for nanofiber mats in an environmentally benign and cost effective manner. However, our recent infrared thermal measurements on polymer melt jets in electrospinning have revealed rapid quenching by ambient air, an order of magnitude faster than predicted by the classical Kase and Matsuo correlation. This drastic heat transfer enhancement can be linked to electrohydrodynamic (EHD) effects. Analysis of EHD-driven air flow was performed and included into a comprehensive model for polymer melt electrospinning. The analysis was validated by excellent agreement of both predicted jet radius and temperature profiles with experimental results for electrospinning of Nylon-6 (N6), polypropylene (PP), and polylactic acid (PLA) melts. Based on this analysis, we discuss process modifications that alleviate the undesirable quenching.

Thursday 11:35 Coronado/DeVargas NM21

Analyzing curing reactions by simultaneous rheometry and FTIR spectroscopy to determine interactions between chemical and mechanical properties of materials

Manfred Feustel[1], Cornelia Küchenmeister[2], and Jint Nijman[2]
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In order to understand the properties of a material, and the interrelated dependence of these properties more than just one analytical technique is required. Techniques complementing rheological measurements are e.g. GPC, thermal analysis, microscopy, and FT-IR spectroscopy. Although most techniques can record dynamic progressions, they cannot detect interactions when used in parallel. This requires their combination in one instrument to analyze a sample the same time under exactly the same conditions.

In this paper we present the combination of a rheometer and a FT-IR spectrometer. With the Rheonaut module a rheometer can be coupled to the side port of standard FT-IR spectrometer to collect rheological data and mid-infrared spectra simultaneously. The optical module features an infrared transmitting element with a high refractive index as the optical sensor based on the ATR principle. The advantage of this technique compared to standard infrared transmission spectroscopy or specular reflection spectroscopy is that the sample thickness can be adjusted to the rheological needs and is independent from the infrared spectroscopy requirements.

Applications include the tracking of curing reactions in a shear flow while monitoring the appearance and disappearance of chemical bonds. Measurements of the curing of a PU resin shows that in the early stage of the curing the rheological properties are dominated by the formation of associated urethane where the later stage is dominated by amide bond formation. Additional curing reaction data of an epoxy resin and a PU foam in a shear flow are presented. The simultaneously acquired mid-infrared spectral data reveals that the inflection points in both G' and G" are reflected in absorbance bands representing specific molecular bonds of functional groups. Such knowledge opens an in-depth understanding of how physical properties and molecular structures generated by a chemical process correlate which each other.

Thursday 12:00 Coronado/DeVargas NM22

Numerical and experimental studies on flow of linear and branched polyethylenes through axisymmetric and planar die

Vivek Ganvir[1], Ashish Lele[2], B P Gautham[1], Rochish Thaokar[3], and Harshwardhan Pol[2]
[1]TRDDC, Tata Consultancy Services Ltd, Pune 411013, India; [2]Polymer Science and Engineering, National Chemical Laboratory, Pune, India; [3]Chemical Engineering, Indian Institute of Technology, Bombay, Mumbai, India

Polymer flow simulations and extrudate swell prediction has shown significant difficulties due to two key reasons. The first is the appropriate representation of the constitutive behavior of the polymer melt. The second is regarding the simulation of the free surface, which requires special techniques in the traditionally used Eulerian framework. We have simulated extrudate swell using an Arbitrary Lagrangian Eulerian (ALE) technique based finite element formulation and the same has been validated by comparing the results with reported numerical and experimental studies. In the present work we compare our ALE simulations with our own experimental data on the extrudate swell of commercial grade LLDPE and LDPE resins. The resins were characterized for their rheological behavior in both shear and uniaxial extension. ALE simulations were performed using molecular constitutive model like eXtended Pom-Pom (XPP) for branched (LDPE) and PTT for linear LLDPE. The simulated extrudate swell showed good match with the experimental data. It was found that the swell values of LPDE through planar die are higher than the axisymmetric die. Further, flow birefringence and pressure drop measurements were done using a 10:1 contraction-expansion (CE) slit geometry in a MultiPass Rheometer. Simulated pressure drop and contours of the principle stress difference were compared with experimental data and were found to match well.

Symposium FD
Micro- and Nano-Fluidics

Organizers: Siva Vanapalli and Anubhav Tripathi

Thursday 8:05 Peralta/Lamy FD15

Making microfluidic channels from biopolymer gels - some issues and opportunities

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Microfluidics operates with little inertia, high surface-to-volume ratios and large elasticity numbers and it has found use as a platform for a wide range of applications. Fabrication of microfluidic channels using soft lithography with cross-linked elastomers such as polydimethylsiloxane (PDMS) is a relatively mature technology, and microfluidic devices can be reliably and reproducibly manufactured. Many of the polymers used are, to some extent, permeable to oxygen or other gases, but are usually impermeable to liquids. Conversely, biopolymer gels will often allow or facilitate diffusion of liquids into the gel. Here, a technique for fabricating microfluidic channels using gelatin will be demonstrated. Some of the major difficulties and challenges, along with their solution, will be presented. Finally, some of the opportunities available using gelatin microchannels rather than PDMS will be discussed.

Thursday 8:30 Peralta/Lamy FD16

Microfluidic fabrication of magnetic and fluorescent chains using polymer capsules as building blocks

Kunqiang Jiang[1], Chanda Arya[2], Don L. DeVoe[3], and Srinivasa R. Raghavan[2]
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We describe a microfluidic approach to generate monodisperse building blocks that can be further connected on-chip into higher-order structures. Our building blocks are capsules of the biopolymer chitosan, which are created by contacting an aqueous solution of chitosan at a microfluidic T-junction with a stream of hexadecane containing a nonionic detergent. In the process, monodisperse chitosan-bearing droplets are passively sheared off from the injected flow, and these are interfacially crosslinked downstream by a solution of glutaraldehyde (GA). Robust monodisperse microcapsules of adjustable size are thus produced, and capsule properties are easily varied by introducing payloads such as magnetic nanoparticles and/or fluorescent dyes into the chitosan. We then demonstrate the linking of individual capsules into chains of precise length, again using GA as the chemical "glue". Chain flexibility can also be tuned by adjusting the crosslinking conditions: in the case of magnetic chains, both rigid chains that can be rotated by an external magnetic field as well as semiflexible chains that show a beating motion can be created. The arrangement of capsules within a chain can also be controlled, e.g., to generate chains with alternating fluorescent and non-fluorescent capsules. Such capsule chains could find application as microfluidic mixers, delivery vehicles, microscale sensors, or as miniature biomimetic robots. In addition to chains, the approach outlined here can be extended towards "bottom-up" manufacturing of a variety of complex microstructures.

Thursday 8:55 Peralta/Lamy FD17

Transient vortex dynamics in a planar 4:1 contraction microchannel flow

Daewoong Lee, Kyung Hyun Ahn, and Seung Jong Lee
School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Republic of Korea

When non-Newtonian fluids flow through microfabricated contraction channel, the flow shows distinctive flow patterns at elevated Deborah number due to its viscoelasticity. As the fluid elasticity or flow rate increases, flow pattern develops from Newtonian-like flow to unstable flow. In between those flows, divergent shape and vortex enhancement region occur. The flow development is affected by the type of contraction (planar or axisymmetric), contraction ratio, flow rate, and the rheological properties of fluids. There were many studies in this field, however, steady state was mainly focused and transient state was not fully investigated. One reason is that it is difficult to get to transient state with dilute solutions. In this study, transient state was investigated experimentally using a planar microchannel of 4:1 contraction geometry (width of expansion part: 200 μm, width of contraction part: 50 μm, and channel depth: 70 μm), with l viscoelastic solutions of different concentration. (PEO, molecular weight = 5,000,000) When concentrated aqueous solutions of polyethylene oxide (PEO) with high molecular weight flow through a contraction channel, the transient state can be more easily observed before the flow becomes unstable. In this research, as the concentration of PEO solution increased, the flow development changed at a specific concentration. After that, the flow showed vortices with periodic fluctuations. Unstable flows also showed fluctuating vortices, but they were not periodic with no trace of pattern formation. This periodic fluctuation was assumed as 'transient state'. In that state, both symmetric and unsymmetric fluctuating vortices had particular frequency.

Thursday 9:20 Peralta/Lamy FD18

Microfluidics enhanced enzyme immobilization for sensitive H_2O_2 biosensing

Amy Shen, Donglai Lu, and Joshua Cardiel
University of Washington, Seattle, WA 98195, United States

A novel and versatile processing method based on microfluidics is developed for the formation of nanoporous scaffold with in-situ enzyme immobilization for highly sensitive biosensor applications [1]. Our new approach used microfluidic devices to facilitate the single throughput, in-situ process to immobilize enzyme in a nanoporous scaffold that can retain the enzymes' native stabilities and reactivities. The nanoporous gel provides the favorable host matrix that isolates the enzyme molecules, protecting them from self aggregation and leaching, while providing essentially the same local aqueous microenvironment as in biological media. The nanoporous scaffold based biosensor shows high sensitivity, stability, selectivity, and good precision. This flow induced immobilziation technique opens up new pathways for designing simple, fast, biocompatible, and cost-effective process for enhanced sensor performance.

Reference: [1] Donglai Lu, Joshua Cardiel, Guozhong Cao and Amy Q. Shen, Nanoporous scaffold with immobilized enzymes during flow induced gelation for sensitive H_2O_2 biosensing, Advanced Materials, in press, 2010.

Thursday 10:20 Peralta/Lamy FD19

Challenges measuring the response of viscoelastic materials during LAOS experiments

Aly J. Franck
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A key experimental problem, well known from transient experiments of highly elastic fluids such as polymers melts, filled systems, gels, etc. in parallel plate or cone-plate configuration is the appearance of a non consistent stress response at high shear rates or shear deformations. The flow artifacts responsible for this effect includes fracturing of the sample, expelling of the sample from the gap, slip and/or shear banding. These phenomena show as soon as the material behavior transitions from the linear into the non-linear regime and makes the interpretation of the results obtained during LAOS experiments difficult, even impossible. It appears that the significance of these artfacts increases with increasing elasticity of the sample. The presence of even harmonics in the shear stress and uneven harmonics in the normal stress in the non-linear region can be related to flow asymmetries resulting from these flow artifacts.

In order to eliminate, reduce or delay these boundary effects to higher strain, a variety of approaches such as using guard rings, closed gap, surface treatments, partitioned plates, etc. have been tried out.

The extend of the effect of these flow phenomena on the stress response at large amplitudes is quantified for a typical viscoelastic and a yield stress material and the validity of the various approaches to control the flow at the sample rim is evaluated.

Thursday 10:45 Peralta/Lamy FD20

Nanopattern insert molding and evaluation of pattern surface by applying automatic image analysis techniques on the S.E.M. images

Kim Sung Ho[1], Sul In Hwan[2], Song Young Seok[3], Jeong Jun-ho[4], and Youn Jae Ryoun[1]

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Nanopatterning techniques have been developed to fabricate optical, magnetic, chemical, biological, and Micro/nano electronics devices. But the methods of verifying its quality are not easy and sufficient. Investigating nanopatterns formability is important for particularly repeatable patterns such as antireflection film. Nanopattern insert molding is a new method to produce nanopatterns on polymeric surface with high resolution, good productivity, and low cost. A disposable polymeric film, made of polyvinyl alcohol (PVA), was used for the stamp with nanopatterns on its surface. The nanoimprinted PVA film was inserted into the cavity and the polymer melt was injected into the mold. The water soluble PVA film was used as the inserted template to overcome difficulties of releasing the nanopatterned film from the substrate. To evaluate the generated nanopatterns' shape regularity, image processing techniques were applied to the SEM images which have larger field of view than the AFM data. The proposed evaluation method was used for nanopatterns from a several different processing conditions and the nanopatterns' shape regularity was measured automatically and quantitatively.

Thursday 11:10 Peralta/Lamy FD21

High throughput rheology

Suraj S. Deshmukh, Matthew Bishop, Jodi Mecca, Eddie Gee, Daniel Dermody, and Jonathan Zieman

Core R&D, The Dow Chemical Company, Midland, MI 48642, United States

Rheological characterization is a crucial screen for gauging the performance of a wide range of commercial products including paints, water soluble polymers, shampoos etc. Measurement of simple rheological functions such as viscosity and complex rheological properties such as elasticity and LAOS functions have traditionally been a labor intensive and tedious task for researchers. The Rheology workflow is a scientific process starting from design of experiments to formulation to rheological characterization and finally data analysis. In our work, we have endeavored to remove the bottlenecks in this scientific process making this is a rapid, efficient and fairly accurate High Throughput Rheology workflow. A number of tools that are part of this workflow have been developed over the past few years including some of the world's first high throughput rheometers and viscometers. I will outline the development of a novel high throughput viscometer which in conjunction with an automated cone and plate rheometer that includes automated sample handling, loading and cleaning systems make this an efficient screening and measurement process. Further, validation of these instruments will be described including systematic experimental observations and model simulated results which were used to identify optimum operating and test conditions. Also, rapid data visualization tools while maintaining the analysis in the hands of the experienced experimentalist will be outlined.

Thursday 11:35 Peralta/Lamy FD22

Fluid-structure interaction analysis on the film wrinkling problem of a film insert molded part

HwaJin OH[1], YoungSeok Song[2], and JaeRyoun Youn[1]

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Back-injection of polymeric liquid to preformed films, also known as film insert molding (FIM), provides the surface quality of polymeric parts. The back-injection material is responsible for mechanical and thermal properties of the part, especially such as stiffness and thermal expansion. In the back-injection, molding it is important to ensure that the inserted films are not wrinkled by the injection of molten polymers. In this study, FIM was carried out with utilizing PC/ABS alloy and PMMA/ABS film. The wrinkling of films was observed by the atomic force microscope (AFM). Numerical simulations were performed to understand the mechanism of the film wrinkling and optimize the processing conditions of FIM for high precision parts by using commercial packages including Hypermesh™, Moldflow™, and COMSOL™. A critical shear rate for the film wrinkling of a center garnish part, was determined based on the deformation energy of plate. It was found that the critical shear rate calculated numerically was in good agreement with that of the film insert molded parts.

Thursday 12:00 Peralta/Lamy FD23

DNA dynamics in the presence of crowding agents

Patrick S. Doyle[1], Jing Tang[2], and Jeremy Jones[2]
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In the past decade, single molecule microscopy has emerged a valuable technique for studying the conformation and dynamics of model polymer systems such as DNA. The ability to visualize single molecules gives new insight into polymer rheology and separation processes. To date, the majority of work has focused on DNA in good solvents, such as the buffer solutions that are commonly in electrophoresis. A few studies have examined the effects of modulated ionic conditions, but these still remain in the good solvent regime. Here we explore the role of added crowding agents which give rise to attractive depletion interactions among DNA segments. We explore the change of DNA size, equilibrium dynamics (diffusivity and relaxation times) and non-equilibrium stretching dynamics in elongational electric fields. New regimes are encountered in all cases and scaling theories developed to explain them.

Symposium SA
Self-Assembling, Associative, and Gel-like Systems

Organizers: Ferenc Horkay and Matthew W. Liberatore

Thursday 8:05 O'Keeffe/Milagro SA27

Self-assembly of side group liquid crystalline block copolymers in a nematic solvent

Zuleikha Kurji, Rohan Hule, Paul Pirogovsky, and Julia A. Kornfield
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Structural studies clarify the origin of the rheological properties of solutions of Side-Group Liquid Crystalline Polymers (SGLCPs) and coil-SGLCP block copolymers dissolved in a nematic liquid crystal. The local chain conformation and self-assembled morphology of coil-SGLCP diblock copolymers are investigated using SANS, USANS and TEM. The innate orientational order of the mesogen couples with the flexible backbone in the SGLCP block. Two distinct types of mesogen chemistry and orientational coupling are examined that produce either a prolate or oblate spontaneous anisotropy of the SGLCP conformation in a small molecule nematic solvent. The spontaneous anisotropy of the SGLCP block facilitates formation of unusually large, anisotropic self-assembled microstructures that display a remarkable restructuring across the nematic-to-isotropic transition temperature of the thermotropic solvent driven by favorable solvation of the coil. Morphological and conformational characteristics of these coil-SGLCP diblocks open new opportunities in responsive LC interfaces, as well as reversible LC gels.

Thursday 8:30 O'Keeffe/Milagro SA28

Development of an in-situ rheological method to characterize fatty acid crystallization in complex fluids

Prachi Thareja[1], Carrie B. Street[1], Kevin Hermanson[2], Martin Vethamuthu[2], and Norman J. Wagner[1]
[1]Chemical Engineering, University of Delaware, Newark, DE, United States; [2]Unilever R & D, Trumbull, CT, United States

Skin-care creams are complex systems whose rheology directly affects their tactile properties or their sensory perception. To better understand the rheology of this complex system, we have designed an experimental model formulation. The formulation consists of two synthetic surfactants and a fatty acid (crystallization temperature 55°C) in water The formulations are prepared and then rheologically measured under a well controlled thermal and shear protocol using a rheometer tool called the starch pasting cell (SPC). This tool consists of a rotating impeller with blades in a temperature controlled cylindrical cup. The components of the formulations are mixed in SPC at 70°C, followed by 1°C/min cooling under shear to 25°C. Further micro structural evolution at 25°C is probed by small amplitude oscillatory shear (SAOS). SPC rheometry shows $G'\sim10^5$ Pa resulting from the formation of a solid fatty-acid crystal network is obtained. SAXS and Polarized light microscopy at 70°C show the presence of swollen lamellar phase. After cooling to 25°C, initially formed lamellar mesophase provides a template for crystallization. The crystals further grow and aggregate forming a network with a minimum critical 5-7 wt% of fatty acid required to achieve percolation and build high modulus structures. The maximum in modulus is observed at 10 wt% fatty acid which becomes approximately independent of wt% of fatty acid beyond 18 wt%. The same qualitative trend is also observed in yield stress and yield strain for these formulations. Optical microscopy shows the change in crystal morphology from long needle-like at 10 wt% fatty acid to smaller irregular platelets at 15 wt% and beyond, indicating the difference in rheological properties arise from the different crystal morphology. We hypothesize that the fatty acid crystal network consists of crystal aggregates linked by regions consisting of non crystallizing synthetic surfactants, rendering the desired paste-like characteristics to the formulation.

Thursday 8:55 O’Keeffe/Milagro SA29

Micellization and gelation of F127 solutions with methyl paraben and the kinetics of ordering using rheology, DSC, and small angle x-ray scattering

Norman A. Meznarich and Brian J. Love
Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States

The reverse thermal gelation behavior of Pluronic F127 PEO-PPO-PEO triblock copolymer solutions has been studied as a drug-delivery vehicle or for formulated injectables. Previously we have characterized the thermodynamics and kinetics of the gelation behavior when F127 solutions were heated at different ramping rates. Expanding upon this work, we have probed the kinetic effects on F127 gelation due to the addition of pharmaceuticals using rheology and DSC. Saturated methyl paraben (MP) was added to F127 solutions ranging from 10-30% w/v and tested on the rheometer at heating rates between 0.1°C/min and 10°C/min. Power law and log-Boltzmann sigmoidal analyses show that the presence of MP increases the rate of gelation (roughly 3-fold increase in speed) for intermediate F127 concentrations. A large decrease in gel temperature (approximately 15°C) occurs as well, a result that has been previously reported in the literature. We found that the presence of MP suppresses the micellization endotherm using DSC, to the point that no endotherm is discernable when MP is added to saturation. This athermal micellization phenomenon gives insight into the interactions between MP and F127 that result in the observed rheological changes in gelation behavior seen with F127 + MP solutions. The evolving structure in these F127 solutions (with and without MP) will be further examined using time-resolved SAXS on the X10A beamline at Brookhaven in June 2010 by heating these solutions at controlled rates using a hot stage. A more refined microstructural evaluation of triblock copolymer dynamic ordering will lead to a better understanding of both the driving force and kinetics of association of amphiphilic copolymers in solution.

Thursday 9:20 O’Keeffe/Milagro SA30

The mathematics of myth: Yield stress behavior as a limit of nonmonotone constitutive theories

Michael Renardy
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We formulate a model which can describe fluids with a nonmonotone shear stress / shear rate relationship. It is shown how yield stress fluids arise as a limiting case of such a model. Differences between critical stresses for “fast” and “slow” yielding, hysteresis phenomena and thixotropy are naturally explained by the model.

Thursday 10:20 O’Keeffe/Milagro SA31

Microscopic nature of yield stress

Oleg Verbitsky and Daphne Weihs
Faculty of Biomedical Engineering, Technion-Israel Institute of Technology, Haifa, Israel

Yield stress is a complex macroscopic phenomenon, which is still being heavily debated and not well-understood on any scale. Many cross-linked gels have been shown to exhibit a resistance to applied stresses up to a critical value, the yield stress, above which they exhibit flow. While the breakage of cross-links may explain the resistance, the exact microscopic origin of the yield stress is still unknown. In gels, and especially in biological gels, the local structure is heterogeneous and can vary with time, thus making localized measurements crucial. We explore the microscopic nature of yield stress in polymeric gels using microrheology to measure flow phenomena on a micron scale in polymeric gels.

We compare and contrast particle-tracking microrheology data with classical, macroscopic rheology of yield-stress gels. In addition, we use controlled on-microscope-stage perturbations to study the dynamics of yielding in gels. Transient gel disruption is achieved by applying using low-intensity ultrasound, which produces sample-wide effects. Those experiments provide enhanced time-resolution of the gel response and allow us to evaluate break-down and recovery of yielding structures, revealing not only local changes in structure but local gel dynamics as well. We present data showing Maxwell-like dynamics as well as sub-diffusion within a local trap in different gels. In addition, the response following perturbation provided an indication of local, structural dynamics.

Thursday 10:45 O’Keeffe/Milagro SA32

Large amplitude oscillatory shear and elastic wave propagation in the VCM model for wormlike micellar solutions

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The VCM constitutive model (Vasquez, McKinley, Cook, J. Non-Newtonian Fluid Mech.,44(2007)) successfully describes steady and transient flows of entangled micellar solutions for a number of different deformation histories (including steady and transient shearing and also extensional deformations). The VCM equations are derived from network theory and describe the coupled evolution of two micellar species. They incorporate the scission/reforming of the elastically active network “segments”, thus mimicking many features of wormlike micellar solutions. In a shear-rate controlled flow, (for example cylindrical Taylor-Couette flow) the initially homogeneous flow loses stability beyond a

critical deformation rate and develops shear bands with a high shear rate band forming near the interior (moving) wall, and a low shear rate band forming towards the outer (stationary) wall.

In this talk, the behavior of the (inertialess) VCM model is examined in Large Amplitude Oscillatory Shear flow (LAOS). The LAOS predictions for the two species model are compared with those of a limiting case (corresponding to a single entangled species in a viscous solvent). Comparisons are made through the use of Pipkin diagrams and Lissajous figures of the resultant flow states observed. With the addition of inertia to the governing equations an elastic wave propagates through the sample. This elastic wave can perturb the inertialess steady state (base) flow sufficiently that multiple interacting bands, as opposed to two uniquely-determined shear bands, are possible. The critical value of the Elasticity number leading to different banding structures will be discussed.

Thursday 11:10 O'Keeffe/Milagro SA33

Simultaneous velocimetric and rheometric (RheoPIV) study of the yielding and slip behavior of gels

Christopher J. Dimitriou[1], Gareth H. McKinley[1], and Ramachandran Venkatesan[2]
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In this talk, the rheology of two widely-distinct yield stress gels are studied in order to understand the connection between bulk yielding behavior and the evolution of local heterogeneities within the gel under an imposed shear stress or shear rate. This is accomplished through the use of a RheoPIV system that utilizes Particle Image Velocimetry (PIV) to visualize local velocity fields within a sample that is simultaneously undergoing shear in a rheometer test cell.

The first gel that is studied is a model wax-oil system that exhibits rheological behavior similar to waxy crude oils. The experimental protocols that have been developed for flow assurance rheometry are described here - specifically how we combine localized measurements of wall slip and instantaneous deformation fields (using seed particles and PIV techniques) to complement bulk rheological measurements. The RheoPIV system is used to study model wax-oil systems when cooled to temperatures below their wax appearance temperature (WAT) to form a gelled state. RheoPIV Measurements under steady shearing conditions show complex spatiotemporal dynamics in the evolution of the observed velocity field. These dynamics are due to a breakdown of solid gel fragments over time.

The second gel that is studied is a carbopol microgel. The carbopol gel is a more idealized yield stress fluid that exhibits no thixotropic behavior. However, like the model wax-oil system, the carbopol gel can yield either through the mechanism of interfacial slip, or bulk deformation. We carry out a detailed study of the slip behavior of the carbopol gel, by imposing steady and oscillatory stresses on the gel and directly observing the slip behavior. Measurements of instantaneous velocity fields under oscillatory stress indicate that the carbopol exhibits a dynamic slip behavior that depends on both the stress and its rate of change, whereas the slip behavior under steady shear can be approximated using a slip constitutive law that relates slip velocity to shear stress.

Thursday 11:35 O'Keeffe/Milagro SA34

Elasto-viscoplastic model for thixotropic liquids

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It was shown in a previous publication (J. Non-Newtonian Fluid Mech. 164 (2009) 66-75) that the main non-Newtonian effects observed in thixotropic liquids are well predicted by a model that employs a scalar structure parameter in conjunction with a Maxwell model whose parameters depend on the structure parameter. Here it is shown that the inclusion of a retardation time on the stress equation further increases the predictive capability of the model. The new model involves two evolution equations, a Jeffreys-like one for the stress and the other for the structure parameter. Simple ideas are employed to describe the microstructure, and, as a result, a model with a clear physical basis is obtained. In addition to the flow curve, which by construction is exactly predicted, it is shown that the model is able to predict correctly the behavior observed in the usual rheometric transient flows, among which: abrupt changes in shear rate (microstructure buildup or breakdown experiments); abrupt changes in shear stress (viscosity bifurcation experiments); and oscillatory tests (amplitude sweep and frequency sweep). Even rather complex thixotropic effects are also faithfully predicted, such as the shear rate overshoot observed in constant-stress experiments with pre-sheared samples, reported in J. Rheol. 46 (2002) 573-589. The model is frame-indifferent and applicable to complex flows.

Symposium GR
General Rheology

Organizers: Jacinta C. Conrad and Jian Wang

Thursday 8:05 Kearney GR5

Rheology of Ziegler-Natta and metallocene high-density polyethylenes: Broad molecular weight distribution effects

Mahmoud Ansari[1], Savvas G. Hatzikiriakos[1], Ashish M. Sukhadia[2], and David C. Rohlfing[2]
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The linear viscoelastic properties of two series of Ziegler-Natta and metallocene HDPEs of broad molecular weight distribution (MWD) have been studied. Correlations between zero shear viscosity and molecular weight and molecular weight distribution show that the breadth of the molecular weight distribution (MWD) for m-HDPEs plays a significant role. Other interesting correlations between the crossover modulus and steady state compliance with MWD of both these classes of polymers have also been derived. Finally, the steady-shear viscosities from capillary rheometry are compared with LVE data to check the applicability of the empirical Cox-Merz rule. It is shown that the original Cox-Merz rule is applicable for ZN-HDPEs, while it fails for m-HDPEs. A theoretical Cox-Merz correction proposed by Milner (J. Rheol, 40, 303-315, 1996) seems to apply in the case of m-HDPEs. Keywords: Ziegler-Natta HDPE, metallocene HDPE, Cox-Merz rule, molecular weight distribution, Zero shear viscosity.

Thursday 8:30 Kearney GR6

Transient rheology of long glass fibers in a polymeric matrix

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The purpose of this research is to understand the transient fiber orientation and the associated rheology of long glass fiber (> 1mm) reinforced polypropylene, in a well-defined simple shear flow, to extend the results and knowledge gained from these fundamental experiments to the use of simulating (more complex) molding processes. Specifically, we are interested in associating the rheological behavior of glass fiber reinforced polypropylene with the transient evolution of fiber orientation in simple shear flow in an effort to ultimately model fiber orientation in complex flow. A sliding plate rheometer was designed to measure stress growth in the startup and cessation of steady shear flow. Two fiber orientation models were investigated to predict the transient orientation of the long glass fiber system. One model, the Folgar-Tucker model (FT), has been particularly useful for short glass fiber systems and was used in this paper to assess its performance with long glass fibers. A second fiber orientation model, one that accounts for the flexibility of long fibers as opposed to rigid rod models commonly used for short fibers, was investigated and results were also compared with experimentally measured values of orientation. The accuracy of these models, when used with the stress tensor predictions of Lipscomb, was evaluated by comparing the model predictions against experimental stress growth data. Samples consisting of 10% wt. glass fiber in polypropylene with an average fiber length of 4 mm were prepared with random initial orientation and were sheared at different rates. Model predictions showed that fiber flexibility has the effect of retarding transient fiber orientation but provides poor rheological predictions with the chosen stress model. Additionally, it was shown that the predictions of the Folgar-Tucker model are not able to capture the dynamics of neither the orientation evolution nor the stress growth evolution that was measured experimentally.

Thursday 8:55 Kearney GR7

Changes in xanthan rheology and drag reduction with solvent conditions

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An understanding of the rheology of polyelectrolyte solutions in various solvent conditions is critical to their efficient use in industry. Xanthan concentrations ranging from dilute to concentrated in both water and salt solution are studied using oscillatory and shear rheology. In salt free solution, the scaling of xanthan viscosity with concentration agrees well with theoretical predictions. Three critical concentrations (c*, ce, and cD) marking changes in the viscosity scaling behavior in water are determined. In 50 mM NaCl, the viscosity scaling is well described by theory for a neutral polymers and two critical concentrations (c*, ce) are observed. As expected for polyelectrolytes, the viscosity of xanthan is observed to decrease significantly upon addition of salt for concentrations in the semidilute unentangled regime. However, for xanthan concentrations above cD, the zero shear rate viscosity increases by a factor of four in the presence of 50 mM NaCl. Similar increases in viscosity upon addition of salt are measured for several other polyelectrolytes (HPAM, Carrageenan, Welan). When the sizes of the added salt cations are changed, the larger salt cations produce a greater increase in the viscosity for xanthan concentrations above cD. For ions of similar size and differing valency, the divalent salts produce a higher viscosity than the monovalent salt. Ionic bridging between polyelectrolyte chains is hypothesized to account for the higher viscosity for the divalent salts. In turbulent pipe flow, drag reduction effectiveness increases with increasing xanthan concentration for the homogeneous case. Measurable reduction in the drag is achieved for xanthan concentrations as low as 20 ppm. When an entangled stock solution is diluted to 60 ppm (dilute regime), the drag reduction is significantly higher than the homogeneous

case. This increase in drag reduction effectiveness is hypothesized to be caused by residual entanglements resulting from the stock solution dilution.

Thursday 9:20 Kearney GR8

Rheological and optical models experimental investigations of encapsulation defects in coextruded multilayer polymers

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The aim of this work has been to gain a fundamental understanding with rheological and optical tools of the mechanisms governing encapsulation in the coextrusion process. Model polymers and commercial materials of varying viscosities and structures were investigated. The study rendered it possible to decouple the influence of viscoelastic parameters, thereby highlighting a number of macroscopic effects that were governed by the interdiffusion of macromolecular chains at the interface. The model polymers were based on poly (dimethylsiloxane) of varying molar masses. The encapsulation of two drops or melt particles placed in close vicinity of each other was monitored with a CCD camera at regular intervals time. The effects of viscosity, surface tension and relaxation time on the sintering kinetics were discussed. The coupling between rheological and optical studies showed that the viscosity of the material was a key parameter and that it had a considerable influence on the kinetics of coalescence. Industrial materials based on PVDF/PMMA, which were completely miscible and fully characterized, were selected. The kinetics of coalescence were assessed at several temperatures (i.e., viscosity ratios) and compared to the kinetics of coalescence of PVDF/PVDF and PMMA/PMMA. The observed development represented the signature of the kinetics of diffusion where the macromolecular chains intertwined and gradually became replaced by a more robust interphase. Finally, the same approach was applied to functionalized polymers. Two pairs of reactive polymers at interfaces based on PE-GMA (glycidyl methacrylate)/PVDF-g-AM (maleic anhydride) as well as a non-reactive material at an interface based on PVDF/PE were selected. The results of an optical investigation of the coalescence kinetics of two drops corroborated those obtained through rheology of the bilayer systems. The observed phenomena and the results were analyzed based on the physicochemical mechanisms involved in the diffusion/reaction interfaces.

Thursday 10:20 Kearney GR9

Is there a relation between the relaxation time measured in CaBER experiments and the first normal stress coefficient?

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We investigate a variety of different semidilute polymer solutions in shear and elongational flow. The shear flow is created in the cone-plate-geometry of a commercial rheometer. We use capillary thinning of a filament that is formed by a polymer solution in the Capillary Breakup Extensional Rheometer (CaBER) as an elongational flow. We compare the relaxation time measured in the CaBER with relaxation times based on the first normal stress difference and the zero shear polymer viscosity that we measure in our rheometer. All of these three measurable quantities depend on different fluid parameters - the viscosity of the solvent, the polymer concentration within the solution, and the molecular weight of the polymers - and on the shear rate (in the shear flow measurements). Nevertheless, we find that the first normal stress coefficient depends quadratically on the CaBER relaxation time. Several scaling laws are presented that could help to explain this empiric relation.

Thursday 10:45 Kearney GR10

Torsional flow of viscoelastic polymer solution over soft materials

Neelamegam Raju and Shankar Vishwanathan
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Flow instabilities happen all around us in both desirable and undesirable situations, but an in depth understanding still bewilders us. In viscoelastic solutions wherein the fluid inertia is negligible, the elasticity of the polymer solution drives a plethora of instability modes. In this work we investigate the elastically driven instability of a viscoelastic polymer solution over a rigid base and a soft gel. A rheological flow experiment is carried on a polymer solution between torsional plates with varying values of shear rate. It gives rise to various instability modes from base flow to elastic turbulence, a manifestation of the time dependent change in viscosity. When the polymer solution is placed over a soft gel the time dependent flow structures become non existent. Similar instability modes do exist when the polymer solution is placed over a high modulus gel. We postulate that the instability observed between rigid surfaces is suppressed when there is flow of a polymer solution past soft gel. We supplement our rheological observations with flow visualization and FFT to provide a molecular level analysis of the flow structures.

Thursday 11:10 Kearney GR11

Sound propagation in a vibrating bed of granular material

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An experimental device is used to examine sound propagation in an oscillating bed of granular material. Several authors have examined the effects of vertical and horizontal vibrations in granular materials (see for example ref.1). Several flow patterns may appear, which include heaping, arching, small amplitude suface waves, large amplitude surface waves and convective cycles rotating in opposite directions together with lateral waves. Furthermore, the basic parameters involved in the above cases are a dimensionless acceleration parameter involving the frequency and amplitude of oscillations with the acceleration of gravity and a dimensionless number of layers of granular material. The present paper examines the superposition of sound waves upon the flow patterns mentioned above. Since the sound waves will follow the path of less resistance, the propagation will be modified for each type of vibration; therefore, attenuation may be increased or decreased, with a possibility of a resonance frequency appearing in a re-circulatory motion. These effects will be presented and analyzed.

References: 1. Jaimes.J.,Joseph,G.G.,Herrea-Velarde,J.R.,Geffroy,E.&Mena,B., Rev.Mex.Fis. 48 (6) (2002).

Thursday 11:35 Kearney GR12

Rheological tracking of phase separation kinetics in block copolymer solutions

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The manner in which solvent is removed during the solution-casting of block copolymer films has a significant influence on the polymer morphology in the final film due to both thermodynamic and kinetic effects, which in turn governs film properties. While scattering and microscopy are useful in studying the preferred ordered structures formed during drying, rheology has proven to be a valuable tool for tracking ordering kinetics of block copolymer systems. However, a majority of the work concerning phase separation has focused on monitoring the constant-concentration ordering kinetics following shallow temperature quenches through the order-disorder transition. In order to better understand the phase separation of solution-cast films, it is important that the ordering during a drying process as the film transitions through various concentrations be understood. This work is aimed at demonstrating the efficacy of rheology in tracking phase separation in block copolymer solutions, and applying this technique to monitoring the ordering kinetics as solution-cast films are isothermally dried from the dilute form. At the present time, the kinetics of films cast from polystyrene-b-polybutadiene or polystyrene-b-polybutadiene-b-polystyrene, solutions in solvents of varying selectivity are being studied. In addition to rheological measurements, microscopy has been used in conjunction with small angle x-ray scattering to determine the phase diagram and confirm the growth of ordered structures during drying of SB and SBS solutions. In-situ SAXS measurements have also been made during the drying process to enhance the understanding of the growth mechanism and rheological data.

Thursday 12:00 Kearney GR13

Effect of drop size distribution shape upon emulsion stability

Ian M. Klink, Robert L. Powell, Ronald J. Phillips, and Stephanie R. Dungan

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A discretized population balance has been developed utilizing the moving pivot technique in order to understand effects of the droplet distribution shape upon the dispersion stability. Simulations show that the rate of shear-induced coalescence is independent of average drop size, and depends only upon the shape of the distribution. Monodisperse systems show the fastest rate of coalescence. Lognormal and step distributions show decreases in the rate of coalescence up to 75% and 25%, respectively, with increases in the width of the distribution. Multimodal distributions show intermediate decreases in the rate of coalescence with increases in the width. Furthermore, since the rate of coalescence is a function of the shape of the drop size distribution, improving the resolution with which the drop size distribution is measured can substantially increase the observed rate of coalescence. Measurements of the evolution of the droplet size distribution which fail to capture drops at the upper end of the size range, due to limitations in the measurement technique, can seriously underestimate the coalescence rate. This is the case even when the majority of droplets are still within the measurement window. At long times, systems undergoing Brownian and shear aggregation approach time-independent, self-similar distributions, though the asymptotic distribution shapes for each mechanism are fundamentally different. Brownian systems approach a bell-shaped form with a well-defined average size, while shear systems evolve towards a distribution that is a monotonically decreasing function of droplet size, with no such 'characteristic' size. Other distributions undergoing shear aggregation retain 'fingerprints' of the initial distribution at small drop sizes even as the rest of the distribution approaches the long-time asymptotic behavior.

Poster Session

Symposium PO
Poster Session

Organizers: Anne M. Grillet and Ali Mohraz

Wednesday 5:30 Sweeney E-F PO2

The rheology of cellulose suspensions: Nanocrystalline cellulose (NCC) and conventional wood pulp fibre suspensions

Sadaf Shafiei-Sabet[1], Babak Derakhshandeh[1], Wadood Y. Hamad[2], and Savvas G. Hatzikiriakos[1]
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Cellulose is the main constituent in woody plants and the most renewable bioresource and therefore the development of advanced fiber products based on wood pulps is of great interest. Cellulose fibers can be disintegrated into substructures by sulphuric acid hydrolysis which results in fully crystalline rod-like particles termed nano-crystalline cellulose (NCC). The NCC particles have anionic surface groups which lead to electrostatic stabilization of the NCC suspensions. These particles are able to form chiral-nematic liquid crystal phases above a critical concentration. All these properties combined with biocompatibility, non-toxicity and biodegradability make NCC a very promising material for nanotechnology. The rheology of NCC suspensions at different concentration have been investigated in this work and the rheological properties have been correlated with the microstructure. The shear dependence viscosity profiles of the studied NCC suspensions show model behaviour for liquid crystalline polymers (two shear thinning regions at very low and high shear rates separated by a plateau at intermediate shear rates). The effects of ultrasonic treatment on the rheological behaviour of these suspensions have also been studied, showing a viscosity drop which has been found to be concentration dependant. The rheological behaviour of NCC suspensions at different concentration has been compared with those of conventional wood fiber suspensions. Both suspensions exhibit yielding and shear thinning behaviour. Yield stress is found to be increasing more rapidly in NCC suspensions as a function of mass concentration compared with that of wood fibre suspensions.

Wednesday 5:30 Sweeney E-F PO3

The constant shear stress rheology of concentrated colloidal dispersions

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The Brownian contribution to the suspension stress depends solely on the particle configuration and the intrinsic hydrodynamic interactions among the constituent colloids. As the hydrodynamic contribution to the stress is linearly and instantaneously proportional to the material rate of strain, the rheology of suspensions deformed at constant shear stress may be probed by varying the rate of strain relative to the difference between the constant, applied shear stress and the resultant Brownian stress. Accelerated Stokesian dynamics simulations, using a new log-linear algorithm for computing the Brownian forces on the colloids, are employed to compute the rheology and shear-induced diffusivity of concentrated colloidal dispersions. Unlike constant strain rate simulations, this approach makes the sub-yield stress behavior of concentrated dispersions directly observable. Additionally, this approach offers statistical and computational advantages over the usual constant strain rate simulation methodology.

Wednesday 5:30 Sweeney E-F PO4

Shear thickening of chemical mechanical polishing slurries using high shear rheology

Nathan C. Crawford and Matthew W. Liberatore
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Chemical Mechanical Polishing (CMP) is a fundamental technology used in the semiconductor manufacturing industry to polish and planarize a wide range of materials for the fabrication of logic devices, memory chips, and other microelectronic-mechanical devices. The CMP slurry is a mixture of a colloidal abrasive, a carrier liquid (usually water) and active chemicals that attack the material to be removed. During the polishing process, it has been estimated that the slurry will undergo shear rates in excess of 10^6 s^{-1}. Under this extreme shear environment, it is hypothesized that individual slurry particles begin to interact and collide with one another forming large aggregates (> 0.5 μm), called hydroclusters. These hydroclusters cause the slurry to portray solid-like behavior leading to the formation of defects such as scratches, gouges, pits, and corrosion during polishing. On the order of 10-15% of failed integrated circuits can be linked to CMP induced defects which is estimated to be $4.5 to $9 billion of lost production per year. Our overall effort seeks to obtain a detailed understanding of the high shear rheological behavior of CMP slurries as well as changes in particle characteristics, both temporary and permanent. Utilizing high shear rheology to mimic the CMP process, the goal is to correlate shear thickening of the CMP slurry to the formation of aggregates (or hydroclusters). The slurries of interest are a highly concentrated fumed silica suspension in water with added KOH buffer. A controlled stress rheometer with a

parallel plate geometry at small gaps measures the non-linear rheological responses of the high solids slurry. Rheo-optical techniques will be used to identify the formation, shape, and size of hydroclusters generated under shear.

Wednesday 5:30 Sweeney E-F PO5

Mixing and segregation of particle suspensions in 2D chaotic flows

Bu Xu and James F. Gilchrist
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This work simulates segregation of non-colloidal particle suspensions in a two dimensional time-periodic flow. Two different mixing protocols having alternating moving boundaries in a cavity known to generate chaotic advection with the same energy input rate are applied to the suspension. A diffusive flux model is used to capture the essence of shear-induced migration. In this system, fluid deformation drives both mixing and segregation where the local rheology is a function of particle volume fraction. The impact of flow topology and shear migration are investigated. As a result of the complex interplay between these two aspects, the concentration profile ranges from that representing the underlying topology to that of steady flow in a lid-driven cavity, depending on the strength of mixing versus migration. In this system, increasing the size of chaotic regions does not result in enhanced mixing. These results challenge conventional wisdom in designing small-scale flows for mixing and separation in micro-scale applications.

Wednesday 5:30 Sweeney E-F PO6

Mesoscopic coarsening of colloidal gels due to shear

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At intermediate volume fractions, colloids with short ranged attraction form a gel; a percolated network structure with a finite yield stress. Colloidal gels are encountered in drug delivery systems, food products, cosmetics, paints, coatings and more. The long time response of such systems can show catastrophic delayed yielding in both shear and compression. The structure of this gel can be described on a single particle, mesoscopic strand, or macroscopic length scale. Herein we explore the role of mesoscopic ordering due to simple shear on the strength of colloidal gels with simultaneous confocal microscopy and rheology. To achieve this we built a rheoconfocal with a couette geometry, allowing us to image the shear plane quickly and directly. We find that a large anisotropy develops within the gel structure making it highly susceptible to fracture in one direction. We also find that the macroscopic elastic modulus does not significantly change during this anisotropic ordering while yielding is greatly affected. These results suggest that the mesoscopic, not just the individual particle interactions, define the macroscopic behavior of colloidal gels.

Wednesday 5:30 Sweeney E-F PO7

Guided motion of self-propelled magnetic colloidal particles by Brownian dynamics simulations

Glenn C. Vidal-Urquiza, Carlos Rinaldi, and Ubaldo M. Córdova-Figueroa
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Self-propulsion of artificial nano- and microscale objects by the transformation of chemical energy into motion is one of the most fascinating and exciting challenges currently studied. Intense investigations about this have been developed due to their potential appliation in diverse areas of nanotechnology. However, it has been shown in recent experiments that autonomous motion of the so-called ‘catalytic’ motors is hindered by their rotary Brownian motion and thus preventing its potential to be fully realized. On the other hand, such limitation could be relaxed with colloidal particles sensitive to external magnetic fields. The present study investigates the short and long-time diffusive behavior of a catalytically driven ‘magnetic’ colloidal particle immersed in a dispersion of reactant particles subject to a magnetic field using Brownian dynamics simulations. The strength of the magnetic field is controlled by the Langevin parameter, which physically measures the relative importance of magnetic to Brownian torques, and dictates the spatiotemporal behavior of the particle. The rotational and translational self-diffusivity is measured for different surface reaction speeds, particle sizes, reactant particle concentrations, magnetic dipole orientations, and Langevin parameters. Finally, a theory to determine the long-time self-diffusivity and time-averaged particle velocity is developed and compared to the simulation results.

Wednesday 5:30 Sweeney E-F PO8

Studies on spreading of suspensions on solid substrates

Jeongin Han[1], Hongrok Shin[1], Chongyoup Kim[1], and Seong Jae Lee[2]
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In most printing processes ink drops, particle laden fluids, spread and dry on solid surfaces of differing contact angles. Even though there have been many studies on the contact line movement of pure liquids, studies on the capillary spreading of suspensions on solid surfaces are rare until now. In this research, the capillary spreading of suspension drops on solid surfaces was investigated experimentally. The suspension was prepared by dispersing spherical particles of polystyrene in glycerin. A 30µL drop was placed on the solid surface and observed the capillary spreading from side. Both the contact angle and contact line speed were extracted through the image processing technique. Parametric studies were performed by varying the size of particles (0.35 - 5.7µm, mono-disperse), particle loading (0 - 0.3) and wettability of the surface (amine and OTS treated surfaces). The experimental result shows that the Hoffman-Tanner-Voinov model (Capillary number=$\kappa(\theta^3 - \theta_{eq}^3)$; κ: a constant) held as in the case of pure liquid. As particle loading increases κ increases. κ value for the suspension of particle loading of 0.01 was larger than that of pure liquid. It was observed that particles were aligned along the contact line and the liquid drained out of the suspension forming a wedge-shaped particle-free region between the contact line and aligned particles.

Wednesday 5:30 Sweeney E-F PO9

Complex behaviors of alumina suspension in a modified capillary rheometer

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Rheological properties of suspension is normally measured by conventional rotational rheometers. However they have limited range of shear rates to be applied, and are not suitable for highly concentrated suspension system. Therefore a newly-designed rheometer is needed to overcome these shortcomings. In the present study a commercial capillary rheometer(RH7; Malvern Instrument) was modified to examine rheological characteristics of highly concentrated suspension especially at high shear rates. Model system was alumina suspension with different concentrations and pH's. Silicone oil was also adapted as Newtonian fluid for comparison. Resultant data at low shear rates were in good agreement with those obtained from rotational rheometers(ARES & AR-G2; TA Instrument). Higher shear rates measurements were then available by using this modified capillary rheometer. It was also designed to observe, in real time, fluid motion of concentrated suspension in a transparent capillary. PMMA or cupper particles were injected as a tracer for visualization and results exhibited complex behaviors of shear flow such as yielding, jamming, and shear banding even though only simple shear was applied. Pressure fluctuation was monitored and analyzed to interpret flow instabilities, and also effects of concentration and pH on the pressure was demonstrated. We suspect that these are attributed to microstructure of concentrated suspension.

Wednesday 5:30 Sweeney E-F PO10

Hyper-aging dynamics of aqueous Laponite-polyethylene oxide suspensions

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When a jammed colloidal system is subjected to a stimulus, the response generated is not only dependent on the time (t) for which the stimulus is applied but also on an aging time (or waiting time) of the sample. Such behavior causes failure of time - translational invariance. In this work we have used aqueous Laponite-PEO suspension, which shows strong time dependent evolution of its physical properties. We carried out creep time - aging time superposition on this material to get dependence of relaxation time on waiting time as a function of time elapsed since preparation of the sample. We observe that the relaxation time shows exponential dependence on aging time in the liquid regime where $G'' > G'$. When the system enters glassy regime ($G' > G''$), relaxation time shows hyper-aging behavior with power law dependence on aging time having coefficient of 6. The dependence of relaxation time on aging time becomes weaker for the experiments carried out on a later date since preparation eventually showing a linear dependence 80 days after preparation. Interestingly we observe qualitative agreement between the predictions of general linear viscoelastic model for aging materials and the creep behavior of Laponite-PEO suspension showing hyper-aging dynamics.

Wednesday 5:30 Sweeney E-F PO11

Rheological behavior and microstructures of concentrated particles gels

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In this work we show the influence of microstructure on the rheological and mechanical properties of highly concentrated colloidal particle gels. By using an in-situ mechanism based on enzyme-catalyzed internal reactions, we are able to form gels of highly concentrated particles, without disturbing the microstructures that develop during the gelation process. These gels can be produced by two different destabilization mechanisms: Either the pH of the suspension is shifted towards the isoelectric point (Δ pH-method), or the ionic strength of the suspension is increased at a constant pH (Δ I-method). The two destabilization mechanisms lead to gels of significantly different rheological behavior and microstructure. Results suggest an increase of elastic and yield properties of concentrated particle gels with decreasing homogeneity of their microstructures.

Wednesday 5:30 Sweeney E-F PO12

Atomization characteristics of impinging jets of gel material containing nanoparticles

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In this study, we investigated the spray behavior and the mean diameter of drops to characterize the doublet like-on-like impinging jet atomization (orifice diameter=0.7mm, impinging angle, $2\theta=90°$) of water and water-base Carbopol gels with or without SUS nanoparticles. The spray patterns of gel materials had four different types and the "rimless sheet with ray shaped shedding" was the unique pattern which did not appear in the Newtonian fluids like water. Under the equilibrium condition, the ratio of the maximum length to the maximum width of sheet was different for water (2.1) and for two gel materials (1.7). The sheet sizes of the water and the pure Carbopol gel increased with increase in jet velocity, but sheet size did not change in the case of the Carbopol gel containing SUS particles. Due to the high viscosity of gel materials, the

amplification of sinusoidal wave was mitigated and, consequently the spreading angle toward the perpendicular direction of the sheet was lower compared with the angle for water. The drop SMD (Sauter mean diameter) obtained from the Rosin-Rammler distribution decreased with the increase in jet velocity and it converged to an asymptotic value for the materials tested here. The asymptotic SMDs of water and Carbopol gels were 100 and 75 - 77 microns, respectively. The addition of nanoparticles did not affect the asymptotic SMD, but the jet velocity at the asymptotic condition decreased with the addition of nanoparticles.

Wednesday 5:30 Sweeney E-F PO14

Physical aging of colloidal glasses after concentration jumps

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For our experiments, we synthesized particles comprised of PS (polystyrene) cores, and the shell composed of a highly swellable or thermosensitive polymer, cross-linked PNIPAAM (poly-N-isopropylacrylamide). After drying under high vacuum, PS-PNIPAAM samples are suspended in water, and the particles had an average core diameter of 283nm and 13nm thickness of thin layers by conventional transmission electron microscopy (TEM), with a size polydispersity of about 6.2%, and 5.5% respectively. However, the diameter of particles is about 430nm by dynamic light scattering (DLS) in water at ambient temperature. The size by transmission electron microscopy is smaller than that by dynamic light scattering is due to shrinkage of the layers during conventional TEM. The thermosensitive particles undergo shrinkage with increasing temperature and we use this feature to perform “concentration jumps” with the PS-PNIPAAM colloidal dispersions in the vicinity of the concentration glass transition. Subsequent to the concentration jump, we perform measurements of the linear viscoelastic response ($G(t,t_e)$; $G'(\omega,t_e)$; $G''(\omega,t_e)$) of the colloidal system in a way that we monitor the state of the non-equilibrium glass as a function of the aging time t_e. The results are compared with those expected in the Kovacs’ catalogue of experiments in structural recovery of glassy polymers, viz., intrinsic isotherms, asymmetry of approach and memory events [1].

[1] A.J. Kovacs, Fortschritte der Hochpolymeren-Forschung, 3, 394-507 (1963).

Wednesday 5:30 Sweeney E-F PO15

Frequency and interaction dependence of yielding in microgel particles

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We investigate the yielding behavior of microgel suspensions in water, studied by bulk dynamic rheology. The interaction between the particles can be conveniently tuned from attractive to repulsive by varying the pH of the system from acidic to basic conditions. At elevated pH, under repulsive interaction, the microgel particles swell and show a high modulus. During the strain sweeps the system shows a single peak in the loss modulus during yielding. This is in sharp contrast to the situation at low pH where the system is under attractive conditions and has a smaller complex modulus due to partial collapse of the particles. Here, yielding occurs with a display of two peaks in the loss modulus. While the magnitude of the low strain peak is frequency independent, the high strain peak decreases in size in strain sweeps conducted at lower frequencies. We propose that these results may be considered in the framework of a two-step yielding mechanism as recently advanced for attractive colloidal glasses. In this context, systems with purely repulsive interactions show a single step yielding due to particle cage escape. Yielding is attended by increased viscous dissipation, manifest as a peak in the loss modulus. In attractive systems however, there is an additional peak at lower strains due to the breaking of bonds between particles which occurs in advance of full fluidization at much larger strains. The hydrodynamic versus thermodynamic origins of the dissipation account for the difference in the observed frequency dependence of the yielding signatures.

Wednesday 5:30 Sweeney E-F PO16

Kinetic characterization of a laponite-based photorheological hydrogel system

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Photorheological systems hold promise as functional materials allowing the *in-situ* modification of rheological properties via light illumination. These systems have an advantage over magnetorheological or electrorheological systems in that continued power is required in order to maintain their changed viscoelastic behavior, whereas a lasting change can be affected using a temporary exposure to light in a photorheological system. Sun *et al.* [1] have developed a system utilizing laponite nanoparticles and the photoacid generator (PAG) diphenyliodonium-2-carboxylate monohydrate. Here we have reported on the gelation kinetics of this system using PAG concentrations ranging from 5 to 20 mM, and UV intensities ranging from 100 to 150 mW/cm^2. We found that increasing PAG concentration sped up the gelation process, however an upper limit to this acceleration was observed between 13 and 20 mM. UV intensity was linearly proportional to the rate of gelation. In addition, we have completed a similar series of tests using a second PAG, (4-methylphenyl) diphenylsulfonium triflate, and have compared the efficacy of this new PAG against the old one. We observed that photogelation could be achieved using a lower concentration of the new PAG, indicating a greater activity or efficiency in causing the gelation to form. Further studies detailing the thermal sensitivity to the pH activity of these two PAGs are presented as the gelation process can be activated via either light or thermal stimuli. Despite the improved activity of the new PAG, there is still a significant lag time (a few minutes) between the start of illumination and the onset of gelation. Our work efforts are geared towards improving the efficiency of this system so that it responds more quickly to UV exposure.

[1] Sun et al. *Photogelling Colloidal Dispersions Based on Light-Activated Assembly of Nanoparticles.* Journal Of The American Chemical Society (2009) vol. 131 (20) pp. 7135-7141

Wednesday 5:30 Sweeney E-F PO17

Electrorheological response of dense strontium titanyl oxalate suspensions

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Strontium Titanyl Oxalate (STO) particles were synthesized using a new method of precipitating the STO water solution by adding alcohol. When dispersed in silicon oil, dense STO suspensions exhibit an extremely high yield static stress in the presence of an electric field (> 200kPa at 5kV/mm) at low current density. We also find that the yield stress increases roughly linearly with applied field. This behavior is a key characteristic of a polar molecule dominated electrorheological (PM-ER) effect. By reducing the STO concentration a crossover to the quadratic scaling known from regular ER fluids is observed. Heating the sample suppresses the magnitude of the PM-ER effect, suggesting that residual water content plays an important role in the performance. Additional rheological measurements reveal several aspects that are unusual for simple field-activated fluids. This includes a certain amount of time as well as history dependence, which manifests itself in stiffening under low shear and irreversible strength decrements after reaching a critical strain. In the field-activated state, there are indications of the creation of a thin (a few particles wide) shear band that might be responsible for some of the observed anomalies.

Wednesday 5:30 Sweeney E-F PO18

Static and dynamic polarized and depolarized light scattering from sepiolite suspensions

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Interest in nanocomposites utilizing anisotropic particles such as rods and plates is increasing due to the enhanced properties relative to spherical particles. Characterization of these particles of high aspect ratio presents additional challenges. Light scattering can be used to determine the average length of the rodlike sepiolite clay particles in aqueous suspension. As is typical of asymmetric particles, dispersion into individual particles is challenging. For this study, the sepiolite particles were dispersed in water by treating the surface with TSPP. The high quality of the dispersion was evidenced by the q^{-1} dependence of the light scattering intensity. The initial slope of the light scattering intensity as a function of the scattering vector q yields the mean square radius of gyration, R_g from which an average length can be determined. Dynamic light scattering yields the mutual diffusion coefficient, from which another average length can be determined. Although the optical anisotropy of the sepiolite particles is small, depolarized measurements could also be carried out. The angular dependence of the depolarized scattering yields a measure of R_g that is independent of the optical anisotropy. Dynamic depolarized light scattering yields the rotational diffusion coefficient, D_R, from which another independent measure of the rod length is determined. The nominal average length for the sepiolite studied here is about 1 micron.

Wednesday 5:30 Sweeney E-F PO19

Transient and oscillatory magnetorheology of dilute ferrofluids from Brownian dynamics simulations

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Ferrofluids, suspensions of magnetic nanoparticles undergoing translational and rotational Brownian motion in a non-magnetic carrier fluid, are a class of soft magnetic matter for which the viscosity and rheology can be modified through applied magnetic fields. Most prior theoretical and experimental work on the rheology of ferrofluids has focused on the steady state dependence of the suspension viscosity on magnetic field amplitude and rate of deformation. Here we report simulation predictions of the magnetorheology of ferrofluids under transient and oscillatory shear conditions. In the case of transient response to a step change in the magnitude of the shear rate it is found that the approach to steady state can be monotonic or oscillatory depending on the relative magnitudes of the magnetic field, shear rate, and particle rotational relaxation time. In the case of oscillatory shear the in-phase and out-of-phase components of the complex viscosity are found depend on the magnitude of the magnetic field and frequency of the shear wave, following a Debye-like model with characteristic time equal to the field-dependent rotational relaxation time of the nanoparticles. Both effects indicate an apparent elastic character to the rheology of these suspensions, even though they are seen in the dilute limit in which there are negligible particle-particle interactions and as such there is no chain formation. The simulated behavior is thus the result of the interplay of magnetic and hydrodynamic couples acting on the particles and the effects of thermal rotational motion.

Wednesday 5:30 Sweeney E-F PO20

Rheological characterization of a ferrofluid consisting of permanently magnetized nanoparticles

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Most ferrofluids, dilute suspensions of magnetic nanoparticles in non-magnetic carrier liquids, consist of magnetizable particles whose magnetic dipole can freely rotate and as such their magnetorheological behavior depends solely on chain formation due to particle-particle interactions. We have prepared and characterized ferrofluids consisting of magnetized particles whose magnetic dipoles are rigidly locked onto the particle. As a result of this, the rheology of these ferrofluids is affected also by hindered particle rotation resulting from a balance of hydrodynamic and

magnetic torques. For ferrofluids with low (~0.005) magnetic fraction but relatively high volume fractions (~0.2) we observe the usual magnetic field dependent shear thinning behavior associated with common ferrofluids. However, we also observe a magnetic field dependent yield stress of up to 10 Pa at magnetic fields of up to 0.4 T. Experiments under small amplitude oscillatory shear indicate a transition from viscous to elastic behavior at a critical magnetic field which depends on the frequency of the oscillatory shear. At low applied magnetic fields both moduli are independent of the magnetic field and increase with the frequency of the oscillatory shear. At high applied magnetic fields both the loss and storage modulus seem to asymptote to a power law dependence on the magnetic field magnitude.

Wednesday 5:30 Sweeney E-F PO21

Non-standard geometries for rheological characterization of complex fluids

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Traditional rotational rheometry has been dealing with ideal flow conditions (viscometric flows) using plate-plate, cone-plate or concentric cylinder geometries to characterize complex materials, preferably in the linear viscoelastic region. Complex fluids, however, are often difficult to measure under these conditions. Sedimentation during the test or slippage at the interface of the sample and tool has a significant effect on the results and reduces the accessible testing range of the instruments. Furthermore the flow is complex and the material behaves most of the time non-linear, the calculation of a true or representative deformation or deformation rate is an issue. Based on a Couette analogy for the mixing elements, average deformation and stress coefficients are determined which relate the motor rotation speed to the material deformation rate and the measured torque to the stress. With this experimental setup complex systems can be easily characterized and the processability determined and not only of foods, but also for a wide variety of materials including building materials, cosmetic creams and lotions. To prove the validity of the Couette analogy, flow curve and dynamic spectrum have been compared for some typical complex fluids like salad dressing and cosmetic cream with different types of non-standard flow geometries and the standard Couette.

Wednesday 5:30 Sweeney E-F PO22

New techniques for measuring very fast changes in materials using oscillatory rheometry

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Melting, crystallization and (UV-) curing processes can be followed by oscillatory rheological measurements since the build-up or break-down of a structure in the sample is reflected in the change of the viscoelastic properties (G', G", etc.) of that sample. The data gained from rheological measurements can be directly associated with the performance and properties of a product such as the melting, crystallization or curing time or the final strength of a material.

Monitoring changes in materials using standard oscillatory rheometry becomes very difficult if not impossible when these changes happen very fast, i.e. when the values of G' and G" change by several orders of magnitudes within a few seconds. This is because in a standard oscillation experiment the strain and stress sine wave data are sampled during exactly one oscillation period in order to calculate one rheological data point (G', G" etc.): At a constant frequency of 1 Hz the time between two data points is 1 s, at 10 Hz this is 0,1 s. This is obviously not fast enough for monitoring an UV-light induced fast curing reaction or the melting of wax which only takes a few seconds.

In order to be able to monitor such very fast changes in materials new techniques were developed which allow for a maximum data acquisition rate for the rheological data (G', G", etc.), in both controlled stress and controlled deformation mode, of 500 Hz, i.e. a time of 2 ms between to data points, independent of the oscillation frequency.

We will present details on the technical realization of the new techniques and show the experimental results of measurements on UV-curing materials as well as measurements of melting and crystallization processes.

Wednesday 5:30 Sweeney E-F PO23

Numerical investigation of the slotted plate rheometer for yield stress fluids

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The slotted plate rheometer has already been successfully applied to the rheological measurements for yield stress fluids (Zhu, et al. 2001). Using a Computational Fluid Dynamics (CFD) method, the flow structure and shear stress distributions of the slotted plate can be investigated numerically. The yield stress fluid is modeled by a modified Generalized Newtonian Fluid (GNF) model, with which the pre-yield material is treated as a highly viscous fluid instead of an elastic solid. The ‘slip length’ method is adopted for modeling wall slip boundary conditions. The steady state flow field is obtained by solving the 3-D incompressible N-S equations. Based on the simulation results, the plate edge and slot size effects are discussed. The results show that higher measurement accuracy can be reached by using a thinner plate with a sharper front edge since it can reduce the resistance caused by the front edge. Wall slip effects can be significantly reduced by opening slots on the plate and by increasing the slot number and slot area ratio, defined as the ratio of the slot area to the plate area. Our study provides a numerical analysis tool for optimizing such a novel rheometer design.

Wednesday 5:30 Sweeney E-F PO24

A microfluidic device for measurement of the apparent viscosity of non-Newtonian fluids

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Progress in micro-fluidics has created opportunities for studying the flow behavior of non-Newtonian fluids at micrometer scales in regimes not accessible by conventional rheometry. Here, we investigate the use of a microfluidic comparator technique for measuring the apparent viscosity of non-Newtonian fluids. In the comparator technique, a fluid with known properties is introduced in one microchannel and an unknown fluid in an adjacent connected channel. Varying the flow rate of the unknown fluid and balancing the interface of the co-flowing streams enables measurement of the apparent viscosity of the unknown fluid over a broad range of shear rates. As a first step we used Newtonian glycerol solutions which showed good comparison with conventional rheometery. Subsequently, the apparent viscosity of 10-1000 ppm of polyethylene oxide solutions were studied, and the microfluidic comparator showed that these solutions were shear-thinning consistent with conventional rheometry. Finally, the apparent viscosity of red blood cell suspensions of varying hematocrit were investigated in microchannels of different aspect ratios. Testing of these various fluids, enabled us to benchmark the sensitivity and limits of operation of this microfluidic viscometer.

Wednesday 5:30 Sweeney E-F PO25

Parallel superposition studies on paint using ARES G2 rheometer

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Paints are commonly used under a certain shear condition. Traditionally, the flow behavior and the viscoelastic properties of paint were investigated separately. To study the viscoelasticity of paint materials at the application shear conditions, a combined steady shear and oscillatory motions need to be applied to the sample simultaneously. It is challenge to use a controlled stress rheometer to perform this type of analysis because two individual closed loops (i.e. controlled rate and strain) are needed at the same time. The ARES G2 rheometer is a pure controlled strain rheometer. The motor can apply accurate shear rate and oscillatory strain simultaneously. The ARES G2 is the ideal rheometer to perform the parallel superposition studies on viscoelastic fluids such as paints.

Wednesday 5:30 Sweeney E-F PO26

Experimental and modeling protocols for a micro-parallel plate rheometer

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We present a new device, the Micro Parallel Plate Rheometer (MPPR), for viscoelastic inverse characterization. The device is designed to evaluate the role of linear and non-linear viscoelasticity in flow, and diffusive transport relevant to biological systems. In particular, we are interested in studying the cilliary transport of mucus in the lung. Inference of dynamic moduli, and onset of nonlinear harmonic generation, are based on a generalization of the Ferry-Sawyer-Adler shear wave model to finite depth samples, and nonlinear constitutive laws, given in [1-2]. We apply the method using a 5mg/ml Hyaluronic acid solution, at several applied strains and frequencies. Further mathematical analysis allows us to extend these experimental findings to different regimes within the parameter space. In addition, we investigate the effects of considering various non-linear constitutive models.

[1] Mitran et al J. Non-Newtonian Fluid Mech. 154, 120-135 (2008). [2] Lindley et al J. Non-Newtonian Fluid Mech 156, 112-120 (2009).

Wednesday 5:30 Sweeney E-F PO27

Correlation of wall slip and the second stress harmonic in Fourier space

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Slip is a phenomenon that appears in many high solid content food and personal care formulations. It is a phenomenon that can be characterized quite easily on a rotational rheometer by using smooth and serrated geometries and comparing the shear rate viscometry results. In the literature, it is suggested that by using LAOS, this slip can be characterized by an increase in the second stress harmonic in Fourier space. This paper investigates that claim for a commercial concentrated emulsion.

Wednesday 5:30 Sweeney E-F PO28

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

David J. Moonay

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

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

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

Wednesday 5:30 Sweeney E-F PO29

Survey of trends in the harmonic intensity with harmonic number

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FT Rheology analysis of Large Amplitude Oscillatory Strain testing relies on the ability to resolve the higher harmonic amplitudes of the stress response to a sinusoidal strain. While the entire spectrum of higher harmonic amplitudes is recognized as contributing importantly to the material response to deformation, the majority of applications of FT Rheology have relied primarily on the analysis of the third harmonic. This is due, in part, to the difficulty of accurately resolving harmonic signals beyond the third. Improvements in rheometer design have decreased the underlying noise in the deformation input and increased the sensitivity of the ensuing torque measurement. This enables improved resolution of those harmonics greater than the third. In order to facilitate treatment of higher harmonic data, unifying trends between the harmonic intensity and the harmonic number are desirable. Such trends have previously been identified for linear polymers. Additional classes of materials are examined for common behavior.

Wednesday 5:30 Sweeney E-F PO30

Large amplitude oscillatory strain (LAOS) testing on select materials with analysis by Fourier transform rheological methods

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In recent years, the use of Large Amplitude Oscillatory Strain (LAOS) as a way of characterizing structured materials has increased greatly. It is hoped that the LAOS approach can provide insights into the molecular architecture of materials that conventional dynamic testing cannot. Earlier usage of the LAOS method focused on variables such as the intensity ratios of the higher harmonics to the fundamental and the phase angle of the higher harmonics. Recent upgrades to commercially available software now enable us to obtain quantities such as the Fourier coefficients and the Chebyshev polynomial coefficients. The goal of the present work is to illustrate how the respective quantities are determined and to demonstrate the usefulness of the quantities that are now readily obtained with current software, such as the Chebyshev polynomial coefficients. Results on automotive sealants and viscoelastic liquids will be presented

Wednesday 5:30 Sweeney E-F PO31

Shear flow mediated elongational flow in soft glassy materials

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Soft glassy materials like gels, foams, colloidal suspensions, emulsions etc., possess non-equilibrium, three dimensional jammed structures. Application of a stress field on such materials leads to partial or complete un-jamming depending on the yield stress of the material. In this work, we study the deformation behaviour of thin films of such materials simultaneously subjected to the application of two creep flow fields, namely, constant shear stress and constant engineering normal stress fields. We find that when a shear flow field is imposed on an elongational flow field, a larger strain gets induced in the material at a given time. The magnitude of the strain increases with an increase in shear stress. Further, we observe that the strain response at lower normal stresses and higher shear stresses is similar to that at higher normal stresses and lower shear stresses. All the strain - time curves corresponding to different combinations of normal and shear stresses were found to have same curvature leading to a superposition upon horizontal shifting.

Wednesday 5:30 Sweeney E-F PO32

Evidence of time dependent behaviour in gels under LAOS

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LAOS (Large Amplitude Oscillatory Shear) is becoming an increasingly used technique for measuring many different types of samples, but not all sample types respond in the same way to the shear. In this work we studied commercially available gel networks to investigate the responses during large amplitude oscillation. The stress/strain Lissajous plots reached equilibrium within the first period of oscillation, but the Normal force/strain Lissajous plots showed a reduction in the normal force over consecutive periods of oscillation.

Wednesday 5:30 Sweeney E-F PO33

Large amplitude oscillatory shear (LAOS) of shear thickening fluids

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Shear Thickening Fluids (STFs) are concentrated colloidal suspensions that exhibit increases in viscosity under high shear rates of deformation. Recent research has moved toward exploiting the exceptional damping properties of STFs for use in applications such as personal protective armor, medical devices and sports equipment. These applications motivate a more fundamental understanding of the nonlinear rheological response of STFs under large amplitude oscillatory shear (LAOS) deformations. LAOS measurements are performed on a well-studied, model shear thickening colloidal silica dispersion (Kalman, D.P. et al., ACS Appl. Mater. Interfaces 2009, 1, (11), 2602-2612) and compared to steady shear. Lissajous-Bowditch diagrams are interpreted within the framework of our understanding of shear thickening under steady shearing. The nonlinear regime analysis as developed by Ewoldt et al. (Ewoldt, R.H. et al. J. Rheol. 2008, 52, (6), 1427-1458) enables us to quantify the instantaneous viscosities and elastic moduli throughout an oscillatory shear deformation cycle. Unlike the shear thinning regime, we observe a common "saturated viscosity" in the shear thickened regime over a range of frequencies. Analysis of the oscillatory stress response suggests maximal STF hydrocluster formation at zero strain and maximum shear rate over a deformation cycle. A basic understanding of an STF's oscillatory stress response is obtained, indicating this nonlinear regime analysis could be useful in further investigations of STFs under dynamic deformations. Finally, new methods of obtaining constitutive equation properties from LAOS experiments are demonstrated.

Wednesday 5:30 Sweeney E-F PO34

Characterization of yield stress and slip behavior of skin/hair care gels using steady flow and LAOS measurements and their correlation with sensorial attributes

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Gels made with three different polymers widely used as rheology modifiers in cosmetic formulations (Crosslinked poly(acrylic acid), crosslinked methyl vinyl ether/maleic anhydride copolymer, and crosslinked vinyl pyrrolidone/acrylic acid copolymer) were characterized by rheological and sensory evaluation methods to determine the relationship between sensorial perception and rheological parameters. Both conventional rheological characterization methods and a more recent method, Fourier Transform Rheology with Large Amplitude Oscillatory Flow data (LAOS), were utilized to characterize the material with and without wall slip. Sensorial analyses were implemented in-vivo to evaluate the perceived ease of initial and rub-out spreadability, cushion, pick-up, and slipperiness attributes of the gels. Results were statistically analyzed by analysis of variance (ANOVA), principle component analysis (PCA) and linear regression analysis. Sensory characteristics discriminated the three materials and PCA and linear regression analyses revealed that sensory attributes could be well predicted by rheological methods. Rheological experiments, without wall slip, revealed that gel strength in the linear viscoelastic region and yield stress of these materials are similar, but exhibit significantly different wall slip and thixotropy behavior in the low shear rate region under wall slip conditions. In particular, the rheological parameters and sensorial perception of 1% crosslinked vinyl pyrrolidone/acrylic acid copolymer are significantly affected by wall slip and/or thixotropy related shear banding phenomena.

Wednesday 5:30 Sweeney E-F PO35

Effect of mixing energy on the rheology and dewaterability of polymer flocculated mature fine tailings

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High-molecular-weight polymer flocculants are being used for dewatering of mature fine tailings (MFT) so as to reclaim containment ponds for terrestrial use. MFT is fines solids waste from hot water bitumen extraction process of the oil sands; suspended in 84% by volume water that won't be released by natural self-weight consolidation. Flocculation is undertaken so as to release the water by self-weight, as in rim-ditching, or as a feed for centrifuge dewatering. In stirred vessel mixing there is wide variation in the effective shear rate and inhomogenous mixture is produced owing to the shear thinning and yield stress of the flocs. Controlled mixing conditions are therefore needed to relate the rheological properties to dewaterability of flocculated MFT. A close-clearance, single-flight helical impeller was used as a tool in a rheometer. Newtonian and non-Newtonian samples were used to determine the cell constants. The flocculation were conducted as function of shear rate and mixing time. The dewaterability of these flocs were evaluated by capillary suction time (CST) method. The CST initially decreased and then increased with increasing mixing time. The inflection point of the CST was shorter at higher shear rates of mixing. However, the minimum CST were

superimposable when presented in terms of the mixing energy. The viscosity, shear yield stress and elastic modulus showed initial increase to a peak, followed by a decrease that then leveled to steady values. This trend reflects the actions the mixing initiates; from polymer spreading to finally shear thinning. The peak in these properties occurred at shorter mixing times than for well dewatering samples. This study proves that the unambiguous process control factor for generating a well dewatering polymer treated MFT is the mixing energy.

Wednesday 5:30 Sweeney E-F PO36

Jetting of low viscoelasticity low viscosity polymeric solutions

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This paper describes recent work concerning the way fluid viscoelasticity affects drop formation at an ink jet printhead and also filament break up mechanisms downstream of the printhead. A series of matched viscosity polymeric solutions were prepared with a solvent base as a mixture of diethyl phthalate, dioctyl phthalate and containing different concentrations of mono disperse polystyrene of molecular weight 110000 kg/kmol. High frequency viscoelastic measurements were performed using a piezo axial vibrator (PAV), that enabled the quantification of the linear viscoelasticity of the fluids at high frequency (1 hz - 10 khz). PAV data measurements showed the viscoelasticity of the fluid developed as a function of polymer loading with a Maxwellian like behaviour. Additional capillary filament thinning and breakup experiments were also carried out using a Cambridge "Trimaster" (CTM) filament stretching rheometer and this enabled transient extensional viscosity and break up data to be obtained. The jetting behaviour of the rheologically characterized fluids were compared using a Xaar 1001 printhead. High speed photographs of the jetting behaviour was recorded with a SLR camera using a nanoflash duration light for the illumination. The results demonstrate that there is a clear correlation between the viscoelasticity detected in the fluids and the jetting behaviour, whilst other factors, such as the base viscosity have been held constant for this series of fluids.

Wednesday 5:30 Sweeney E-F PO37

The sensitivity and stability of non-isothermal film blowing process

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Employing transient simulation technique in Hyun et al. (JNNFM, 2004), frequency response method has been applied in this study to investigate the sensitivity of nonisothermal film blowing process with respect to sinusoidal ongoing disturbances. Amplitudes of film thickness, bubble radius, and cross-sectional area at freezeline height to various sinusoidal disturbances (e.g., disturbances at flow rate, take-up velocity, cooling, air amount inside the bubble, etc) have been obtained, showing the resonance peaks along the frequency regime. It has been confirmed that frequency at the first resoant peak correspond to the imaginary part of the first leading eigenvalue from linear stability analysis. Sensitivity results in three multiple states exhibits somewhat different patterns. Also, effects of the process conditions such as drawdown ratio, blow-up ratio, cooling, fluid viscoelasticity on the sensitivity as well as the stability in this system have been scrutinized.

Wednesday 5:30 Sweeney E-F PO38

Rinsing of rheologically complex fluids

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The everyday act of rinsing a surface is often overlooked. Perhaps every time we touch water, rinsing occurs in one way or another. For our purposes, rinsing occurs when a jet of liquid (water) ablates another liquid coating a substrate. As the rinsing liquid progresses over the coating liquid, something peculiar occurs with certain coating fluids. Dubbed penetration, this is when the interfaces of the two liquids become indistinguishable. Recent research in the Fuller laboratory indicates that this phenomenon arises in viscoelastic fluids, and specifically in shear thinning fluids. To better understand this phenomenon of penetration, further research was undertaken. A rinsing transition potentially exists at a critical viscosity-ratio, where penetration into these coating fluids begins. To determine this viscosity-ratio, other factors must be held constant. The use of aqueous Newtonian solutions is effective for answering this penetration question, because their viscosities can be easily manipulated. In this experiment a glycerine solution coats the substrate while water is used to rinse. The viscosity of the aqueous glycerine solution is varied between trials to understand at what viscosity-ratio the interfaces of the liquids begin to exhibit penetration.

Wednesday 5:30 Sweeney E-F PO39

Operability windows and sensitivity in slot coating bead regime using 1-D and 2-D models

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Slot coating which has been indispensable for the manufacture of flat panel displays and long-life secondary batteries, can be susceptible to unexpected disturbances at high speed conditions, giving rise to many kinds of undesirable defects. Operability coating windows for both Newtonian and shear-thinning non-Newtonian liquids have been investigated using simplified 1-D viscocapillary model in slot coating bead

flow regime. Stable coating windows free from leaking and bead break-up from 1-D model have been determined, quantitatively coinciding with those by 2-D calculations using Fluent CFD package and FEM code. Also, the sensitivity of the slot coating flow via frequency response method, measuring the amplitude of final wet coating thickness with respect to ongoing sinusoidal disturbances has been sought from both viscocapillary and 2-D models as in the stability case. It has been revealed that the viscocapillary model is quite a quick and efficient tool for the enhancement of productivity and processability in coating systems.

Wednesday 5:30 Sweeney E-F PO40

The effect of ink rheology on impinging velocity and diameter of drop in drop-on-demand inkjet system

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As the inkjet printing technology is widen its application to bio and electronic industries beyond household or office inkjet printers, many different kinds of inks have to be handled. However, inks have not been characterized properly and the processing conditions have been sought mostly through trial and error basis. Considering the importance of the inkjet technology, in the present research, we investigated the generation of inkjet droplets to give an insight into the processing of non-Newtonian fluids for various applications by using a drop-on-demand (DOD) inkjet printing system. As “inks,” Newtonian fluids (water, ethylene glycol, water-glycerin mixture), shear-thinning fluids (aqueous solutions of xanthan gum) and viscoelastic fluids (aqueous solutions of polyethylene oxide) were prepared. Aqueous solutions of PEDOT:PSS were also prepared which is widely used in electronic industries as a conducting polymer. The diameter and velocity of droplet were measured while varying the wave form of the bipolar shape (dwell and echo voltages) to the piezoelectric inkjet head and the effects of the rheological properties were examined. We chose the operating window for each ink at which a single stable drop without satellites was obtained and examined the jetting characteristics. The result shows that the impinging velocity of Newtonian fluids is not strongly affected by the viscosity as far as jetting is possible. However the impinging velocity of xanthan gum solution is lowered when the zero shear viscosity increases while the viscosity at the jetting condition is estimated to be approximately the same. Elasticity lowers the droplet velocity. The drop diameter increases less than 20% with the change in viscosity (1 - 100mPa.s) and/or dwell and echo voltages (20 - 70V). It appears that shear thinning is the most important parameter in jetting of highly viscous inks.

Wednesday 5:30 Sweeney E-F PO41

Viscoelastic properties of ultrathin polymer films using the liquid dewetting technique

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There is considerable interest in studying the rheological behavior of polymers at the nanometer size scale. A novel bubble inflation method was developed in our lab to directly study the equi-biaxial viscoelastic response of ultrathin polymer films.[1] While Bidiguel and Fretigny have proposed a new liquid dewetting technique that also provides a measurement of the equi-biaxial creep response of ultrathin films.[2] The two methods give contradictory results, viz., the bubble inflation work shows both large reductions in Tg and in the ‘rubbery plateau regime’ creep compliance while the dewetting experiment shows no change in rubbery plateau compliance and only small reductions in the T_g. This latter result is also contrary to literature reports of large T_g reductions in freely standing polystyrene (PS) films[3]. To investigate the reasons for these differences, a similar dewetting device to that of Bidiguel and Fretigny was built in our labs and peliminary results show that we can successfully replicate their results for polystyrene films dewetting from glycerol. We are also investigating annealing time and molecular weight. Furthermore, the original device was limited to systems with large differences in index of refraction between polymer film and substrate, e.g., PS/glycerol, and we have developed the technique so that a wider range of materials can be investigated.

References: [1] O’ Connell P. A. and McKenna G. B., “Rheological Measurements of the Thermoviscoelastic Response of Ultrathin Polymer Films”, Science, 307, 1760-1763 (2005). [2] H. Bodiguel and C. Fretigny, “Viscoelastic dewetting of a polymer film on a liquid substrate,” Eur.Phys. J. E., 19, 185-193 (2006). [3] K. Dalnoki-Veress, J. A. Forrest, P. G. de Gennes and J. R. Dutcher, J. Phys. IV., 10, 221-226 (2000).

Wednesday 5:30 Sweeney E-F PO42

Glass transition behavior of epoxy films subjected to CO_2 pressure changes

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The glass transition temperature of polymers has attracted wide interest from the polymer physics community. However, the glass transition concentration is less widely investigated. In the present work, we study the glass transition concentration (as the CO_2 pressure P_{CO2}) of a thin epoxy film (approximately 60 μm) measured during depressurization after pressurizing the system with CO_2 to above the glass transition concentration/pressure for the temperatures investigated. The samples used in the study were thin films of an epoxy-terminated diglycidyl ether of bisphenol A cured with an amine-terminated poly (propylene oxide). Two types of Pressure-change (P-change) experiments were performed: (a) At a fixed depressurization rate of 0.0016 MPa/s and at different temperatures of 75^oC, 72^oC and 69^oC respectively; (b) At a fixed temperature of 69^oC and different depressurization rates of 0.0032 MPa/s, 0.0016 MPa/s, and 0.0008 MPa/s respectively. The preliminary experimental results are reported: P_{CO2} for the glass transition ($P_{CO2,g}$) depends on both temperature and depressurization rate. $P_{CO2,g}$ increases as temperature rises when the depressurization rate is constant while $P_{CO2,g}$ decreases as the depressurization rate increases at a constant temperature. Details of the responses are presented.

Wednesday 5:30 Sweeney E-F PO43

Modulus and work of adhesion for polystyrene surfaces: A comparison of particle embedment and AFM methods of measurement

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There is considerable interest in the development of methods to determine surface properties of materials at the submicron to nanometer size scales. In the present work we show two different methods of obtaining the work of adhesion and modulus of glassy polystyrene: spontaneous particle embedment and atomic force microscopy (AFM).Polystyrene (PS) films were prepared by solvent casting to create a smooth surface. SiO_2 particles having diameters of 204±11 nm, as determined by particle height measurements on a Si surface, were dispersed onto the PS surface and the embedment depth determined from the difference between the average particle diameter and the AFM determined particle height above the surface. The embedment depth was fitted to JKR[1](Johnson, Kendall, Roberts) and DMT models[2](Derjagin, Muller, Toropov) to determine the shear modulus and the work of adhesion. The AFM was also used to directly examine the surface properties using the force distance curve[3] during the approach and pull-off cycle. Pull-off force was generated by the adhesion between the silicon nitride tip and PS surface and the embedment curve was generated as the tip in hard contact with the PS surface. The peak value of pull-off force was used to evaluate the work of adhesion and the embedment curve can be used to estimate the elastic modulus. Comparison of the results of two methods for both the modulus and the work of adhesion will be reported.

References: [1] K. L. Johnson, K. Kendall and A. D. Roberts, P. Roy. Soc. Lond. A, 324, 301-313 (1971). [2] Derjaguin B.V., Muller V.M., Toropov Yu.P., J. Colloid Interface Sci. 53, 314 (1975). [3] F. Benmouna and D. Johannsmann, Langmuir, 20,188-193 (2004).

Wednesday 5:30 Sweeney E-F PO44

Novel approach to design a reusable adhesive by using bilayers of fine-tuned rheological properties

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The performance of an adhesive is strongly dependant on its rheological properties. A good adhesive must be “liquid” enough to wet the surface during bonding while at the same time it should have sufficient cohesive strength to resist the stress during separation. The importance of rheology is even more prominent for pressure sensitive adhesives (PSA) which employs viscoelastic dissipation to enhance adhesion. However, while viscous component increases adhesion, it compromises over reusability because of permanent deformation and particulate contamination. We propose that a bi-layer adhesive having a viscoleastic bulk with thin elastic skin may offer an optimized solution. In this work, the effect of elastic modulus and coating thickness of bilayer was investigated to study the adhesion performance. Cross-linked polydimethylsiloxane (PDMS) elastomer has been used as a model adhesive in this work. Modulus of PDMS has been varied from 0.3 to 0.006 MPa by changing its cross-linking density. The gradient in elastic properties and coating layer thickness shows influence on adhesive strength of bilayer system. The data reveals that higher elastic modulus coating maintains better reusability as compared to its low elastic modulus counterpart without sacrificing adhesion strength. This strategy of adhesive design by selectively using its rheological properties may find much potential use such as bio-medical tapes and anti-fouling coatings.

Wednesday 5:30 Sweeney E-F PO45

Extension of the beam theory for the polymer bio-transducers with low aspect ratios and viscoelastic characteristics

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Polydimethylsiloxane (PDMS) based micropillars (or microcantilevers) have been widely used as bio-transducers for measurement of cellular forces on the order of pN to μN. The accuracy depends on appropriate modeling to convert the micropillar deformations into corresponding reaction forces. The traditional approach is based on Euler beam theory with the consideration of a linear elastic slender beam. However, the low aspect ratio of PDMS micropillars does not satisfy the slender beam requirement. Consequently, Timoshenko beam theory, appropriate for a beam with low aspect ratio, should be used. In addition, the inherently time-dependent behavior in PDMS has to be considered for accurate force conversion. In this work, the Timoshenko beam theory, along with the consideration of viscoelastic behavior of PDMS, was used to model the mechanical response of micropillars. The viscoelastic behavior of PDMS was characterized by the stress relaxation nanoindentation, and the relaxation function was extracted and described by a generalized Maxwell model. The bending of rectangular micropillars was performed by a wedge indenter. The viscoelastic Timoshenko beam formula was used to calculate the mechanical response of the micropillar, and the results were compared with measurement data. The calculated reaction forces agreed well with the experimental data at three different loading rates. Parametric study was conducted to evaluate the accuracy of the viscoelastic Timoshenko beam model by comparing the reaction forces calculated from the elastic Euler beam, elastic Timoshenko beam, and viscoelastic Euler beam model at various aspect ratios and loading rates. The extension of modeling from elastic Euler beam theory to viscoelastic Timoshenko beam theory has improved the accuracy for the conversion of the PDMS micropillar deformations to forces, which will benefit the polymer-based micro bio-transducer applications.

Wednesday 5:30 Sweeney E-F PO46

Multiple particle collision dynamics simulation of the rheology of polymer solutions

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Many important phenomena underlying the physics of complex fluids occur on length and time scales that cannot be accessed by Molecular Dynamics (MD) simulations. Multiple Particle Collision Dynamics (MPCD) is a mesoscale simulation method that coarse grains the solvent while preserving the hydrodynamics, thus enabling simulations over longer length and time scales as compared to MD simulations.

In this work, the MPCD method is used to study the physical behavior of complex fluids, the specific systems of interest being the dilute and semi-dilute solutions of polymers and wormlike micelles. Calculations are performed to investigate the structural (e.g. radius of gyration), dynamic (e.g. diffusion coefficient), and rheological (e.g. viscosity) properties of these complex fluids. Simulation results are compared with experimental results and theoretical predictions for these properties.

Wednesday 5:30 Sweeney E-F PO47

Nonlinear flow behavior of polybutadiene solution in the absence of wall slip

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Wall slip is an important phenomenon in many rheological experiments. To avoid it and better examine the existence of shear banding observed by S. Q. Wang [1], a non-stick interface has been developed by taking a solution of polybutadiene dissolved in toluene and then coated onto mica. This thin polybutadiene layer is further crosslinked with dicumyl peroxide and applied to both plates of the rheometer to prevent interfacial slip between the polymer (polybutadiene in its own oligomer) sample and platen surfaces. Experiments are being conducted over a series of shear rates to observe the shear velocity profile of the polybutadiene/oligomer solution between two parallel plates with our self-designed particle tracking velocimetry (PTV) device. The ultimate goal of the research is to determine the range of conditions over which shear banding is a steady state behavior, as suggested by S. Q. Wang [1], or if it is just a transient behavior. The special nature of the interface, by preventing slip, also provides the means to better determine if the shear banding is a manifestation of surface slip or is an inherent material instability.

[1] P. Tapadia and S. Q. Wang, Phys. Rev. Lett. 96, 016001 (2006)

Wednesday 5:30 Sweeney E-F PO48

Modeling of linear rheology of comb polymer melts

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We extended the time marching algorithm for predicting linear rheology of comb polymer melts. We considered the possibility of fluctuations with respect to all branching points along the backbone, after relaxation of all side branches. The model is applied to combs from different chemistries and structural parameters. It is shown that in the extreme case, when the frictional obstacles from relaxed side branches are significant the backbone segments would fluctuate with respect to the closest branching point, like a Cayley-tree molecule, which is well captured by multi fluctuations modes approach. On the other hand, when the extra friction from relaxed branches are ignorable, the segments would rather fluctuating with respect to the middle of the molecule, just like a linear chain, which can be captured by considering only three fluctuations modes. The model is able to predict the relaxation behavior of combs with branches of unentangled to several entanglement lengths, from different chemistries without a need to use the hopping distance parameter p2 or manually determination of the extent of tube dilation. Taking into account the contribution of monomeric friction of backbone segments in the total drag, modification of early time fluctuations, and consideration of tube dilation as a continuous function evolving through time are believed to be responsible for the capability of time marching algorithm in correct prediction of the extra drag coming from relaxed side branches.

Wednesday 5:30 Sweeney E-F PO49

Non-equilibrium phenomena in reversible associating polymers

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A novel hybrid MD/MC simulation technique is employed to study telechelic polymers[1]. At low temperature or high concentration, their end-groups interconnect and the polymers form a reversible network gel. The glassiness in rheological response observed in our simulations resembles that found in other complex fluids, such as liquid crystals, wormlike micelles, and the actin network in a human cell. In this poster we will show several examples of glassy behavior (e.g. shear induced transitions, creep, and memory of previous deformations). In addition, we will report the spatial and temporal properties of the polymeric networks and correlate them with the macroscopic response.

[1] Baljon et al, J. Chem. Phys. 126, 044907 (2007)

Wednesday 5:30 Sweeney E-F PO50

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

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Worm-like micellar (WLM) solutions exhibit unusual flow behavior under shear. Specifically, there have been recent studies elucidating the formation of shear banding, i.e., the splitting of a viscometric flow into bands of different local shear rates. In the present study, we investigate further the nonlinear shear rheology of cationic surfactant solutions in conjunction with small angle light scattering (SALS): specifically near the miscibility gap of 40mM Erucyl bis(hydroxyethyl) methylammonium chloride (EHAC) and sodium salicylate (NaSal), by using a rheo-SALS instrument (TA instruments) developed in our group at the University of Delaware. Isotropic solutions of a high NaSal concentration (200-800mM), show shear-banding that manifests rheologically as a stress plateau between 25 to 55°C. Interestingly, this stress plateau is observed to be independent of the temperature, but the critical shear rates vary systematically with temperature. The SALS pattern in flow-vorticity plane show no scattering below the critical shear rate and a "butterfly" pattern with enhanced scattering in the flow direction. This is indicative of a shear induced phase separation (SIPS) with large structures aligned along the vorticity direction. The isotropic solutions with low NaSal (< 20mM) do not show any evidence of shear-banding or SIPS. We observe a maximum in zero shear viscosity for which the NaSal concentration is independent of the temperature. This behavior is unlike that of cationic WLM surfactant solutions that exhibit shear banding in the vicinity of an isotropic-nematic phase transition, pointing to the possibility of different underlying mechanisms driving shear banding in highly branched WLM solutions.

Wednesday 5:30 Sweeney E-F PO51

Effect of AN content, viscosity of SAN on the morphology and rheological properties of PC/SAN blends

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PC/ABS blend is one of the important commercial blends which can be used for various fileds such as appliance housing, automobile interior part and mobile phone housing. In order to maintain the surface quality of the injection molded product, it is necessary to understand the interface between two phases. As a model case, here we have studied PC/SAN blends via their morphology and related rheological properties with various AN content in SAN phase. From the measured dynamic storage modulus and loss modulus, weighted stress relaxation spectrum can be calculated. Interfacial relaxation times can be correlated with dynamic surface tension by using Palierne emulsion model. It will serve as a basis to understand the effect of g-ABS composition on the morphological and rheological properties of PC/ABS blend in the long run.

Wednesday 5:30 Sweeney E-F PO52

Rheo-NMR studies of complex spatiotemporal dynamics in wormlike micelle systems

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Recent experiment and simulation of wormlike micelle systems indicate complex spatiotemporal dynamics occur under shear flow. Surfactant systems under the correct conditions can self-assemble into long flexible cylindrical aggregates called wormlike micelles, which exhibit complex rheological behavior. Above a critical micelle concentration, a highly entangled network is formed with the additional complication of constant dissociation and recombination of micellar chains. Due to this, the linear mechanical response is viscoelastic and classically Maxwellian with a single relaxation time. A shear banding transition occurs in the nonlinear response, characterized by a plateau in the shear stress versus shear rate flow curve, where the flow field is inhomogeneous with macroscopic regions of varying shear rates. Instabilities at the band interface manifest as complex spatiotemporal dynamics of the three dimensional flow field. Nuclear Magnetic Resonance (NMR) techniques provide a unique perspective on the complex fluid flow behavior of wormlike micellar systems. NMR velocimetry measurements can probe flow structure in any direction. Improvements in rapid velocimetry techniques allows investigation of the temporal flow field fluctuations, which in combination with spatially localized information on molecular order obtained with deuterium NMR, provides information on the coupling between flow and microstructure. The semidilute surfactant system of cetyltrimethylammonium bromide (CTAB) and sodium nitrate in water and deuterated water at a concentration and temperature far from the isotropic to nematic phase transition exhibits complex behavior under shear, as revealed by spatially and spectrally resolved NMR measurements.

Wednesday 5:30 Sweeney E-F PO53

Conformational dynamics of a single chain of submicron-sized polyelectrolyte in simple flow fields

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Understanding the conformational dynamics of polyelectrolyte chain by single molecule detection has been motivated in areas of nanobio research, holding promise for studies of rheological system as well. Our previous studies [Phys. Rev. E, 2009; J. Chem. Phys., 2007] on a single wormlike chain of xanthan polyelectrolytes have recently been extended with focusing on its behavior in flow fields. The mesoscale coarse-

graining is based on the nonlinear bead-spring model (i.e., FENE) with long-range electrostatic and hydrodynamic interactions between pairs of beads. Our Brownian dynamics (BD) simulations provide that the size increses in no-flos case with decreasing screening effect are well reproduced by previously obtained experimental data. Coil-to-rodlike transition is predicted by estimating the static structure factor and the characteristic stretching ratio between end-to-end distance and gyration radius. Compared to the case of uniform flow field, the chain conformation in simple shear fields follows plateau, transition, and slight change regions, as the flow strength increases. Translational self-diffusion is determined from the mean-square displacement with the lag time in each Beownian trajectory, taking into account velocity fluctuations in the time interval. In this presentation, we also reports the single molecule tracking performed on fluorescein-labeled xanthan using an inverted epi-fluorescence microscope. Subsequently, the degree of discrepancy between simulation results and experimental data obtained by quantifying the image motion will be discussed.

Wednesday 5:30 Sweeney E-F PO54

Rheological and thermal behavior of poly(L-lactic acid)/poly(caprolactone) melt and solution blends

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Melt and solution blends of PLA and PCL in compositions ranging from 95:5 weight percent (PLA:PCL) to 5:95 were fabricated and tested for rheological and thermal property behavior. Melt blends were mixed in a mini-compounder under constant temperature and screw speed settings. The polymer systems were allowed to mix with recirculation for 5 minutes which was determined to be enough time to affect an adequate mix by an NMR-based quality of mix test. The polymer blend was then extruded through a 0.75mm die and collected. Solution blends of the same compositions were prepared from low concentration chloroform solutions that were allowed to equilibrate for 24 hours. Films of the blended polymers were cast in a dry room environment and allowed to dry under quiescent conditions for 24 hours followed by drying under vacuum at 40°C for 24 hours. Standard and temperature-modulated differential scanning calorimetry was performed to assess the thermal behavior of each blend as a function of composition and blending technique. Blend crystallinity was calculated and shown to be dependent on the blending technique. These results also indicate the complexity of this blend system due to the apparent overlap of the PCL phase crystalline melt and PLA phase glass transition. The rheological response of the blended samples shows similar transitions when measured with small amplitude oscillatory shear frequency sweeps as a function of composition and temperature. Results will be reported on our attempt to deconvolute the PCL crystalline melt from the PLA glass transition through rheological measurements.

Wednesday 5:30 Sweeney E-F PO55

Effects of insoluble surfactants in head-on collisions of two equal-sized polymer drops in a polymer matrix

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Boundary integral simulations were used to study the coalescence via head-on collision of two equal-sized viscous drops in a matrix of equal viscosity in a hyperbolic extensional flow, for low Reynolds number, in the presence of insoluble surfactants. The parameters were chosen to mimic the experiments of Yoon et al. [Phys. Fluids **19**, 023102 (2007)], which were performed in a 4-roll mill to measure the drainage time of two Polybutadiene (PBd) drops in a Polydimethylsiloxane (PDMS) matrix, with asymmetric PBd-COO-NH3+PDMS block-copolymers as compatibilizers. In these experiments a discontinuous transition in the drainage time was found for low compatibilizer concentrations (Γ_{eq}) as the Capillary number was increased. Moreover, the drainage time was independent of Γ_{eq}, for $\Gamma_{eq} > \Gamma^*$.

We employed the code developed in Dai and Leal [Phys. Fluids **20**, 040802 (2008)], using an equation of state based on mean field theory of block-copolymer which matches the experimental surface tension data very well. By changing the interfacial diffusivity (D_s), i.e. the interfacial Peclet number (Pe_s) and interface concentration, i.e. the Marangoni number (Ma), we identified the mechanism underlying the transition and the range of Ma and Pe_s for which this phenomenon takes place. Decreasing diffusion slowed down significantly the coalescence process. Our simulations matched the experimental data for high Γ_{eq} by simultaneously decreasing Ds, with respect to the one previously estimated using Lodge and Dalvi's expression [Phys. Rev. Lett. **75**, 657-660 (1995)], and increasing the attractive force in the thin film. It is likely that this increased attraction is a consequence of the entropic attraction due to the formation of two facing dry brushes in a homopolymer matrix at the drop interfaces. Our results show the importance of a precise determination of the block-copolymer interfacial diffusivity either experimentally or theoretically to design effective stabilizers.

Wednesday 5:30 Sweeney E-F PO56

Rheological behavior and relaxation phenomena of immiscible blends of polypropylene and polystyrene

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A new method, using creep measurements to study the long-time linear relaxation mechanisms in immiscible blends was developed. Dynamic experiments were performed to analyze the shorter time relaxation processes, while the long time portions of the weighted relaxation spectrum was probed by means of incomplete creep test followed by recovery. A composite retardation spectrum was constructed combining the results of dynamic and creep experiments. The extended retardation spectrum was then converted to an extended relaxation spectrum and other linear viscoelastic (LVE) material functions over a broader viscoelastic window. This procedure was tested using immiscible blends of polypropylene/polystyrene. It was observed that the extended relaxation spectrum depicts well the long-time relaxation processes and differs from the spectrum obtained using only dynamic measurements at longer times.

Wednesday 5:30 Sweeney E-F PO57

Effect of compatibilizer viscosity and miscibility on blend mixing and multi-layer stability

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Copolymer compatibilizers are widely used for blending immiscible polymers and the viscosity ratio between the compatibilizing copolymer and the other polymers has an important influence on the mixing efficiency and final blend morphology. We utilized the newly developed planar polymer micro-mixer (PPMM) to determine the effect of compatibilizer properties on the transition from layered structures to dispersed domains in a model three component system. Specifically, we investigated the stability of polystyrene (PS)/styrene-ethylene-propylene copolymer (SEP)/polypropylene (PP) system by observing the formation and breakup of layered structures as the blend system traverses a series of split and recombine mixing elements as well as through straight flow channels. The flow pattern was observed on-line through a sapphire window of the mixer and the morphology was examined off-line by coherent anti-stokes Raman scattering (CARS) microscopy (for 3-D chemical imaging) as well as SEM. Surprisingly, the layered structure in the compatibilized blend is less stable than that in the uncompatibilized one, but the final dispersed structure does exhibit a finer domain size. The results show that the viscosity ratio of the compatibilizer relative to the other polymers controls the multi-layer stability while its reduced interfacial tension controls the final domain size.

Wednesday 5:30 Sweeney E-F PO58

Polymer-polymer interfacial slip velocity

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Polymeric liquids often exhibit slip at either liquid-solid or liquid-liquid interfaces. Such slip phenomena have important roles in physical properties of blends, polymer processing, and properties of final products. We had used a sliding plate rheometer to study the polymer-polymer interfacial slip and used multilayer films to control interfacial area. Both direct and indirect measurements had shown that slip velocity did not show a sudden increase at a critical shear stress as predicted by Brochard-Wyart and de Gennes [C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre l'Univers 317, 13 (1993)]. In this study, we performed slip measurement study with bi- and tri-layer samples of nearly monodisperse pairs of polybutadiene (PB)/polystyrene (PS) and poly(methyl methacrylate) (PMMA)/PS to eliminate the effect of broad molecular weight distribution. Results and comparison with our previous studies will be presented.

Wednesday 5:30 Sweeney E-F PO59

Rheological and neutron reflectivity studies of grafted polystyrene against polystyrene melt under shear

Leslie A. Sasa[1], Eric J. Yearley[2], Michael S. Jablin[2], Robert D. Gilbertson[2], Adrienne Lavine[1], Jaroslaw Majewski[2], and Rex P. Hjelm[2]
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Current theory concerning the behavior of end-grafted polymers in contact with a polymer melt under shear states that shear thinning is due to slippage of the melt next to the interfacial polymer at higher shear rates. The end-grafted polymer, which is initially entangled with the melt at rest or at low shear rates, elongates with increasing shear rate. It results in complete disentanglement at a sufficiently high critical shear rate. Although the phenomenon of slip near the bound polymer interface has been demonstrated, the molecular scale events have not. The objective of this study is to understand the molecular-scale events that lead to this slippage.

To study this, a Neutron Rheometer in the cone and plate geometry has been built at the Los Alamos Neutron Science Center to perform neutron reflectivity simultaneously with rheological studies to study the structure of the interfacial region between a highly viscous deuterated polystyrene melt and polystyrene (PS) grafted to a solid surface under shear. Shear thinning was observed as well as a change in the density profile of the grafted PS when transitioning from a static to a shearing state. Throughout all of the experiments, the amount of bound polymer was conserved, showing that the grafted PS was not sheared off the quartz. When transitioning from no shear to shear, the structural characteristics of the end-grafted PS change. This also occurs when the system changes from a higher shear rate back down to rest, indicating that the grafted PS does not relax back to its original state. In two of the zero shear measurements, a depletion layer appeared in the reflectivity results. When the system changes from one shear rate to another higher shear rate, however, the reflectivity pattern stays the same within experimental error. This indicates that the structure of the grafted PS remains the same. The structural changes of the grafted polymer under shear appear as metastable states. Thus, current theories may need to be revised.

Wednesday 5:30 Sweeney E-F PO60

Small-angle neutron scattering and rheological investigation of linear polystyrene in a high flow environment

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The rheological properties of entangled polymers, according to the current tube theories, are attributed to the entanglement of the chains with other neighboring chains and their ensuing escape through the network when an external stress is placed on the system. One example of polymeric nonlinear behavior is shear thinning, where viscosity decreases as a function of shear rate. A typical molecular-level explanation for this response of entangled polymers is that the structural conformations of the polymers in the melt state are altered when escaping their respective "tubes."

While contemporary work supports the tube theory concepts involving the shear thinning phenomena, there is currently only a small set of studies that characterize the response of the polymer chain in this state. The implementation of small-angle neutron scattering with the Los Alamos Neutron Science Center Neutron Rheometer in the couette configuration has provided information on the conformational behavior at the molecular and nanoscales of polymers under shear stress, while correlating these structures with the simultaneously measured rheological properties.

Small-angle neutron scattering and rheological measurements were performed at the Los Alamos Neutron Science Center and the High Flux Isotope Reactor on high molecular weight polystyrene. From the rheological data, it was found that the experiments exhibited monotonic shear thinning. However, although the neutron scattering pattern of the polystyrene melt at a relatively lower shear rate was anisotropic, indicative of chain extension along the shear direction, the anisotropy decreased at higher shear rates. The results show that the determining factors of shear thinning in a smooth couette environment may involve more than just the behavior of the polymer in the bulk. These effects may be explained in part by the current tube theories, yet these present results indicate an additional term due to wall slippage is in play at higher shear rates.

Wednesday 5:30 Sweeney E-F PO61

History effects and postcooling flow properties of waxy oils

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It is well known that below the crystallization temperature the rheology of waxy oils changes from a Newtonian to an extremely complex non-Newtonian behavior, which is temperature- and shear-rate-history dependent. However, the history effects on the postcooling flow properties of waxy oils remain not fully understood. In this paper we perform temperature ramps and stress-amplitude-sweeps with waxy oils and compare the results obtained with the ones found in the literature. In addition, we highlight the effects of the holding time and of the cooling and shear rate histories on the microstructure, and consequently on the rheology. Finally, we discuss in detail the possible sources of rheological measurement errors.

Wednesday 5:30 Sweeney E-F PO62

Mechanics of microstructured emulsions

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Emulsions – metastable suspensions of droplets of one fluid dispersed within another – can be concentrated over a wide range of volume fractions, due to droplet deformability. Here, we study the rheological properties of microstructured emulsions over a range of volume fractions.

Wednesday 5:30 Sweeney E-F PO63

The impact of copolymer brush stretching on the emulsification of droplets in immiscible polymer blends

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Using rheo-optical techniques, we investigated the impact of interfacial wetting of symmetric diblock copolymers (BCPs) on the emulsification and coalescence of polydimethylsiloxane (PDMS) droplets in polyethylene-propylene (PEP). Anionic polymerization was used to synthesize matrix homopolymers and PDMS-b-PEP copolymers with low polydispersity (PDI ˜ 1.02). Molecular weights of these components were varied to ensure that the inner block of the copolymer inside the droplet was collapsed and dry, whereas the outer block of the copolymer outside of the droplet was stretched and wet. Droplet coalescence and interfacial surface tensions were measured using rheo-optical experiments with a Linkam shearing stage. Subsequent to droplet breakup at high shear stress, the BCPs mitigated shear-induced coalescence at lower shear stresses. Increased BCP stretching was inferred from surface tension measurements, which indicate that BCP stretching causes the droplet surface to saturate at lower BCP coverage in line with theoretical predictions. Droplet aggregation was detected with further reductions in shear stress. The aggregates form when attractive forces dominate the forces related to shearing flow. Ultimately, expressions relating volume fraction, aggregation shear rate and surface coverage are developed to enable interfacial parameters to be considered when engineering polymer dispersions.

Wednesday 5:30 Sweeney E-F PO64

Vorticity and velocity banding in shear thickening solutions of wormlike micelles

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An equimolar mixture of cetylpyridinium chloride and sodium salicylate exhibits pronounced shear thickening and vorticity bands (alternating transparent and turbid bands) in non-linear flow regime. Rheological, flow visualization and rheo-SALS studies indicate a stress driven mechanism for the development of shear bands. A combination of rheo-NMR and UVP shows that not only vorticity bands, but also radial bands coexist in this system. To access the microscopic structure in these bands, time-resolved SANS measurements are performed in a transparent Couette geometry. These triggered experiments show that the transparent and turbid bands are composed of different kinds of highly anisotropic structures. Analysis of the structure factor indicates that long wormlike micelles are strongly aligned in flow direction in the turbid state and this alignment is destroyed to some extent in the transparent state.

Wednesday 5:30 Sweeney E-F PO65

Accurate measurements of shear induced vesicle deformation by reflection interference contrast microscopy

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The behavior of individual blood cells subjected to a flow close to a vessel or a tube wall has generated a great number of experimental and theoretical studies intended to acquire a solid basis for understanding blood rheology. Recently, polymer vesicles have emerged as appropriate tunable systems that can provide valuable information in experiments that simulate conditions encountered in vascular flow. In particular, tracking the position and deformation of these artificial soft shells is vital when studying the effect of an increasing shear rate that eventually produces unbinding of vesicles adhered onto a substrate. Here we formulate the use of an improved non-planar image formation theory of reflection interference contrast microscopy (RICM) to analyze RICM images from such situations. The resulting procedure, called Generalized Inverse RICM, yields the location of the vesicle in three dimensions as well as a direct an accurate measurement of its shape near a surface. Because the use of the complete non-planar theory is computationally expensive, we also present a simplified model based on a single ray contribution which allows a faster but still accurate measurement of the deformation of the vesicle.

Wednesday 5:30 Sweeney E-F PO66

Yielding and shear induced structure formation in emulsions with attractive interactions

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The yielding behavior of dense colloidal suspensions is a strong function of the nature of the particle-particle interactions in the system. The addition of a non-adsorbing polymer to hard sphere colloidal glasses induces a short-range attraction and has been shown to lead to re-entrant behavior resulting in the formation of attractive colloidal glasses. Recent results [K. N. Pham, J. Rheol. 52(2), 649-679 (2008)] indicate that such attractive colloidal glasses display a two-step yielding, as opposed to the single yielding transition observed in the hard sphere case. In this framework, the first yielding step at low strains corresponds to the breaking of attractive bonds between particles. The second yielding transition occurs at significantly larger strains and is attributed to a cage breaking process. From this perspective, we examine the yielding behavior of an oil-in-water emulsion system with attractive interactions using dynamic bulk rheology. In strain sweep experiments, the system shows a linear regime with constant elastic and viscous moduli at low strain values (< 1%). On increasing strains beyond 1%, the system yields with a pronounced bump in the viscous modulus, a sharp decrease in the elastic modulus and a crossover between the two, indicating significant fluidization of the system. This one step yielding is different from the two-step yielding paradigm advanced for attractive particulate suspension systems. However, an increase in the complex modulus is observed at yet higher strains (~100%), with both the elastic and viscous components showing small peaks. The onset of this behavior is composition dependent with peaks shifting to lower strain values on increasing volume fraction of the dispersed phase. We speculate that this display is due to the formation of shear induced structures in these systems at high strains.

Wednesday 5:30 Sweeney E-F PO67

Scaling of flow transitions and droplet size in a microfluidic flow focusing device

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We study the various flow transitions that occur in a microfluidic flow-focusing device when the flow rates of the two immiscible Newtonian phases are varied. Consistent with previous studies, depending on the flow rates, we find that the dispersed phase breaks up to yield droplets via squeezing, dripping and jetting mechanisms. At extremely high flow rates of the inner and outer phase, we observe no droplet production, but simply co-flowing laminar streams. The crossover from dripping to jetting behavior is found to occur when the outer phase Weber number is approximately unity indicating that convective instabilities cause jetting. The transition from droplet generation to laminar stream occurs at about inner phase Reynolds number of unity suggesting the shift in behavior is being driven by inertial forces. The droplet size variation with flow rate in the squeezing, dripping and jetting behaviors will also be presented.

Wednesday 5:30 Sweeney E-F PO68

The effect of interfacially segregated particles on foam shear modulus

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The ability of colloidal particles to efficiently stabilize fluid interfaces has been known for more than a century. Research into exploiting this ability to control foam/emulsion stability by tuning particle size, concentration, and wettability has long been a subject of interest, with early work on 'less-characterized'particles enabling general conclusions to be drawn on the colloid-stabilization mechanism, and more recent studies using "model" colloids further elucidating the details of the stabilization mechanism. Despite the history of interest in particle-laden foams and emulsions, there is still very little known about the rheology of these materials. Recent work by Cohen-Addad et al. pointed out that for high particle volume fractions, these systems resemble wet granular materials whose rigidity is due to attraction via capillary bridges and hard core repulsion between neighboring grains, whereas in the absence of particles, elasticity arises from the interfacial tension between phases. They posed the question of how foam rigidity changed upon the addition of solid grains and described a "rigidity percolation" of foam when working with particles of size commensurate with the foam cells. Here we investigate a different regime, where particles are much smaller than foam cells. Particles are also chosen such that they preferentially segregate to the gas-liquid interface. In this case, foam linear viscoelastic moduli increase even faster with particle concentration than in the case of larger, wetted particles. Under some conditions, a lack of dependence of the shear modulus on foam cell size is also demonstrated. These and other observations will be discussed as a starting point to understanding the role surface adsorbed particles play in determining the rheological characteristics of foam.

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Wednesday 5:30 Sweeney E-F PO70

Investigating the energy dissipation of a shear-thickening fluid impregnated fibers using the split Hopkinson pressure bar technique

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According to the recent literature, the impregnation of shear-thickening fluids (STF) into the Kevlar fabrics showed an enhanced ballistic performance. However, there is only limited insight into the detailed mechanisms to correlate the local fiber and STF interaction to understand the global beneficial properties. In this poster, a split Hopkinson pressure bar technique is implemented to understand the energy dissipation mechanisms of the fibers impregnated with shear thickening colloidal suspensions. These suspensions are shown to exhibit dramatic shear thickening and extensional thickening when evaluated using rotational rheometry and filament stretching rheometry. We will discuss the possible dissipation mechanisms of the fiber impregnated with the STF.

Wednesday 5:30 Sweeney E-F PO71

Surface mechanical properties of an epoxy nanocomposite and PS through embedment of submicron particles

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Epoxy resins are widely used in microelectronics, aerospace and other industrial applications. Addition of polyehedral oligomeric silsesquioxane (POSS) to epoxies has been found to improve the existing properties. Though there is significant effort to investigate curing, chemistry and viscoelastic behavior of the epoxy/POSS composites, there have been few attempts to explore the surface mechanical properties. In the present work, we undertake an investigation of the surface modulus of an epoxy/POSS composite at room temperature (far below the glass transition temperature) through a particle embedment experiment in which the Johnson, Kendall and Robert's (JKR) model [1] is used to extract the modulus from the particle embedment depth measured by AFM. Silica and gold particles of sub-micron size in dilute solution were dispersed on a disc-shaped sample of the composite and the embedment depths of the particles into the surface were determined by measuring the particle heights above the surface and subtracting that from the average particle diameter. The embedment depth was used in the JKR model with the driving force of embedment being the work of adhesion between the particle and the epoxy [2,3]. Surprisingly, the calculated modulus values were found to be close to the rubbery modulus values obtained from macroscopic measurements at a temperature of 20ºC above the glass transition temperature. Similar experiments were also performed for a linear chain, non-crosslinked polymer, polystyrene, and it was also found that the estimated surface modulus values are much lower than the bulk glassy modulus. We also examine the magnitude of the stresses in the embedment experiment to establish the range of expected linearity of the mechanical response.

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Wednesday 5:30 Sweeney E-F PO72

Linear viscoelastic response of graphene oxide reinforced polystyrene nanocomposites

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Graphene oxides are monolayers of graphite oxide, which have mechanical strength comparable to carbon nanotubes. To investigate the behavior of graphene oxide nanocomposites, we have undertaken an investigation of the viscoelastic properties of polystyrene reinforced with graphene oxide at different volume fractions to 4.5%. The polystyrene/graphene oxide composites (PSGO) were prepared at the different volume fractions by ultrasonication in solution and subsequent solvent removal. Dynamic moduli and steady shear viscosity were measured for the PSGO composites and master curves were constructed using time temperature superposition. The temperature dependence of the horizontal shift factors of the PSGO systems is found to be weaker than for polystyrene, the glass transition temperature seems to be modestly reduced by the incorporation of the graphene sheets into the polymer. Interestingly, though frequently used to disperse nanofillers into polymers, little concern is usually given to the effects of sonication on the polymer itself. We also present results showing that sonication can lead to significant degradation of the polymer, though not enough to account for the observed changes in melt viscosity and glass transition temperature.

Wednesday 5:30 Sweeney E-F PO73

Effect of treatment method on rheology of latex-blended PS/MWCNT composites

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Polystyrene/multi-walled carbon nanotube (PS/MWCNT) composites were prepared via latex technology and their rheological properties were investigated to elucidate the effect of treatment method on the dispersion of MWCNTs. First, the monodisperse PS latex of 500 nm size was synthesized by emulsifier-free emulsion polymerization. Prior to mixing the PS latex with MWCNTs, chemical and physical treatments such as acid treatment and ultrasonic treatment were employed to improve the dispersion state of highly entangled MWCNTs. Then the MWCNTs were dispersed in deionized water and mixed with the PS latex. Finally, PS/MWCNT composites were prepared by freeze-drying and compression molding. From these composites, morphology and rheological properties were investigated. The composite prepared with either acid treatment or ultrasonic treatment showed substantially increased rheological properties with increasing MWCNT content, indicating an excellent dispersion of MWCNTs. However, the composite prepared with combined treatment of the two showed only slightly increased rheological properties with MWCNT content due to the breakage of MWCNTs, although the highly dispersed state of shortened MWCNTs was maintained. Electrical properties of the composites were also investigated depending on the treatment method.

Wednesday 5:30 Sweeney E-F PO74

Control of thermal degradation of polylactic acid (PLA)-clay nanocomposites during processing

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Thermal degradation of polylactic acid (PLA) is still a challenging issue for industrial applications. Moreover, the presence of clay in PLA enhances the degradation rate; consequently the thermal stability of PLA nanocomposites is quite low as compared to neat PLA. PLA-layered silicate nanocomposites based on semicrystalline PLA containing 2 wt% of modified nanoclay (Cloisite 30B) were compounded by melt mixing. Two different rheological test methods, i.e. time-temperature superposition (TTS) and time sweep tests were employed to examine the extent of thermal degradation. To control the thermal degradation of these nanocomposites during processing, three different types of chain extenders including polycarbodiimide (PCDI), tris (nonylphenyl) phosphate (TNPP), and Joncryl ®ADR were used. The results demonstrated that the addition of 2, 1, and 1 wt% of PCDI, TNPP and Joncryl® ADR, respectively, could stabilize the rheological properties of the nanocomposites containing 2 wt% of nanoclay. DSC results revealed that the value of the glass transition temperature (T_g) and the degree of crystallization increased in the nanocomposites containing TNPP and Joncryl ®ADR as compared to the non-stabilized composite; however, the cold crystallization temperatures (T_{cc}) of these nanocomposites tended to shift to lower values. As evidenced by TGA results, in TNPP-enriched nanocomposites, the temperature at which degradation started was postponed to higher temperature (360 °C as compared to 300°C for non-stabilized PLA nanocomposites), even more than that of the neat PLA (334 °C). A significant increase in the viscosity of the TNPP or Joncryl ®ADR-enriched nanocomposites suggested that the presence of such chain extenders not only controls the thermal degradation, but it could also increase the molecular weight of the PLA matrix.

Wednesday 5:30 Sweeney E-F PO75

Rheological study of the gel transition of sodium alginate solutions with dispersed particle inclusions

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Physical biopolymer gels are ideal candidates for the drug delivery of solid pharmaceutical drugs. Nevertheless, inclusion of particles may affect the gelation of these systems. In this work, we evaluate the effects of particle size and concentration on the thermal gelation of a model biopolymer-particle system. The studied system consists of a pharmaceutical grade sodium alginate (NaAlg) and submicron silica particles (d_{DLS} = 0.22 or 0.78 μm) synthesized by the Stöber method. Silica loadings between 0 to 1.5 wt% were dispersed by ultrasonication in a 1.5 wt% aqueous NaAlg solution at 70°C. The gelation temperature, which characterizes the gel transition, was determined by viscosity measurements during cooling ramps (50 to 0°C @ 2°C/min) at constant stress (1 Pa) in a double gap Couette fixture in a Rheologica StressTech HR stress-controlled rheometer outfitted with an external temperature controller. The gelation temperature was unaffected by addition of silica particles up to a silica loading of 1.0 wt% independently of particle size. Above a loading of 1.0 wt%, the temperature was observed to level up by at least 1.5 °C. Results suggest that the silica particles promote the gelation of NaAlg.

Wednesday 5:30 Sweeney E-F PO76

Effect of particle shape and concentration on the rheology and structure of thermotropic liquid crystalline polymer nanocomposites

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Currently, many thermotropic liquid crystalline polymers (LCPs) are specialty materials of high commercial value due to their outstanding mechanical properties. In some cases, fillers are used to enhance their thermal or chemical properties. Nevertheless, the use of fillers is limited due to their detrimental effect on the ordering. Nanoparticles have the potential to provide additional functionalities at lower loadings without affecting the LCP matrix. In this work, we evaluated the effect of nanoparticle shape and concentration on the physical properties of poly(4-benzoic acid-co-ethylene teraphthalate) (PHBA-PET), a model thermotropic liquid crystalline copolymer. Composite films were produced by direct melt-blending of the polymer with up to 1.5 vol% of either silica spheres, halloysite rods, carbon nanotubes, or montmorillonite platelets in a Thermo-Haake MiniLab2 twin-screw extruder. Our results indicate a strong correlation between particle anisotropy and the microstructure of the LCP. Spherical particles have a detrimental effect as evidenced by the reduction and eventual disappearance of the characteristic SAXS peak and the change of the frequency scaling of the linear viscoelastic moduli of the melt with increasing particle concentration. On the other hand, composites with rodlike particles are mainly unaffected, but plate-like particles seem to further promote anisotropy. Additional results on the thermal transitions, mechanical properties and morphology of the fracture planes will be presented.

Wednesday 5:30 Sweeney E-F PO77

Rheology and phase behavior of lyotropic liquid crystalline polymers loaded with MWCNTs

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Liquid crystalline polymers (LCPs) are interesting fluids due to their inherent orientational order and self-organizing properties. Orientation enhances and allows for the control of the mechanical, electrical and thermal properties. Yet, physical properties may be affected by inclusion of particles due to disturbances in the orientation and degree of anisotropy. However, anisotropic particles, such as rodlike nanoparticles, should not significantly affect the phase transition neither the structure of the liquid crystal, due to their geometric similarity with the polymer molecules. In this research, we determine the particle loading effect of carboxylated multiwalled carbon nanotubes (MWCNTs) on the phase behavior of hydroxypropylcellulose solutions using both steady-state rheology and polarized optical microscopy. The steady-state viscosity was obtained as a function of frequency using a stress controlled rheometer and a plate-plate geometry at room temperature. We also evaluate the particle loading effect on the linear viscoelastic properties of those solutions. Loadings up to 0.45 wt% of nanoparticles did not show a significant effect in the phase transitions of the matrix. Concentration scaling laws are within experimental error of those for neat polymer solutions. Additionally, the addition of the particles modifies the magnitude of the linear viscoelastic moduli, but the frequency scaling in the terminal region is conserved. Thus, we can conclude that addition of low concentrations (i.e. up to 0.45 wt%) of nanotubes do not affect the microstructure of the LCP solutions.

Wednesday 5:30 Sweeney E-F PO78

Processing of nanocomposites PLA/Graphene using a novel elongational mixing device

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Expanded grafite was added to Polylactide acid (PLA) in an internal mixer and then fully mixed in a novel elongational mixing device designed at the LIPHT, University of Strasbourg. The operation of the mixing device is based on the multiple passages of the material, piston driven, trough two capillary conducts inducing high elongational stresses at the exit and the entrance of them. From SEM analysis it can be seen that highly homogeneous materials were obtained at several processing conditions, it means, different number of cycles and speeds of the reciprocant pistons. Also, domains of particles ranged from some tens to hundreds nanometers across the observed samples. X-ray analysis confirmed the existence of nanometric and exfoliated domains trough comparison, between reference non-exfoliated samples and those from the process, of relative intensities about the characteristic graphite peak. DMA results showed a T_g shift of about 10 C of nanocomposites with respect to pristine polymer. This is the first time a device of this nature is employed for this purpose, so that intense work has to be done in order to optimize process conditions needed for a consistent production of graphene/polymer nanocomposites.

Wednesday 5:30 Sweeney E-F PO79

Non-Newtonian displacement flow in a Hele-Shaw cell

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Viscous fingering in non-Newtonian fluids in a rectangular Hele-Shaw cell was investigated numerically and experimentally. Applications include displacement of heavy crude oil in reservoirs. Visualization experiments were performed using Xanthan Gum and a Newtonian mineral oil. The channel, made of transparent glass, is 120mm wide and 650mm long, and the gap between the glass plates is 0.70mm. A digital camera is used to capture images of the interface between the fluids during the flow. A fully 3-D numerical simulation of this displacement flow is also performed, using the finite volume technique and the Volume-of-Fluid method to solve the governing equations. The main parameters that govern this flow are the viscosity ratio, the rheological capillary number, and the (dimensionless) flow rate. The Reynolds number is kept low for all cases investigated, to ensure negligible inertia. The interface shape is given for different values of the governing parameters.

Wednesday 5:30 Sweeney E-F PO80

Viscosity and accelerated aging of biomass pyrolysis oils

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Bio-oil, produced from the pyrolysis of lignocellulosic biomass, is a renewable and carbon neutral fuel that is gaining more attention as a replacement for petroleum-based fuel oils. Bio-oils, also known as biomass pyrolysis oils and other similar names, are produced from the thermochemical conversion of the three main cellulosic biomass components: cellulose, hemicellulose, and lignin. The resulting product is a dark brown liquid with a distinct smoky aroma containing over 300 different organic compounds. Elemental analysis shows that the oils are mainly carbon, oxygen, and hydrogen with nitrogen, sulfur, and inorganics present in much lower concentrations. Unfortunately, bio-oils have drawbacks that prevent wide use as a fuel. Namely, bio-oil has a high water content (~15-30%) and high oxygen content (~44-60%), which reduce the heating value of the oil. Bio-oil is also acidic (pH of ~2-4) and contains some compounds that will repolymerize. Over time, the oil's viscosity will increase due to repolymerization of the reactive species (known as aging) and the oil may become unstable and separate into two phases during storage. The viscosity of the bio-oils was explored as a function of feedstock, temperature, pH and other variables. In addition, to measure the real-time aging and viscosity change of the bio-oils, a TA Instruments AR-G2 rheometer fitted with a pressure cell geometry was used. Viscosity flow curves were generated at 10, 25, and 40^{o}C after 0, 8, and 24 hours of aging at 90^{o}C. All of the raw oil samples saw increases in viscosity after 8 and 24 hours of aging, with some becoming as much as 13 times thicker. The aged samples were more Newtonian and had weaker shear thinning behavior. All of the samples remained one phase after aging. The water content of the oil samples also increased with aging.

Wednesday 5:30 Sweeney E-F PO81

Structure and micromechanics of amyloid nanofibrils

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Many proteins of diverse sequence, structure and function form amyloid fibrils after partially unfolding. These highly ordered nanofibrils exhibit superior mechanical properties. Since the formation is a simple self-assembly process and amyloids are biocompatible and robust under extreme conditions, they are attractive candidates for applications in materials science, tissue engineering and food science. Our aim is to understand and control the relation between the structure of amyloid fibrils on the supramolecular scale and the ultimate structure and mechanics of the self-assembled networks on the macroscopic scale. We study the self-assembly of the milk protein ß-lactoglobulin, which is the major protein in whey. Polyphenols are a possible candidate to control amyloid formation and stability, as it was found that these flavonoids interact specifically with amyloids. We will show an analysis of fibril yield, diameter, length, and structure performed using a combination of turbidity assays, atomic force microscopy and microscopy. Moreover, we will show first measurements of the micromechanics of individual fibrils. The next step is to measure the emergent rheology of networks on the mesoscopic scale using micro- and macrorheology. The resulting fundamental insights are essential for the rational design of novel edible and biodegradable biomaterials and for optimizing industrial food processing.

Wednesday 5:30 Sweeney E-F PO83

Linear and nonlinear rheological investigations of high-solids biomass slurries for bio-refinery applications

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The enzymatic digestion of cellulosic biomasses, such as corn stover and switchgrass, to create biofuels, such as ethanol, is economically competitive only when working at high solids fractions. Therefore, the production of cellulosic ethanol involves working with high-solids slurries which are notoriously difficult to transport due to their high viscosity, requiring large, powerful pumps. As a result, it is particularly important to understand the rheological properties of these suspensions. Dilute-acid pretreated corn stover suspensions have been found to be strongly shear-thinning, be viscoelastic, and exhibit a significant concentration-dependent yield stress, which dominated the flow behavior. Methods for measuring the yield stress include unidirectional shear and small-amplitude and large-amplitude oscillatory shear experiments, using vane-in-cup and roughened parallel plate geometries. At low oscillatory strains (~0.1%), G' is roughly an order of magnitude larger than G". Elastic Lissajous plots (stress versus strain) appeared nearly linear, while viscous Lissajous plots (stress versus strain rate) appeared nearly

circular on appropriately scales axes, indicating linear viscoelastic behavior with elastic stresses dominating. At higher oscillatory strains (greater than about 10%), both G' and G" drop an order of magnitude or more, and cross over at sufficiently high oscillatory strains (~ 15-20%). Within this region elastic Lissajous plots appeared elliptical, while viscous Lissajous plots appeared as distorted ellipses, indicating nonlinear viscoelastic behavior and the presence of bulk elastic flow. Nonlinear constitutive models, such as the elastic Bingham model, were used to characterize the flows and to serve as an aid to connect viscosities and yield stresses measured during unidirectional and oscillatory shear flows.

Wednesday 5:30 Sweeney E-F PO84

High pressure rheology of methane hydrates: Effects of temperature, salt content, and hydrate structure

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A unique high pressure rheology apparatus is used to study the in-situ formation of methane hydrates from a water in oil emulsion. Viscosity and pressure of the hydrate slurry are measured during nucleation, growth, aggregation, and dissociation. Also, the yield stress is determined after an 8 hour annealing period. In this study, the effects of experiment temperature (0-16 ^{o}C), salt content (e.g., 3.5 wt%), and hydrate structure (sI vs. sII) are evaluated. A large increase in viscosity is associated with hydrate nucleation. This spike occurs after a random time (typically 20 minutes to 200 minutes) because hydrate nucleation is a stochastic process. The viscosity reaches a peak, which decreases with increasing temperature. After this peak, we propose at least two aggregation phenomena competitively affect the viscosity. Shear forces from aggregate collisions reduce viscosity while particle-particle adhesion forces (these increase with temperature) cause re-aggregation and thus increase viscosity. In our system, these forces are balanced at around 2 ^{o}C. Below 2 ^{o}C, adhesive forces dominate, while above 2 ^{o}C, shear forces dominate.

Wednesday 5:30 Sweeney E-F PO85

Wall slip behavior of a sodium carboxyl methyl cellulose based hydrogel during drag and pressure induced flows

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Gel-like soft solids are ubiquitous in the human body, are used as drug delivery vehicles and are processed in myriad biomedical applications. The flow characteristics of such gels are dominated by their wall slip behavior, which complicates their rheological characterization and renders the predictions of how they flow in vivo or in various processing settings very difficult. In this study, a carboxy-methyl based hydrogel system was used to investigate in detail its slip at the wall behavior, i.e., a cellulose derivative with carboxymethyl groups (-CH2-COOH) bound to cellulose backbone. The flow curves and the associated wall slip behavior of the hydrogel incorporated with different concentrations of water was investigated and wall slip behavior characterized as a function of the surface to volume ratio in steady torsional, oscillatory shear, rectangular slit and capillary flows. The wall slip in general gives rise to plug flow in steady torsional, capillary and slit flows under a wide range of drag and pressure induced flow conditions. The wall-slip velocity versus wall shear stress data from all three techniques fall on the same master curve, indicating that the universal wall slip behavior of such gels can be determined independent of the rheometer that is utilized.

Wednesday 5:30 Sweeney E-F PO86

Nonlinear rheology of chewing gum

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Chewing gum provides an excellent everyday example of viscoelastic behavior. It flows when being chewed or pulled slowly between the fingers, stresses in it persist after the deformation has ceased, and recoil occurs when it is suddenly relieved of an externally imposed stress. It also breaks when being blown into bubbles or pulled rapidly. Hence, understanding the rheological properties of chewing and bubble gums is important for application purposes. However, to the best knowledge of the authors, no paper is found in the literature regarding the rheological behavior of chewing gum. Only in a few patents do we find linear viscoelastic data. Despite the fact that chewing involves large, complex, and unsteady deformations, no study has been published that characterizes chewing gum under these deformation regimes. The goal of this initial study was to compare the rheological behavior of selected commercial chewing gums and bubble gums. In particular, the nonlinear viscoelastic behavior was investigated using large amplitude oscillatory shear, and start-up flows (in shear, uniaxial extension, and biaxial extension). Bubble gums were found to show similar small strain moduli to chewing gums but more pronounced strain hardening and greater stress to break in start-up of steady uniaxial extension.

Wednesday 5:30 Sweeney E-F PO87

Effect of complex formation on the thermal gelation and rheology of gelatin-xanthan mixtures

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Protein-polysaccharide mixtures are common systems in food and drug products. It is important to understand their interactions and its effect on structure and rheology, since it may affect processing, product specifications, and even public perception. In this work, we evaluate the thermal

gelation and gel strength of the pharmaceutically-relevant gelatin-xanthan system. The gelation temperature of the mixtures was determined from the discontinuity in the viscosity measured at a constant stress of 1 Pa during cooling at 1 ºC/min in a Rheologica StressTech HR stress-controlled rheometer. As xanthan concentration increased, the transition temperature decreased until no gelation was observed. At much higher concentrations the gelation was observed again. The behavior of the gelation temperature was attributed to the formation of neutral electrostatic complexes. Xanthan has a negative charge due to the carboxylic groups in its side chains, while gelatin is cationic at the studied pHs (which are below its isoelectric point). Further prove was provided by zeta potential measurements which showed an isoelectric point at gelatin to xanthan ratios similar to those where no gelation was observed. The storage modulus ($G^{'}$) was also measured during one hour of aging at a constant temperature of 10 ºC by dynamic oscillatory measurements. For all concentrations, $G^{'}$ decreases with xanthan addition until it reaches a minimum, two orders of magnitude smaller than for pure gelatin solutions. Above the critical gelatin-xanthan ratio, $G^{'}$ increases up to one order of magnitude above that for pure gelatin. The gel modulus was described by mixing arguments for composite gels by assuming that the system consists of a finite dispersion of complexes in either a gelatin or xanthan rich matrix. Addition, of NaCl salt produced a reduction or vanishing of the interactions between the biopolymers, which was attributed to the stabilization of xanthan carboxylic group charges by the sodium ions.

Wednesday 5:30 Sweeney E-F PO88

Effective viscosity of actively swimming algae suspensions

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Suspensions of actively swimming microorganisms exhibit an effective viscosity which may depend on volume fraction, cell shape, and the nature of locomotion (e.g. “pushers” vs. “pullers”). Here we report experimental measurements of shear viscosity for suspensions of unicellular green algae (*Dunaliella primolecta*, a biflagellated “puller”). We use a cone-and-plate rheometer to measure the dynamic shear viscosity for both motile and non-motile suspensions of *D. primolecta* at concentrations ranging from 0.1% to 10% of volume fraction. Viscosity increases with concentration for both cases, but the active suspensions of “pullers” have a comparatively lower effective viscosity than passive suspensions. This observation contrasts recently proposed theories which predict higher effective viscosity for “puller” suspensions compared to non-motile suspensions. Our locomotion study reveals that motile algal cells prefer to align and migrate in the direction of positive shear flow vorticity. It is our belief that such a shear-induced response of the algal cells impacts the resulting effective shear viscosity.

Wednesday 5:30 Sweeney E-F PO89

Rheological evaluation of Cashew gum and Arabic gum at high shear rates

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The rheological behavior of Anacardium occidentale gum (Cashew gum) and Acacia gum (Arabic gum) at different concentrations (1 - 40% w/v) and shear rates (1 - 2000 s-1) was evaluated at 25oC. At shear rates of 1 to about 400 s-1, cashew gum (1-20% w/v) and Arabic gum (1-10% w/v) presented a Newtonian behavior that changed to shear thickening at higher shear rates. Cashew gum solution of 25% showed a Newtonian behavior up to shear rates of 1000 s-1, while the solutions of 30 and 40% showed shear thinning non-Newtonian behavior at all shear rates. Arabic gum (10% w/v) presented Newtonian characteristic up to shear rate of 600 s-1, becoming shear thickening at higher shear rates, while the concentrations of 15- 40 %, clearly presented Newtonian behavior at all shear rates. For cosmetic products, different shear rates may be applied, depending on the operation involved. For example, dispensing a spray from a plastic squeeze bottle may involve shear rates up to 20,000 s-1. Cashew gum viscosity appears to be more dependent on shear rate than the concentration. The opposite was observed with Arabic gum whose viscosity increases with increasing concentrations independent of shear rate. Preliminary results indicate a possible broad scope of application of Cashew gum to replace Arabic gum in food, pharmaceutical and cosmetic industries.

Wednesday 5:30 Sweeney E-F PO90

Rheological behavior of fermented dairy beverages obtained from the ultra-high pressure homogenization

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Ultra-high pressure homogenization (UHPH) at levels of 150, 200 and 250 MPa and inlet temperatures of 10, 15 and 20°C, followed experimental design, was used to pressurize dairy base (UHT skim milk and reconstituted whey powder). This was packaged with lactic probiotic culture, incubated, and allowed to ferment. Pineapple juice, previously sweetened, was added, resulting in fermented dairy beverages. It aimed at evaluating the effect of process. Tests were performed under a steady state condition to assess the flow behavior, and on dynamic condition in order to find viscoelastic properties, comparing to control samples (43°C/60s). The preliminary results suggest that UHPH has the potential to be used in order to model some rheological characteristics of dairy beverages, to favorably modify their rheological behavior. All samples studied exhibited tixotropy, a typical response to a strain sweep showing a linear viscoelastic region and gel characteristic.

Wednesday 5:30 Sweeney E-F PO91

Active microrheology of chemically active particles

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Significant progress in particle manipulation develops a new field of research referred to as active microrheology. Within this concept, one considers local changes in the microstructure of a disperse suspension, which emerge near a forced particle. A nonlinear feedback of this redistribution on the motion of the particle is a focus of the active microrheology. Of especial interest is the manipulation by catalytic particles in a suspension of chemically active particles, which admits to deliver the catalyst to a certain point of a microdevice and to trigger a chemical reaction there. We consider both effective viscosity and long-time self-diffusivity of a catalytic (probe) particle dragged by an external force through a dilute suspension of reactive (bath) particles. Rate of consumption of the reactant is assumed proportional to its local concentration. Neglecting by the hydrodynamic interaction, we derive the boundary value problem which governs the microstructures of the bath particles. Distortion of the microstructure due to both the motion of the probe and the chemical reaction leads to change in the effective viscosity and long-time self-diffusivity. Corrections to both these charactersitics are referred to as microviscosity and microdiffusivity, respectively. The problem is considered analytically in a several limiting cases and numerically otherwise. Due to additional hindrance caused by the bath particles, the microviscosity is always positive, although it decreases with growth of both the external forcing and reaction rate. The increase in the reaction rate can either increase the microdiffusivity (at small intensity of the external forcing) or decrease it (in the adection dominate case).

Wednesday 5:30 Sweeney E-F PO92

Detection of network formation during the thermal denaturation of BSA using optical passive microrheology

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The ability to precisely detect the onset of protein aggregation and draw insights into microstructural characteristics of the evolving microstructure plays a critical role in a variety of biotechnological applications, with therapeutic protein stability being a key one [1]. Rheological techniques are very sensitive to evolution of an aggregating network and although such techniques are being utilized in other fields such as foods, their use has been limited in the biotechnology area. This is primarily due to large sample volume and moderately high viscosity requirements in traditional mechanical rheometry techniques. We propose the application of a method based on optical microrheology for the detection of the onset of protein aggregation and for developing an understanding of the nature of the evolving network structure. Optical microrheology [2,3], which has evolved significantly over the last decade, overcomes the limitations of mechanical rheometry as measurements can be effectively carried out on very dilute samples and require only small sample volumes. The exponent of the tracer mean squared displacement power law fit and the elastic modulus G' emerge as two key parameters in the detection of the on-set of protein aggregation and in understanding the nature of the evolving microstructure. The impact of probe chemistry and probe size on the extracted microrheological response is discussed.

[1] A Saluja et al, “Ultrasonic rheology of a monoclonal antibody (IgG2) solution: implication for physical stability of proteins in high concentration formulations” Journal of Pharmaceutical Sciences (2007) 96, 3181-3195. [2] T A Waigh “Microrheology of complex fluids” Reports of Progress in Physics (2005) 68, 685-742. [3] D Weihs et al, “Bio-microrheology: a frontier in microrheology” Biophysical Journal (2006) 91, 4296-4305.

Wednesday 5:30 Sweeney E-F PO93

Characterization of nanoparticle dispersion by rheological and microrheological techniques

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Nanofluid (NF) is a novel heat transfer fluid prepared by dispersing nanometer-sized solid particles in traditional heat transfer fluids to increase thermal conductivity and thereby heat transfer performance. The increase is known to be as large as tens of a percent. However there have been controversies over the amount of increase and sometimes even over the increase itself among research groups. One of the reasons for the controversies came from the fact that the nanoparticles are not easily dispersed and the status of dispersion has not been fully characterized. In the present research we prepared a class of nanofluids by dispersing alumina nanoparticles (length: 50nm; diameter: 10nm) in water and characterize the dispersion status of the nanofluids by rheological and microrheological measurements. The result shows that the alumina NF shows a constant viscosity when the concentration is lower than 2% while it shows shear banding when particle loading exceeds 3%. The complex viscosity shows a shear-thickening phenomenon implying that there should be strong particle-particle interactions. The microrheological measurement shows a much lower G' and G" than the values obtained by the conventional rheometery, meaning that there exists a larger structure in the suspension than the probe particle size of 1 micrometer. The cryo-SEM images confirm the structure. Ultrasonication and/or milling of the NFs lowered both G' and G". But they recover the properties with the time scale of 1 day. It appears that the aging is one of the important factors that affect the thermal characteristics of NFs.

Wednesday 5:30 Sweeney E-F PO94

Development of multiple-particle-tracking microrheology for fluids experiencing deterministic motion

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In Multiple-Particle-Tracking Microrheology (MPTM), rheological properties of fluids are determined from the Stokes-Einstein theory applied to Brownian motion of small suspended particles. As compared to conventional rheometers, this noncontact method does not have the problem of wall slip effects and requires a very small amount of a test fluid. MPTM measurements are typically performed in a quiescent fluid to ensure all particles are subject to random motion. Unfortunately, it is very difficult if possible to completely eliminate the deterministic motion of a test fluid during measurement because of thermal convection of the fluid, fluctuations and inclination of the experimental platform, and active transport of particles. In this work, we report our first results on development of MPTM that takes into account the deterministic velocity of a test fluid. In our approach, 0.1 or 0.9 um diameter Latex beads were suspended in a fluid located between a glass microscope slide and a glass coverslip. The movement of the particles was visualized through an inverted microscope with 40x and 60x objectives and recorded by a high-speed camera at 30 frames per second. The trajectories of particles were analyzed using a MATLAB code in which the viscosity of a test fluid was determined from the ensemble averaged MSD vs. lag time curves with the deterministic component of the fluid removed under the assumption that the ensemble-averaged velocity for randomly moving particles was equal to zero. We applied this approach to measure the viscosity of water and 5% dextran-water solution at different temperatures. With the elimination of the deterministic component, our results agree well with published viscosity data for these fluids.

Wednesday 5:30 Sweeney E-F PO95

Modeling of nanoconfinement of free radical PMMA polymerization

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In the present work, the mathematical model describe by Verros et al. (2005) to model diffusion controlled free radical bulk polymerization of poly(methyl methacrylate) (PMMA) is extended to account for polymerization in nanopores. The model of Verros et al. (2005) model is capable of describing the conversion and the number and weight average molecular weights as a function of the polymerization time and the process conditions. Nanoconfinement effect is incorporated in the model by assuming that changes in segmental diffusion are related to the entropy loss experienced by the chains using both the Adam-Gibbs model and a prediction by DeGennes. The results indicate that nanoconfinement will lead to higher molecular weights, a broader molecular weight distribution, and faster polymerization. The results are compared to experimental work and implications discussed.

Wednesday 5:30 Sweeney E-F PO96

Rheological examination of sodium alginate gelation

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Reported here are the results of a rheological study of the crosslinking of sodium alginate with calcium chloride. Knowledge concerning the rate of curing of this system is important to its application for sediment stabilization. It is thought that the calcium cation exchanges with sodium, and ties up adjacent chains in a cage-like coordination complex involving the a-L-guluronate residues. While rate studies were carried out by Drageta et al. (1998), their source of calcium ion was calcium carbonate, which slows considerably the crosslinking reaction. For the present work, a sodium alginate was purchased from MP Biomedicals. Variables were polymer concentration and the molar ratio of calcium to polymer. Parallel-disk fixtures were used because they allow rapid loading of the reactive mixture from a dual-barrel syringe equipped with a motionless mixer. G* data were gathered during the cure. Modeling of the cure (G' vs. time) was attempted in terms of a 2nd order reaction of calcium cation with the guluronate residues of the alginate.

Wednesday 5:30 Sweeney E-F PO97

Synthesis and characterization of POSS-containing polyurethane cationomers

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Polyurethane ionomers are industrially important materials used as coatings, adhesives, ink-jet inks, and other applications. In this study, toward the goal of developing waterborne shape memory polymer (SMP) coating as a smart coating material, a series of thermoplastic polyurethane (TPU) ionomers with several different sequence structures having polyhedral oligosilsesquioxane (POSS) as a hard block and poly(e-caprolactone) (PCL) as a soft segment was synthesized by means of general polyurethane chemistry with a tertiary amine-chain extender and following quarternization reaction. Thermal, dynamic mechanical, and melt rheological properties were analyzed for the TPUs before and after the ionization to study on the effects of the presence of ionic groups and the sequence structure on higher-ordered structure and physical properties. The distributions of POSS moieties and ionic groups along the chains were found to be very important for the cross-linking structure formation. Aqueous dispersions of PCL-POSS TPU ionomers were prepared and used to coat several elastic substrates. Shape memory properties of the TPU ionomer-coated substrates are reported.

Wednesday 5:30 Sweeney E-F PO98

Simulation results of a new nonlinear parameter Q from FT-rheology using a single mode Pom-Pom model

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We have proposed a new nonlinear coefficient Q from FT-Rheolgy under large amplitude oscillatory shear (LAOS)[Macromolecules 42, 411, 2009]. This parameter Q is defined as $Q = I_{3/1}/\gamma_0^2$ and we also defined zero-strain nonlinearity (inherent nonlinearity), Q_0, as a constant value at relatively small strain amplitude in analogy to other rheological properties, e.g. viscosity. We have already investigated entangled linear monodisperse and comb polymer melts using these nonlinear parameters (Q and Q_0). At the current stagel, we assume that the polymer topology has a strong influence on these nonlinear parameters. This parameter $Q_0(\omega)$ opens up a simple possibility for quantitative comparisons between experiments and simulations under nonlinear oscillatory shear. Consequently we systematically investigated the simulation results of $Q(\gamma_0)$ and $Q_0(\omega)$ from FT-Rheology using constitutive equations, specifically the single mode pom-pom model for H-polymers. We investigated the nonlinear parameter Q within a wide range of frequencies and strain amplitudes varying backbone and side arm length, furthermore the number of arms are varied. One of the main ideas of the pom-pom model is the separation of the two relaxation process of stretch (fast) and orientation (slow) for the two branch point of the H-polymer. Physically, the time separation is the consequence of the different entanglement dynamics. It is found that $Q_0(\omega)$ can detect this separation process if the side arms are entangled. The $Q(\gamma_0)$ from pom-pom model show strain hardening behavior like the experimental results of comb-branched polymer. We also investigated stress vs. strain and stress vs. strain rate curve within a Pipkin diagram for different strain amplitudes and frequencies.

Wednesday 5:30 Sweeney E-F PO99

New global methods for solving frontier problems in nonlinear rheological dynamics

Tony Gomis
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New global approaches based on the Adomian Decomposition Method, the Cherruault Alienor Transformations, and the Homotopy Perturbation Method will be presented.Their power for solving nonlinear, stochastic or deterministic, integral or differential, partial or fractional functional equations from the same unified framing will be outlined.These new global methods will be applied to nonlinear rheological dynamics.

Wednesday 5:30 Sweeney E-F PO100

The direct numerical simulation of dense suspensions of deformable particles

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The lattice-Boltzmann method is coupled to a finite element elastic membrane and a spectrin-level red blood cell model in order to probe the rheology and microstructure of dense suspensions of deformable particles. This method has been shown to be highly scalable on distributed computing resources. Simulations are performed with hundreds of particles in unbounded shear using a Lees-Edwards boundary condition in order to calculate bulk rheological properties and the suspension microstructure. The rheological properties of interest are the suspension viscosity and normal stresses, which include the isotropic particle pressure. For initially spherical elastic capsules, the simulation results clearly capture the transition from compressive particle stresses when no particle deformation is present, to more tensile stresses at higher deformations. This transition in normal stresses includes a sign change in the first normal stress difference. Concurrent with the decrease in compressive particle stresses is a decrease in the particle self diffusivity. Simulations of red blood cells at physiological concentrations with a nonlinear membrane model are also shown and rheological properties are presented.

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Plenary Lectures

8:30 AM Sweeney F

Monday, October 25	**Activated relaxation and rheology of glassy materials: From dense colloidal suspensions to amorphous polymers** Kenneth S. Schweizer *Materials Science and Engineering, Chemical and Biomolecular Engineering, and Chemistry;University of Illinois at Urbana-Champaign*
Tuesday, October 26 *Bingham Lecture*	**A random walk in rheology** Tom C. McLeish *Physics, Durham University*
Wednesday, October 27	**Molecular aspects of flow-induced crystallization of polymers** Julia A. Kornfield *Division of Chemistry and Chemical Engineering, California Institute of Technology*

Social Program

Sunday, October 24	**Welcoming Reception**	7:00 PM – 9:00 PM	Eldorado Hotel – Eldorado Court and Lobby Lounge
Monday, October 25	**Society Reception**	6:30 PM – 9:00 PM	New Mexico History Museum *Sponsored by a generous contribution from Malvern Instruments*
Tuesday, October 26	**Society Business Meeting**	5:30 PM	Convention Center – Sweeney B
	Awards Reception	7:00 PM	La Fonda Hotel – New Mexico and Santa Fe Rooms *Sponsored by a generous contribution from Xpansion Instruments*
	Awards Banquet	8:00 PM	La Fonda Hotel – Ballroom
Wednesday, October 27	**Poster Session Reception**	5:30 PM – 7:30 PM	Convention Center – Sweeney E-F *Sponsored by a generous contribution from Anton-Paar USA*

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