



THE SOCIETY OF RHEOLOGY

86TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Loews Philadelphia Hotel
Philadelphia, Pennsylvania
October 5 - 9, 2014

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Meeting Schedule

Monday, October 6, 2014

	C-A	C-B	C-C	W-A	W-B	W-C
8:30		S. G. Hatzikiriakos (PL1) - <i>MH</i>				
9:20		Coffee Break				
10:00	SC1	BB1	SM1	CR1	BC1	SF1
10:25	SC2	BB2	SM2	CR2	BC2	SF2
10:50	SC3	BB3	SM3	CR3	BC3	SF3
11:15	SC4	BB4	SM4	CR4	BC4	SF4
11:40	SC5	BB5	SM5	CR5	BC5	SF5
12:05		Lunch Break				
1:30	SC6	BB6	SM6	CR6	FR1	SF6
1:55	SC7	BB7	SM7	CR7	FR2	SF7
2:20	SC8	BB8	SM8	CR8	FR3	SF8
2:45	SC9	BB9	SM9	CR9	FR4	SF9
3:10	SC10	BB10	SM10	CR10	FR5	SF10
3:35		Coffee Break				
4:00	SC11	BB11	SM11	CR11	FR6	SF11
4:25	SC12	BB12	SM12	CR12	FR7	SF12
4:50	SC13	BB13	SM13	CR13		SF13
5:15	SC14	BB14	SM14	CR14		SF14
5:40	SC15	BB15	SM15	CR15		SF15
6:05		End				

Tuesday, October 7, 2014

	C-A	C-B	C-C	W-A	W-B	W-C
8:30		N. J. Wagner (PL2) - <i>MH</i>				
9:20		Coffee Break				
10:00	SC16	BB16	SM16	NF1	BC6	CC1
10:25	SC17	BB17	SM17	NF2	BC7	CC2
10:50	SC18	BB18	SM18	NF3	BC8	CC3
11:15	SC19	BB19	SM19	NF4	BC9	CC4
11:40	SC20	BB20	SM20	NF5	BC10	CC5
12:05		Lunch Break / Society Business Meeting				
1:30	SC21	BB21	SM21	NF6	BC11	CC6
1:55	SC22	BB22	SM22	NF7	BC12	CC7
2:20	SC23	BB23	SM23	NF8	BC13	CC8
2:45	SC24	BB24	SM24	NF9	BC14	CC9
3:10	SC25	BB25	SM25	NF10	BC15	CC10
3:35		Coffee Break				
4:00	SC26	BB26	SM26	NF11	BC16	EF1
4:25	SC27	BB27	SM27	NF12	BC17	EF2
4:50	SC28	BB28	SM28	NF13	BC18	EF3
5:15	SC29	BB29	SM29	NF14	BC19	EF4
5:40	SC30	BB30	SM30	NF15	BC20	EF5
6:05		End				
7:00		Awards Reception				
8:00		Awards Banquet				

Wednesday, October 8, 2014

	C-A	C-B	C-C	W-A	W-B	W-C
8:30		S. J. Muller (PL3) - <i>MH</i>				
9:20		Coffee Break				
10:00	SC31	BB31	SM31	NF16	SF16	EF6
10:25	SC32	BB32	SM32	NF17	SF17	EF7
10:50	SC33	BB33	SM33	NF18	SF18	EF8
11:15	SC34	BB34	SM34	NF19	SF19	EF9
11:40	SC35	BB35	SM35	NF20	SF20	EF10
12:05		Lunch Break				
1:30	SC36	BB36	SM36	NF21	SG1	EF11
1:55	SC37	BB37	SM37	NF22	SG2	EF12
2:20	SC38	BB38	SM38	NF23	SG3	EF13
2:45	SC39	BB39	SM39	NF24	SG4	EF14
3:10	SC40	BB40	SM40	NF25	SG5	EF15
3:35		Coffee Break				
4:00	SC41	BB41	SM41	NF26	SG6	EF16
4:25	SC42	BB42	SM42	NF27	SG7	EF17
4:50	SC43	BB43	SM43	NF28	SG8	EF18
5:15	SC44	BB44	SM44	NF29	SG9	EF19
5:40	SC45	BB45	SM45	NF30	SG10	EF20
6:05		End				
6:05		Poster Session & Reception				

Thursday, October 9, 2014

	<i>MH</i>	C-B	C-C	C-D	C-A1	C-A2
8:00		R. H. Ewoldt (AP1) - <i>MH</i>				
8:40	SC46	BB46	SM46	SF21	SG11	EF21
9:05	SC47	BB47	SM47	SF22	SG12	EF22
9:30	SC48	BB48	SM48	SF23	SG13	EF23
9:55		Coffee Break				
10:25	SC49	BB49	SM49	SF24	SG14	EF24
10:50	SC50		SM50	SF25	SG15	EF25
11:15				SF26	SG16	EF26
11:40				SF27	SG17	EF27
12:05		End				

Session and Room Codes

AP = Award Presentations
 BB = Biomaterials and Biological Systems
 BC = Blends, Composites and Multiphase Systems
 CC = Confined and Coupled Systems
 CR = Computational Rheology
 EF = Emulsions, Foams and Interfacial Rheology
 FR = Food Rheology

NF = Non-Newtonian Fluid Mechanics and Stability
 PL = Plenary Lectures
 SC = Suspensions and Colloids
 SF = Self-assembly and Flow-induced Systems/Gels
 SG = Solids and Glasses
 SM = Polymer Solutions and Melts

C-A = Commonwealth A
 C-A1 = Commonwealth A1
 C-A2 = Commonwealth A2
 C-B = Commonwealth B
 C-C = Commonwealth C
 C-D = Commonwealth D
MH = Millennium Hall
 W-A = Washington A
 W-B = Washington B
 W-C = Washington C

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Monday Morning

Symposium PL Plenary Lectures

Monday 8:30 Millennium Hall

PL1

The wall slip of polymer melts: The rule or the exception?

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There is considerable experimental evidence that the classical no-slip boundary condition of Fluid Mechanics is not always a valid assumption for the flow of molten polymers. In fact, molten polymers slip macroscopically at solid surfaces no matter how small are the applied wall shear stresses. Moreover, for linear polymers there exists a critical wall shear stress value at which a transition from a weak to a strong slip occurs. These two modes of slip (weak and strong) are due to flow-induced chain detachment/desorption at the polymer/wall interface and to chain disentanglement of the polymer chains in the bulk from a monolayer of polymer chains adsorbed at the interface depending on the surface energy. In this talk, the slip of linear polymers is discussed with emphasis on the effects of molecular weight and its distribution. A methodology based on double reputation to calculate the slip velocity given the detailed molecular weight distribution of the polymer is also discussed. Finally, proposed slip models, static and dynamic, are also reviewed and their significance on the rheology and flow simulations of molten polymers is discussed.

Symposium SC Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Monday 10:00 Commonwealth A

SC1

The pressure of active matter

John F. Brady, Sho Takatori, and Wen Yan

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One of the distinguishing features of many living systems is their ability to move, to self-propel, to be active. Through their motion, either voluntarily or involuntarily, living systems are able self-assemble: birds flock, fish school, bacteria swarm, etc. But such behavior is not limited to living systems. Recent advances in colloid chemistry have led to the development of synthetic, nonliving particles that are able to undergo autonomous motion by converting chemical energy into mechanical motion and work - chemical swimming. This chemical or biological swimming or intrinsic activity imparts new behaviors to active matter that distinguish it from equilibrium condensed matter systems. Active matter generates its own internal stress, which can drive it far from equilibrium and free it from conventional thermodynamic constraints, and by so doing active matter can control and direct its own behavior and that of its surroundings. This talk will discuss our recent work on the origin of a new source for stress that is responsible for self-assembly and pattern formation in active matter.

Monday 10:25 Commonwealth A

SC2

Active microrheology of hydrodynamically interacting spheres: Normal stresses and osmotic pressure

Henry C. W. Chu¹ and Roseanna Zia²

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In our recent work we developed a non-equilibrium Stokes-Einstein relation (NESER) for colloidal dispersions undergoing microrheological forcing in the absence of hydrodynamic interactions, and showed that the stress in a suspension is given by a balance between fluctuations---diffusive motion---and dissipation---advective motion. We also showed that the osmotic pressure is a measure of the tendency of particles to push outward on system boundaries---diffusion---and is hindered by viscous normal stress. Here we extend the NESER to systems of hydrodynamically interacting colloids via a combination of asymptotic analysis and numerical solution of the Smoluchowski equation. In active microrheology, a Brownian probe is driven by an external force through a complex medium. The strength of probe forcing, F , compared to the entropic restoring force, kT/a , defines a Peclet number, $Pe = F/(kT/a)$, where k is Boltzmann's constant, T is the absolute temperature, and a is the particle size. For weak probe forcing, the linear-response regime, the normal stresses and osmotic pressure scale as Pe^2 . For strong forcing, high Pe , the Brownian component of these quantities scales as $Pe^{\delta-1}$ while both hydrodynamic and interparticle components scale as Pe^{δ} , where $0.8 < \delta < 1$ for strong to negligible hydrodynamic interactions, respectively. Owing to the axisymmetry of the motion about a spherical probe, the second normal stress difference is zero. The dependence of the first normal stress difference on hydrodynamic interactions evolves intricately with Pe and the changing disparity between longitudinal and transverse lubrication forces. In contrast, the osmotic pressure decreases monotonically as hydrodynamics

become more important and relative mobility between particles decreases. We compare results obtained via statistical mechanics to our phenomenological expression for stress-induced migration, which can be viewed as a generalized non-equilibrium Stokes-Einstein relation.

Monday 10:50 Commonwealth A

SC3

Single particle motion in a sheared colloid dispersion

Aditya S. Khair and Toni Bechtel

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In conventional (macro-)rheometry, rheological properties are measured by subjecting a material to a bulk shearing motion, actuated by oppositely moving plates, for example. In contrast, (active) micro-rheological techniques utilize a colloidal "probe" driven through an otherwise quiescent fluid. Here, we illustrate effects arising from combination of micro- and macro- forcings: specifically, we consider a colloidal probe driven at fixed force through a dilute suspension of hard-sphere "bath" particles undergoing simple shear flow. The distortion to the equilibrium suspension microstructure caused by the probe is characterized by a (micro) Peclet number Pe_f (a dimensionless pulling force), and the distortion due to the ambient shear is represented by a (macro) Peclet number Pe_s (a dimensionless shear rate). Using asymptotic expansions at small Peclet numbers (more precisely, $Pe_s^{3/2} \ll Pe_f \ll Pe_s^{1/2} \ll 1$), we demonstrate that a probe forced along the velocity axis of the shear experiences a cross-streamline drift of $O(Pe_s \phi U_s)$, resulting from a nonlinear combination of micro- and macro- microstructural deformations (ϕ is the bath particle volume fraction and U_s is Stokes' settling velocity). The magnitude of the drift velocity is sensitive to the degree of hydrodynamic interactions between the probe and bath particles. Next, we consider a probe forced orthogonal to the imposed shear. Here, the probe experiences a shear-driven modification in rectilinear velocity of $O(Pe_s^{3/2} \phi U_s)$: this non-analytic contribution originates from the microstructural deformation in the shear dominated (outer) region far from the probe. The connexion of this result to recent work on particle sedimentation in orthogonal linear flows is discussed.

Monday 11:15 Commonwealth A

SC4

Force-induced diffusion in hydrodynamically-interacting colloidal dispersions

Nicholas J. Hoh and Roseanna Zia

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The diffusive motion of a Brownian probe is studied as it is driven by a constant external force through a dispersion of hydrodynamically interacting colloids. The influence of hydrodynamic interactions on equilibrium self-diffusivity is well known; here we explore their influence on microrheological force-induced diffusion by systematically tuning the strength of hydrodynamic interactions via an excluded-annulus model. The strength of probe forcing F compared to the entropic restoring force of the bath, kT/a , defines a Peclet number, $Pe = F/(kT/a)$, where k is Boltzmann's constant, T is the absolute temperature, and a is the particle size. The probe diffuses as it is driven through the suspension. This force-induced diffusion, or microdiffusivity, is determined analytically in the limits of small and large Pe and numerically over the full range of Pe . The total diffusivity comprises that of an isolated probe, the entropic hindrance of the equilibrium microstructure, and a contribution due to non-equilibrium interactions between probe and background particles. When hydrodynamic interactions are important, three factors contribute to the microdiffusivity: a hydrodynamic reduction in probe mobility due both to the presence of bath particles and a distortion in their distribution; Brownian flux due to microstructural deformation; and entropic exclusion (collisions). The microdiffusivity tensor is anisotropic and proportional to Pe^2 for weak probe forcing regardless of the importance of hydrodynamic interactions. In contrast, when forcing is strong, the microdiffusivity scales as Pe^δ where the exponent varies with the strength of hydrodynamic interactions. We showed in our recent work that fluctuations of probe motion are intimately tied to the suspension stress; we utilize this detailed understanding of the microdiffusivity in the development of a non-equilibrium equation of state for hydrodynamically interacting colloids.

Monday 11:40 Commonwealth A

SC5

Passive microrheology thanks to multi-speckle diffusing wave spectroscopy

Jonathan Denis¹, Giovanni Brambilla², and Gérard Meunier²

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This work presents a new technique of passive microrheology for the study of the microstructure viscoelastic properties of soft materials like emulsions, polymers. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from thermal energy ($\sim k_B T$). The unique force used to displace the particles is thermal energy which may be 10^{12} times lower than macroscopic mechanical stress. Our technique is based on Diffusing Wave Spectroscopy, an optical technique to determine the scatterers mobility in terms of speed and displacement which are directly related to the samples viscoelastic properties. The determination of a master curve called Mean Square Displacement (MSD) enables to characterize completely the viscoelastic properties of a sample. This paper will present the technique and its different applications for the characterization of soft matters potentially used in foods industry, such as emulsions, hydrogels, organogels and concentrated dispersions.

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Monday 10:00 Commonwealth B

BB1

Monitoring extracellular matrix (ECM) mechanics in 3D in vitro tumor models during fibrosis and invasion processes for rheology-informed cancer therapeutics

Dustin P. Jones, William Hanna, Gwendolyn M. Cramer, Hamid El-Hamidi, Ljubica Petrovic, and Jonathan P. Celli
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It has become increasingly clear that the rheological properties of the tumor microenvironment play multiple crucial roles in regulating growth, invasion and therapeutic response. At the same time, cancer cells themselves in cooperation with stromal partners (e.g. cancer associated fibroblasts) continually alter the mechanical microenvironment in response to extracellular physical and biochemical cues as part of a two-way mechanoregulatory cross talk. Here we describe the use of in vitro three-dimensional tumor models leveraged in combination with in situ quantitative imaging and particle tracking microrheology (PTM) measurements as a means to place cells in customized mechanical microenvironments and evaluate dynamic changes in local matrix mechanics associated with relevant processes in tumor growth and development. In this approach, micron-sized fluorescent spheres incorporated into the ECM serve as probes for passive thermally driven local PTM and traction force measurements, which are co-registered with phenotypic characterization from imaging of the cancer and stromal cells themselves. Specifically, in view of the noted roles of rigidity-dependent stromal crosstalk in pancreatic cancer, we observe and quantify time-dependent increases in matrix stiffness in a 3D co-culture model of PANC-1 pancreatic ductal adenocarcinoma cells co-cultured with MRC-5 normal human fibroblasts. Conversely we report local decreases in matrix stiffness concomitant with invasive fronts when the mechanical microenvironment of the same cells (PANC-1) is probed in conditions which promote an invasive phenotype. Finally we implement this platform to assess treatment response to chemotherapy treatments (gemcitabine and oxaliplatin) and photodynamic therapy (PDT) and evaluate the role of the mechanical microenvironment in therapeutic response as well as the impact of therapeutics on ECM mechanics.

Monday 10:25 Commonwealth B

BB2

Dynamic cell-material interactions measured by passive microrheology

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Scaffolds that mimic aspects of the extracellular matrix while providing a 3D microenvironment cells can degrade and remodel during migration is an area of growing interest with applications in wound healing, tissue engineering and stem cell expansion. Cells do not reside in their microenvironment, they actively reengineer the scaffold to meet specific requirements that maximize the efficiency of cellular processes. Although biomaterials provide an initially well-defined microenvironment for the cells, little is known about the extent of cellular interaction with the matrix. The lack of quantitative and predictable information about this process has limited advances in biomaterial design. To bridge this gap, we use microrheological characterization to quantitatively measure the microenvironment directly around a 3D encapsulated human mesenchymal stem cell (hMSC), the pericellular region, during dynamic remodeling and degradation. hMSCs degrade a synthetic hydrogel network through two pathways, MMP secretion that digests the peptide cross-linker in this scaffold and myosin II regulated adhesion and reversible remodeling of the network. This facile technique measures spatial changes in material properties with sensitivity that can discriminate between areas where the cell adheres to the matrix as well as areas degraded due to cell-secreted matrix metalloproteinase cleavage of the peptide cross-linker. This work provides a foundation and technique to quantitatively capture matrix remodeling during cellular migration, which will further design of tunable synthetic materials that will enhance and direct cell motility.

Monday 10:50 Commonwealth B

BB3

High frequency microrheology of hydrogels formed from peptide enantiomers

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Self-assembled peptide hydrogels are of interest for drug delivery and tissue engineering applications where, for example, biocompatible hydrogels could be used as an artificial cellular scaffold for tissue regeneration in wounds. Applications such as these require control over both the rate of gel formation and the final gel stiffness. Recently, gels formed from racemic mixtures of MAX1, a 20 amino acid long synthetic peptide, and its enantiomer, DMAX1, were found to assemble more rapidly and exhibit an equilibrated storage modulus four times as large as those containing either pure enantiomer. In this talk, we present progress towards a molecular and network level understanding of this phenomena. The viscoelastic properties of the gels are measured using diffusing wave spectroscopy (DWS). Simultaneous photon counting and multispeckle DWS techniques are used to measure the dynamics with lag times over eight orders of magnitude. This enables characterization of the kinetics of gelation along

with the final viscoelastic properties of the gel. The measured plateau modulus is in agreement with that found from bulk rheology, and the results provide the first direct microrheological measurements of semiflexible polymer mechanics in MAX1 systems. Using a theoretical model and material parameters determined from complimentary, independent measurements, the persistence length and bending modulus of the peptide filaments are determined directly from the DWS experiment. The results provide new insights into the fabrication of hydrogel networks with tunable properties using peptide assemblies.

Monday 11:15 Commonwealth B

BB4

Hemofoam: A biopolymer-based foam for treating non-compressible hemorrhage

Srinivasa R. Raghavan, Matthew B. Dowling, and Joseph White

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In modern warfare, 85% of preventable deaths on the battlefield are caused by non-compressible hemorrhage, usually due to high-velocity penetrating shrapnel. Non-compressible hemorrhaging is particularly threatening because the injury is deep within the body where the application of a tourniquet or topical dressing cannot be utilized. One strategy for treating non-compressible battlefield injury is to inject a self-supporting foam into the wound site to prevent fatal blood loss. Towards this end, we have developed an in situ forming "hemofoam" based on previously published concepts from our lab. Utilizing the "cell-gripping" nature of hydrophobically modified (hm) biopolymers, we have produced a biocompatible foaming system. The "cell-gripping" action creates a gel-like structure with blood, which is similar to the action of the body's own clotting cascade. This talk will discuss the formulation of the foam and also the rheology of mixtures of blood and foam. Moreover, we have found that the gelation can be reversed by applying a solution of cyclodextrins (cyclic sugars), which have hydrophobic binding pockets that can sequester the hydrophobic moieties on the polymers, thus releasing the cells. Results with animal injury models suggest that these hm-polymer-based foams are viable hemostatic agents for non-compressible injuries.

Monday 11:40 Commonwealth B

BB5

Micro-heterogeneity metrics for diffusion in soft matter

Paula A. Vasquez¹, John Mellnik², Scott McKinley³, Jacob Witten⁴, David Hill⁵, and Greg Forest²

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Many biological materials are characterized as complex heterogeneous multiphase and multicomponent systems consisting of macromolecules in various stages of organization. These different stages of organization result in multiple characteristic length and timescales in the system. The understanding of such complex structures and dynamics is of major importance in their study. In this talk, we introduce a protocol to characterize micro-heterogeneity based on microrheology data of diffusing probes. The protocol uses established techniques such as Gaussianity of the van Hove correlation function, hierarchical clustering algorithms, and gap statistics to identify statistically distinct clusters based on the distribution of particle paths. The protocol is applied to both numerically simulated data and experimental data for both viscous and viscoelastic materials.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Monday 10:00 Commonwealth C

SM1

Viscoelastic properties of polymer electrolytes: Mechanical and light scattering studies of a model system

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The relation between mechanical and electrical relaxation in polymer electrolytes is an unresolved fundamental problem in polymer physics and has important implications for the application of such materials in electrochemical devices. While the electrical properties of polymer electrolytes have been the subject of numerous studies, their mechanical properties have received much less attention. In this work the viscoelastic properties of poly(propylene glycol) and lithium perchlorate mixtures are investigated by the combination of mechanical measurements and light scattering techniques. The overall viscoelastic behavior of the examined polymer electrolytes resembles that of weakly associating polymers, due to the formation of transient crosslinks by lithium cations. However, no evidence is found for long-lived crosslinks, and the significant increase of viscosity with the increase of salt concentration is primarily caused by the increase of segmental friction. Similarly, the change of glass transition temperature (T_g) is also found to be the main reason for the increase of longitudinal modulus and sound velocity with increasing salt concentration at a given temperature in the Brillouin scattering experiments. Lastly, the Boson peak frequency at T_g in the low-frequency Raman measurement exhibits substantial decrease with increasing salt concentration. Since the sound velocity at T_g measured by Brillouin scattering only shows relatively weak dependence on salt concentration, this result suggests that the characteristic length scale for local elastic constant fluctuation in the poly(propylene glycol) and lithium perchlorate mixtures grows significantly with the addition of lithium salt.

Monday 10:25 Commonwealth C

SM2

Linear viscoelasticity and dielectric spectroscopy of ionomer/plasticizer mixtures: A transition from ionomer to polyelectrolyte

Quan Chen, Tyler Tunic, Nanqi Bao, Jing-Han Helen Wang, and Ralph H. Colby

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Unfavorable interaction between highly polar ion pairs and low polarity polymer medium for ionomers drives their ionic groups to aggregate. In contrast, for polyelectrolytes, the counterions prefer solvation in the polar medium to leave the chain charged, and accordingly strongly stretched due to charge repulsion. Surprisingly, a transition of ionomer to polyelectrolyte with increasing the dielectric constant of the medium has not been critically examined in literature. In this study, linear viscoelastic and dielectric properties of mixtures of ionomer and high dielectric constant nonvolatile plasticizers were examined. The ionomer chains having bulky side chains are not entangled in space. Upon introducing the plasticizer, the terminal relaxation is significantly accelerated and detailed analysis shows that the acceleration is contributed from three mechanisms: (1) a decrease of T_g (2) an increase of dielectric constant due to polar plasticizer and (3) ion solvation that further boost the dielectric constant by breaking the aggregates into individual ion pairs of large dipole moment. The latter two mechanisms weaken the electrostatic interaction between charges, which is the key to the ionomer-polyelectrolyte transition.

Monday 10:50 Commonwealth C

SM3

Linear viscoelasticity of oligomeric sulfonated styrene near the sol-gel transitionQuan Chen¹, Chongwen Huang², Ralph H. Colby¹, and R. A. Weiss²¹*Department of Materials Science and Engineering, Penn State University, State College, PA 16802, United States;* ²*Polymer Engineering, University of Akron, Akron, OH 44325-0301, United States*

Linear viscoelastic elasticity (LVE) of low-ion-content and non-entangled sulfonated polystyrene shows a sol-gel transition when the average number of ions per chain approaches one. This transition can be well understood by regarding the number of ionizable sites over a chain as functionality for chemical crosslinking. For ionomers below but very close to the gel point, the LVE shows power law relaxation similar to chemically crosslinked systems. Nevertheless, such ionomers also show terminal relaxation not seen in chemically crosslinking system, which is controlled by effective breakup of the largest clusters in the sol.^{1,2} Careful analysis of the power law region shows a change in exponent for the frequency dependence of G' from ~ 1 at high frequency to ~ 0.67 at low frequency, which strongly suggests a transition from mean-field percolation to critical percolation region known as the Ginzburg point. A mean-field theory by Rubinstein and Semenov^{1,2} has been modified to include a frequency range for critical percolation close to the gel point. The modified theory predicts well the LVE behavior of the sulfonated polystyrene samples, close to and also well beyond the gel point.

1) Semenov, A.N. and M. Rubinstein, 1998, Thermoreversible gelation in solutions of associative polymers. 1. Statics, *Macromolecules* 31, 1373-1385. 2) Rubinstein, M. and A.N. Semenov, 1998, Thermoreversible gelation in solutions of associating polymers. 2. Linear dynamics, *Macromolecules* 31, 1386-1397.

Monday 11:15 Commonwealth C

SM4

Deconstructing double-network hydrogels: The importance of grafted chains for achieving toughness

R. A. Weiss, Siamak Shams Es-haghi, and Arkady I. Leonov

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

This paper aims to shed light on the microstructure of tough, "double network" (DN) hydrogels synthesized by free-radical polymerization of a monomer within a highly crosslinked polyelectrolyte hydrogel. It also discusses the most efficient topological microstructure for toughness enhancement. Free-radical polymerization of crosslinked AMPS or SAPS hydrogels using a divinyl crosslinker typically contain residual unsaturation due to inefficient reaction of the crosslinking agent. When such networks are used to synthesize a double-network (DN) hydrogel, the polymerization of the second monomer results in grafting of some chains (or network) to the skeleton of the first network. The microstructures of most, if not all, of the previous DN hydrogels reported in the literature were not interpenetrating networks (IPN) or semi-interpenetrating networks (SIPN). Fourier transform infrared (FTIR) characterization of a hydrogel synthesized from the potassium salt of 3-sulfopropyl acrylate (SAPS) and 2-hydroxyethyl acrylate (HEA) demonstrated that polymer chains synthesized during the second polymerization step of a conventional DN hydrogel are grafted to the skeleton of the polyelectrolyte network. Uniaxial tensile tests performed on hydrogels synthesized from SAPS and acrylamide (AAm) indicate that linear or nonlinear polymerization of a second monomer within a network without grafting to the first network, i.e., forming an IPN or SIPN, does not produce a tough hydrogel. A necessary requirement for preparing strong and tough DN hydrogel is that long chains or a second network are grafted to the skeleton of the first network, and the concentration of the grafted chains is a crucial factor in determining the mechanical behavior of the hydrogel.

Monday 11:40 Commonwealth C

SM5

Carrageenan aggregation and gel transition

Florian Nettekheim, David J. Londono, Prashanth Badrinarayanan, Christopher J. Rasmussen, Dennis J. Walls, Yefim Brun, Laura E. Clinger, Christopher D. Chan, and Anne Golematis

Corporate Center for Analytical Science, DuPont, Wilmington, DE 19803, United States

The gel transition for three different types of carrageenan were investigated as a function of temperature and electrolyte concentration (KCl). Carrageenans are prone to forming helical and double helical aggregates, which lead to a significant change in viscosity and eventually gel formation. These aggregates are also a significant impediment for accurate determination of molecular weight by conventional SEC methods. This complication affects understanding of most aspects of the gel transition and appropriate interpretation of material properties. We followed the transition using dynamic rheology, optical rotation, micro-calorimetry, thermal conductivity and investigated structure under the various conditions using X-ray (SAXS, WAXS) and multi-detector SEC. Local interactions are probed by local techniques, such as Optical Rotation and SAXS, and more global techniques probe longer range effects of gelation, microscopy and rheology. Thermal analysis (thermal conductivity, micro-calorimetry) provide the heat signatures of structural transitions as well as the thermal properties of the material.

Symposium CR Computational Rheology

Organizers: Mike Graham and Ravi Prakash Jagadeeshan

Monday 10:00 Washington A

CR1

Computationally efficient algorithms for incorporation of hydrodynamic and excluded volume interactions in Brownian dynamics simulations of high molecular weight polystyrene: An overview of the effective parameters in the coil-stretch transition

Amir Saadat and Bamin Khomami

Chemical and Biomolecular Engineering, University of Tennessee-Knoxville, Knoxville, TN, United States

Excluded volume and hydrodynamic interactions play a central role in macromolecular dynamics under equilibrium and non-equilibrium settings. The high computational cost of incorporating the influence of hydrodynamic interaction in meso-scale simulation of polymer dynamics has motivated much research on development of high fidelity and cost efficient techniques. Among them, the Chebyshev polynomial based techniques and the Krylov subspace methods are most promising. To this end, in this study we have developed a series of semi-implicit predictor-corrector Brownian dynamics algorithms for bead-spring chain micromechanical description of polymers that utilizes either the Chebyshev or the Krylov framework. The algorithm with the highest efficiency and fidelity, namely, the Krylov subspace method, is used to simulate dilute solutions of high molecular weight polystyrene in uniaxial extensional flow [L. Li, R. G. Larson, and T. Sridhar, *J. Rheol.* 44, 291 (2000)]. Finally, the influence of different parameters, namely appropriate inclusion of excluded volume (EV) and hydrodynamic interactions (HI), the level of fine-graining, the type of EV potential, and the type of conservative spring force law on the observed extensional hardening of polystyrene dilute solutions over a broad molecular weight range will be discussed.

Monday 10:25 Washington A

CR2

The effect of concentration, solvent quality and flow type on coil-stretch hysteresis in planar mixed flows of polymer solutions: A Brownian dynamics study

Chandi Sasmal and J. Ravi Prakash

Chemical Engineering, Monash University, Melbourne, Victoria 3800, Australia

A multi-chain Brownian Dynamics (BD) algorithm has been developed that enables the simulation of polymer solutions at finite concentrations in planar mixed flows, which are linear combinations of planar shear and planar extensional flows. The algorithm uses periodic boundary conditions (PBCs), and accounts for lattice deformation due to flow by adopting Less-Edwards PBCs for shear flows and Kraynik-Reinelt PBCs for mixed and extensional flows. Fluctuating intra and intermolecular hydrodynamic interactions are incorporated via the Rotne-Prager-Yamakawa tensor, and excluded volume interactions are modelled by a narrow-Gaussian potential acting pair-wise between segments on polymer chains. Planar mixed flows are characterized by a mixedness parameter, χ and a flow strength parameter, Γ . In the limit of $\chi \rightarrow 0$, the flow is pure shear, while for $\chi \rightarrow 1$, it is purely extensional. In dilute polymer solutions, it has been shown that there exists a critical mixedness parameter, χ_c , below which the flow is shear dominated, while being extension dominated for $\chi > \chi_c$. Here we determine the scaling of χ_c with concentration, solvent quality, and chain length. The correlation between χ_c and the phenomenon of coil-stretch hysteresis has not been extensively studied so far. For dilute polymer solutions, it is well known that the size of the coil-stretch hysteresis window observed in planar mixed flows is significantly influenced by the value of the mixedness parameter, vanishing as $\chi \rightarrow 0$, and having a maximum at $\chi \rightarrow 1$. Here, we study the dynamics of coil-stretch hysteresis under a variety of circumstances, which include varying the concentration, solvent quality and chain length. In particular, we examine the connection between χ_c and the existence of coil-stretch hysteresis.

Monday 10:50 Washington A

CR3

Structure and rheology of polymer solutions from coarse-grained molecular dynamics simulations: Effects of polymer concentration, solvent quality and geometric confinementYutian Yang and Radhakrishna Sureshkumar*Department of Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244, United States*

Structure, dynamics and rheology of solutions of flexible linear polymers are investigated using molecular dynamics (MD) simulations in presence of explicit solvent mediated interactions. Coarse-grained (CG) molecular models and corresponding force fields are employed to describe the polymer, solvent and the underlying physico-chemical interactions. The CG models are validated against atomistic ones by comparing the predictions of certain structure parameters such as persistence length, radius of gyration and radial distribution functions of the monomeric units. We will first present results for the dynamics of a single polymer chain in shear flow. The effects of chain length and shear rate on the configuration statistics, e.g. tumbling frequency and orientation distribution of the end-to-end vector, will be presented and compared to experimental observations and predictions of stochastic dynamics simulations. Further, the effects of solvent-polymer interactions under good, theta and poor solvent conditions as well as geometric confinement in presence of favorable, neutral and unfavorable polymer-wall interactions on the configuration dynamics of a single polymer chain will be also discussed. Specifically, the role of solvent quality will be shown to have a pronounced effect on coil-stretch transition in shear flow. CGMD predictions for the relationship between the zero-shear viscosity and polymer concentration in dilute and semi-dilute regimes will be presented and compared to experiment results. Shear thinning behavior is observed in both dilute and semidilute solutions in non-equilibrium molecular dynamics simulations. Possible approaches to parameterize phenomenological constitutive models using MD simulation data will also be discussed. (Support from the National Science Foundation through grants CBET-1055219 and CDI 1049489 is gratefully acknowledged).

Monday 11:15 Washington A

CR4

Scaling relations for structural and rheological properties of chains of different architectures in dilute solutions: A molecular simulation studyFardin Khabaz and Rajesh Khare*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States*

The chain size and intrinsic viscosity of linear polymer chains in dilute solution have been well studied by experimental and theoretical techniques. On the other hand, the effects of the chain architecture on the size, shape and intrinsic viscosity of polymer chains are not well characterized.

In this work, we have used molecular dynamics (MD) simulations to study the chain structure in and the rheology of dilute polymer solutions containing chains of three types of architectures - comb shaped, H-shaped and star - that are dissolved in a good solvent. The properties of these systems are directly compared with those of the linear chains at the same conditions. The use of MD simulations allows us to explicitly account for the intermolecular interactions as well as the chain topology in these calculations. Quantitative scaling results will be presented for the effect of the chain architecture on the size and shape characteristics of these chains. Furthermore, the intrinsic viscosity of these systems was quantified using a method similar to that used in the experiments. Results will also be presented for the values of the Mark-Houwink exponent for the chains of different architectures.

Monday 11:40 Washington A

CR5

Structure and rheology of surfactant micelle and micelle-nanoparticle solutions from molecular dynamics simulationsAbhinanden Sambasivam, Subas Dhakal, and Radhakrishna Sureshkumar*Department of Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244, United States*

Coarse grained molecular dynamics (MD) simulations [1-2], utilizing the LAMMPS MD simulation package, are used to study the equilibrium structure, shear-induced structure changes and rheology of cationic cylindrical micelle solutions. Systems that consist of up to a million coarse grained particles are simulated in the presence of explicit solvent and salt interactions. By varying the salt and surfactant concentrations, a phase diagram that consists of dilute, semi-dilute and entangled regimes is obtained. Addition of nanoparticles (NPs) to cationic wormlike micelles results in the formation of electrostatically stabilized micelle-NP junctions. The molecular mechanism and the kinetics of such junction formation will be elucidated. The effect of salt concentration and NP volume fraction on the structure and rheology of micelle-NP networks will be discussed. At sufficiently high salt concentrations, it is observed that branching in micelles results in a decrease in zero-shear viscosity of the solution. Non-equilibrium MD simulations are performed for micelle and micelle-NP solutions, showing both shear thickening and shear thinning behavior depending on the salt and surfactant concentration. A shear-induced isotropic to nematic transition was observed for Weissenberg number $Wi > 1$, where Wi is defined as the product of shear rate and the intrinsic structure relaxation time of the system. For $Wi > 1$, micelles align in the flow direction. Mean square displacement of NPs in such solutions suggests that particles could undergo transient trapping due to entanglement constraints arising from the micelle structure.

1. A.V. Sangwai & R. Sureshkumar, *Langmuir*, 27, 6628 (2011). 2. A.V. Sangwai & R. Sureshkumar, *Langmuir*, 28, 1127 (2012).

Symposium BC Blends, Composites and Multiphase Systems

Organizers: Arezoo Adekani and Florian Nettesheim

Monday 10:00 Washington B

BC1

Rheological percolation in polymer nano-composites: Is there a universal scaling ?

Denis Rodrigue and Hojjat Mahi

Chemical Engineering, Université Laval, Quebec, Quebec G1V 0A6, Canada

Considering the importance of percolation threshold on different properties in polymer nano-composites, the aim of this work is to verify possible universal features in the rheological properties of nano-composites close to percolation. To do this, nano-composites based on ethylene vinyl acetate (EVA) containing five different nano-particles including clay, multiwall carbon nanotube (CNT), CaCO₃, talc, and nano-crystalline cellulose (NCC) were prepared and a wide variety of rheological measurements including small amplitude oscillatory shear (SAOS), shear transient and uniaxial extension was investigated. From the results obtained, it was found that depending on particle surface area which is related to size, shape and density of particles, higher property changes were observed for the smallest and most anisometric particles (CNT, clay), followed by anisometric but larger particles (talc and NCC), and the least amount of changes was obtained for spherical particles (CaCO₃). However, regardless of particle characteristics, all the nano-composites showed similar features around percolation. The scaling exponents for data obtained under SAOS and shear transient were around 0.5, which indicates a Rouse dominated behavior in the linear data and a changeover from liquid-like to solid-like behavior in shear transient measurements.

Monday 10:25 Washington B

BC2

Bulk and shear rheology of a silica/polystyrene nanocomposite: Reinforcement and dynamics

Ran Tao and Sindee L. Simon

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

The relationship between the viscoelastic bulk and shear moduli has been discussed and debated for half a century since Leaderman's suggestion that the two responses arise from different molecular mechanisms. In this work, bulk and shear rheological studies were performed on a 10 wt% silica nanoparticle-filled polystyrene nanocomposite sample, using a custom-built pressurizable dilatometer and a commercial rheometer, respectively. Comparison of the bulk and shear moduli between the nanocomposite and neat polystyrene show that the absolute values of the limiting moduli in glassy and rubbery states are higher for the nanocomposite with the increase being in agreement with the lower bound of the rule of mixtures prediction. The KWW β values for the time-dependent bulk moduli are similar for the neat material and the nanocomposite. In addition, the horizontal shift factors have similar temperature dependence and the shape of shear master curves and retardation spectra are also similar. The implication is that the presence of nanoparticles does not significantly change the polymer dynamics associated with glass transition, except to slightly increase the T_g . Furthermore, comparison of the retardation spectra for both samples suggests that the underlying molecular mechanisms for the bulk and shear responses are similar at short times and that the long-time chain modes available to the shear response are not available to the bulk response, consistent with Plazek's earlier findings.

Monday 10:50 Washington B

BC3

Application of double reptation and time-dependent relaxation theory to the linear viscoelasticity of polymer nanocomposites

Xun Chen and Margaret J. Sobkowicz

Plastics Engineering Department, University of Massachusetts Lowell, Lowell, MA 01854, United States

Current research has shown that mechanical property improvements in nanocomposites are mainly related to the suspension state of the fillers and filler-matrix interface. Thus, constructing satisfactory physical models that can be used for quantitatively predicting rheological properties as well as elucidating the mechanism of reinforcement has attracted considerable scientific interest. In this work we employ the double reptation and time-dependent relaxation theories to reproduce the long-term viscoelastic response of polymer nanocomposites. The polymer matrix is assumed partitioned into two fractions: one confined by the fillers ϕ_s , which includes the "bridge chains", and the other the unconfined fraction ϕ_p . Through curve fitting, critical parameters such as mixing rule index β , domain fraction, and reptation time (τ_s and τ_p) are determined. These two reptation times can be equated to the life time for the attachment and entanglement, respectively. In this study, poly(butylene succinate)/silica, polypropylene/silica, polycarbonate/CNT and polyphenylene sulfide/CNT are employed as model polymer nanocomposite systems to test the linear viscoelasticity and applicability of double reptation theory. From stress relaxation tests, those nanocomposites, which show solid-like behavior in low frequency range, display typical polymer melt viscoelastic properties at long relaxation times, indicating that the filler-induced network can be considered to be purely frictional in nature, and the chains can diffuse away from the surface after long-term strain loading. With hydrophobic surface treatment, strong polymer-particle interactions result in much higher confined effect and further lead to longer relaxation time. The fitted curves are in good agreement with the experimental data at long times. The wide applicability of the model indicates that the two phase theory can be extended to the linear rheology of nanofilled polymer melts regardless of filler type.

Monday 11:15 Washington B

BC4

Tethered nanoparticle-polymer composites: Phase behavior and rheologyRahul Mangal and Lynden A. Archer*Chemical and Biomolecular Engineering, Cornell University, ITHACA, NY 14850, United States*

Polymer nanocomposites in which the particle radius (a) approaches the radius of gyration (R_g) of an entangled host polymer have been reported to exhibit an unusual negative reinforcement effect, which leads to an anomalous reduction in relative viscosity at low particle loadings, ϕ . However, the origin of these so-called Non-Einsteinian flow behaviors and their dependence on parameters such as particle content, polymer entanglements and the particle dispersion state is still unclear. Here, we will systematically explore the onset of these effects in composites with well-dispersed nanoparticles as a function of host molecular weights and particle loadings. Using small angle x-ray scattering measurements we confirm that presence of enthalpic interactions between the tethered chains and the host polymer facilitate complete dispersion of the particles in the host at all molecular weights and ϕ studied. Also, we show that the phase stability of the suspensions of tethered N-mer chains in a host of P-mers extends to P/N ratios as high as 160. Rheology experiments indicate that addition of the nanoparticles to an entangled host polymer leads to an unexpected cascade of dynamics affecting the viscosity of the suspension. The effect was found to be strongly dependent on relative size of polymer (R_g) and particle (a). We systematically investigate these unusual behavior using rheology and x-ray photon correlation spectroscopy to elucidate the fundamental origins of non-Einsteinian flow behavior in polymer- nanoparticle composites.

Monday 11:40 Washington B

BC5

Conductive nanocomposites of polyethylene/oxidized polyethylene (PE/OPE) blends with thermally reduced graphene and carbon blackMuhammad Z. Iqbal¹, Travis J. Arnold¹, Sunil P. Lonkar², Ahmed A. Abdala², and Matthew W. Liberatore¹¹*Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States;* ²*Chemical Engineering, The Petroleum Institute, Abu Dhabi, Abu Dhabi 2533, United Arab Emirates*

Designing new polymeric materials by blending two or more different polymers has always been fascinating. Miscibility of the blended polymers decides final properties of the materials. In this presentation, conductive nanocomposites of PE/OPE blends with graphene and carbon black (CB) are reported. Graphene, produced by simultaneous thermal exfoliation and reduction of graphite oxide, is characterized by XRD, Raman, TEM and bulk density measurements. Nanocomposites of 80/20 and 60/40 PE/OPE blends with varying loadings of graphene and CB are prepared via solvent blending. The nanocomposites have been characterized for their rheological, thermal, mechanical, electrical and morphological properties. Blending PE with OPE shows plasticization of PE chains by reducing the zero shear viscosity, η_0 at 160°C. The miscibility behavior of PE and OPE has been analyzed using the Cole-Cole plots. Incorporating graphene increases η_0 of the nanocomposites and at 1 wt% loading, η_0 reaches that of neat PE. Furthermore, ~ 1 order of magnitude increase in shear modulus has been observed at 1 wt% graphene loading. Similar trends have been observed for CB -nanocomposites but at higher CB loadings. Thermo-mechanical analyses show improvement in storage modulus of the nanocomposites with graphene at various temperatures. Fractured-surface morphology via SEM shows the existence of single phase in PE/OPE blends. Moreover, the electrical conductivity and thermogravimetric measurements are also reported at various graphene and CB loadings.

Symposium SF

Self-assembly and Flow-induced Systems/Gels

Organizers: Eric Furst and Anne Grillet

Monday 10:00 Washington C

SF1

Role of dynamical heterogeneity in the rheology of colloidal gelsLilian C. Hsiao¹, Heekyoung Kang², Kyung Hyun Ahn², and Michael J. Solomon¹¹*Chemical Engineering, University of Michigan, Ann Arbor, MI, United States;* ²*School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea*

Colloidal gels are known to exhibit complex structural and dynamical changes when sheared, particularly when the applied flow is strong enough to cause rupture. Here, we investigate the effect of shear-induced dynamical heterogeneity on the nonlinear elasticity of colloidal gels. These gels are comprised of fluorescent, sterically stabilized poly(methyl methacrylate) colloids that are suspended in refractive index and density matched solvents. Non-adsorbing polystyrene is added to induce gelation with weak, short-ranged attraction. We show that step strain deformations introduce a bimodal distribution in the van Hove self-correlation function, pointing to the existence of a fast and slow subpopulation of colloids within sheared gels. A simple modification of mode coupling theory that considers only the contribution of localized dynamics provides excellent agreement with the nonlinear elasticity of these gels across a broad range of deformations. These results experimentally support the concept that yielding causes the erosion of slow, hydrodynamically rigid clusters.

Monday 10:25 Washington C

SF2

Assembly of rod-like particles in nematic liquid crystal filmsIris B. Liu¹, Mohamed A. Gharbi², Daniel A. Beller², Shu Yang³, Randall D. Kamien², and Kathleen J. Stebe¹¹*Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA, United States;* ²*Physics & Astronomy, University of Pennsylvania, Philadelphia, PA, United States;* ³*Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, United States*

Anisotropically shaped colloidal particles immersed in liquid crystals can generate strong elastic interactions. Such particles trapped at fluid interfaces can create capillary interactions that direct their assembly in well-defined orientations. These effects have been considered only recently, and are largely unexplored for complex fluids, in particular the nematic liquid crystal. In this work, we investigate the physics of these systems to explore the influence of particle geometry in colloidal interactions, both in the bulk and at the interface of nematic films. Rod-like particles are fabricated by photolithography and treated to control their anchoring and wetting properties. We report on their behavior in nematic films as a function of particle aspect ratio. When rod-like particles are immersed in the nematic film, they distort the director field to satisfy anchoring properties at their surface. The resulting elastic forces orient the particles along specific directions dictated by the confinement conditions of the nematic film. When particles are trapped at the interface of the nematic film, they distort the interface to satisfy wetting properties. This deformation gives rise to capillary forces between particles that compete with elastic forces. The resulting potential drives assembly of particles into novel structures and recent progress in understanding colloidal interaction is presented.

Monday 10:50 Washington C

SF3

Non-templated fabrication of partially aligned BCC thin film colloidal crystalsMidhun Joy, Tanyakorn Muangnapoh, Mark A. Snyder, and James F. Gilchrist*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States*

Convective deposition of monosized nanoparticles or microspheres on a substrate utilizes an evaporation-driven flow in a thin film formed across the advancing substrate. Confinement in the thin film results in capillary interactions that order particles into hexagonally arranged monolayers with varying domain size. In thicker thin films, random hexagonally packed crystals form through convection steering identified by Brewer et al., *Langmuir*, 2008. In recent work, we have extended the ability to deposit well-ordered hexagonal monolayers by adding lateral vibration in the direction of deposition. This vibration enhances the order parameter, the deposition rate, and enables coatings on relatively hydrophobic surfaces. In this talk, we introduce the discovery of utilizing this process to form BCC crystals from monosized colloids without templating the substrate nor changing the physical and chemical properties of the suspension. Relatively large domains of 3-12 layers cover as much as 50% of the substrate and the orientation of the BCC domains in the polycrystalline layer have a strong orientation relative to the flow direction. While the mechanism is poorly understood, these results are robust across silica and polystyrene particles in size and deposited on substrates such as glass, polystyrene, and PDMS.

Monday 11:15 Washington C

SF4

Viscoelastic focusing of rigid colloids in Poiseuille flowMichael P. Howard, Arash Nikoubashman, Nathan A. Mahynski, and Athanassios Z. Panagiotopoulos*Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States*

A major challenge in microfluidics is the efficient separation and capture of solute particles, which is crucial for many biomedical applications such as cell counting and genomic mapping. One promising method to achieve such separations is viscoelastic focusing, where particles dispersed in a shear-thinning viscoelastic solvent migrate to the centerline of channels under Poiseuille flow at low Reynolds numbers. This centerline focusing effect is contrary to the behavior observed in Newtonian solvents, where particles are pushed outward by flow. However, it is not clear whether this focusing extends to nanoscale solute particles. Although this effect has been recently documented in experiments, a rigorous microscopic description for the focusing mechanism is lacking.

We simulated spherical, nanoscale colloids in a viscoelastic medium under microfluidic slit and tube Poiseuille flow. We employed a hybrid molecular dynamics approach where the underlying Newtonian solvent was explicitly modeled, and viscoelasticity was introduced through microscopic bead-spring polymer chains. We observed that focusing could be achieved even for colloids of comparable size to the polymers, and that this effect could be sustained for Reynolds numbers up to the order of tens. We directly computed the effective forces on the colloids, and found that focusing results from a direct competition between outward hydrodynamic forces and inward viscoelastic stresses.

Monday 11:40 Washington C

SF5

Temperature dependent self-exfoliation of clay polymer nanocompositeHorst H. Winter¹ and Brian Momani²¹*Chemical Eng. and Polymer Science & Eng., University of Massachusetts, Amherst, MA 01002, United States;* ²*Chemical Engineering, University of Massachusetts, Amherst, MA 01003, United States*

Dynamic mechanical spectroscopy and small angle x-ray scattering (SAXS) were used to monitor the structural development of a clay/polymer nanocomposite during self-exfoliation at varying temperature levels in order to determine the temperature dependence of the exfoliation process. Upon mixing organo-clay powder aggregates into end-functionalized polybutadiene, the aggregates break up into individual clay particles (stacks of clay sheets) and, finally, separate into individual clay sheets (which consist of three layers: an aluminum rich center interposed between two

layers composed of silicon, hydrogen, and oxygen) to form a nanocomposite of randomly oriented clay sheets in a polymeric matrix. This very effective "self-exfoliation" mechanism was discovered in 2004 but its origin is still not definitively known. The exceptionality of this mechanism lies in the observation that it occurs rapidly and without requiring shear or sonication. As the clay exfoliation proceeds and the clay surface accessible to the polymer increases, polymer molecules and clay connect into a sample-spanning network, a physical gel, with increasing modulus and decreasing relaxation times. Thus, small amplitude oscillatory shear (SAOS) is a sensitive probe for the evolving structure and is chosen here for exploring the exfoliation dynamics.

Monday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Monday 1:30 Commonwealth A

SC6

Taylor dispersion of a passive tracer in the pressure-driven flow of a concentrated suspension of rigid, non-colloidal spheres

Arun Ramachandran

University of Toronto, Toronto, Canada

It is well known that the axial spreading of a slug of passive tracer in the laminar flow of a Newtonian liquid in a conduit for sufficiently high Peclet numbers is governed by a process called Taylor dispersion. The Taylor dispersion coefficient is related to the characteristic equilibration time, t_c , of solute concentration inhomogeneities over the cross-section of the conduit. The larger this time scale, the larger the Taylor dispersivity, and the greater the axial spreading of the solute. In this work, the Taylor dispersivity of a solute being carried in the suspending fluid of a concentrated suspension of rigid, non-colloidal particles, is analyzed. For suspensions, in addition to molecular diffusion, there are two other mechanisms influencing the characteristic equilibration time t_c : shear-induced self diffusion, and secondary currents driven by second normal stress differences. As shear-induced self diffusion and secondary currents become stronger, the time t_c , and therefore the Taylor dispersivity, are reduced. A scaling analysis is used to demarcate parameter regimes where the three mechanisms can provide a dominant contribution to the Taylor dispersivity. The scaling for Taylor dispersivity is also established in each regime. The trends from scaling analysis are verified with numerical computations. The model for solute transport is based on the phase-averaging approach adopted by Zydney and Colton, but incorporates a self-diffusion tensor based on experimental measurements. Particle migration effects are included by employing the suspension balance model of Nott and Brady along with the constitutive equations of Zarraga and Leighton. A comparison of the theoretical results from this work and experimental measurements of Taylor dispersivity will allow us to validate the models employed for describing shear-induced solute self diffusion and secondary flows.

Monday 1:55 Commonwealth A

SC7

Hydrodynamic lift and flow-induced ordering of deformable particles under flow

Yeng-Long Chen, Chih-Tang Liao, Yi-Fan Wu, and Shih-Hao Wang

Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

Hydrodynamic lift away from a wall of droplets, cells and other soft particles under flow has been well-noted and exploited for fractionation of healthy and diseased cells. We investigate the dependence of the lift force on the particle inertia (characterized by the Reynolds number Re) and the particle deformation (characterized by the particle Weissenberg number Wi) using a combination of lattice Boltzmann and immersed boundary methods. The observed hydrodynamic lift velocities are found to agree with the analysis of Leal et al [1], for hard spheres and droplets for $Re \ll 1$ and $Wi \ll 1$. However, the lift velocity is found to have non-linear weaker dependencies on Re and Wi at moderate Re and Wi . The lift velocity is observed to decrease faster than predicted as the particle moves away from the wall, and a "migration-free" region is found near the center between two plates. In addition, flow-induced disorder-order-disorder transitions are observed for very dense suspensions.

[1] B. P. Ho and L. G. Leal, *J. Fluid Mech.*, 1974, **65**, 365; P. C. H. Chan and L. G. Leal, *J. Fluid Mech.*, 1979, **92**, 131.

Monday 2:20 Commonwealth A

SC8

Fall velocity of a dense ball in oscillatory cross-sheared concentrated suspensions

Frédéric Blanc, Elisabeth Lemaire, and François Peters

CNRS, Université de Nice, LPMC-UMR 7336, Nice 06108, France

The fall velocity of a dense large ball in a suspension of neutrally buoyant non-Brownian particles subjected to horizontal oscillatory shear is studied. As the strain amplitude is increased, the mean velocity increases up to a maximum value before decreasing to the value that it would have in a resting suspension. The higher the frequency is, the stronger the effect is. The falling ball velocity can be largely increased in the presence of the oscillatory cross-shear flow. For instance, for a particle volume fraction of $\phi = 0.47$ it reaches four times the value it has in the unsheared suspension. At small strain amplitudes, it turns out that the velocity of the falling ball is determined by a balance between the steady drag flow, which drives the apparent suspension viscosity toward a high value, and the oscillatory cross-shear, which lessens it. A simple model is proposed to explain the experimental observations at small strain amplitude through the variation of an apparent viscosity. The velocity decrease observed at larger amplitude is not completely understood yet. However, the time variation of the velocity during one cycle suggests that it is not sufficient to consider only an apparent viscosity. Indeed, the vertical motion of the ball is found oscillatory with a frequency twice the frequency of the external shear rate. The amplitude of variation can be larger than the mean velocity, meaning that the dense ball moves upwards during part of one period.

Monday 2:45 Commonwealth A

SC9

Disturbance flows produced by polymeric micelles in simple-shear fieldsBryan A. Rolfe and Yong L. Joo*Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States*

We present results of nonequilibrium coarse-grained simulations demonstrating the complex flow induced by polymeric micelles in simple-shear fields. From a fluid dynamics perspective, micelles occupy the relatively unknown region between vesicles and star polymers. Whereas star polymers, and especially vesicles, have received much attention in the literature, we are the first, to our knowledge, to publish results on the flow behavior surrounding single micelles. We build on our previous work of multi-micelle systems in shear flow, and focus on the role of the micelle corona, the micelle core, and the importance of the Peclet number. Leveraging coarse-grained molecular dynamics and high-performance computing, we are able to explore the length and time-scales necessary to characterize single-micelle dynamics. We have also developed techniques to visualize surface stresses and quantify energy dissipation of the induced flows. With these results, we show that the disturbance flow induced by micelles is both unique from other soft particles, and important to understanding the microrheology of these systems. The results of this work have direct applications to shear-induced self-assembly and electrospinning, where flow disturbances play important role in the positioning of other suspended particles.

Monday 3:10 Commonwealth A

SC10

Flow-induced microstructure and rheology of linear and branched wormlike micelles using rheo-SANS and 1-2 plane flow-SANSJason P. Rich¹, Michael R. Weaver², Kathleen M. Weigandt³, and Gregory S. Smith¹¹*Neutron Sciences, Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States;*²*Analytical Sciences, The Procter & Gamble Co, Mason, OH 45040, United States;* ³*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, United States*

The threadlike microstructures that form by self-assembly in aqueous solutions of amphiphilic molecules have been the subject of numerous studies that link non-Newtonian rheological properties and complex flow behavior with molecular structure and dynamics. Known as wormlike micelles (WLMs), these structures constantly break and reform in equilibrium and have the ability to align under shear, leading to viscoelasticity, shear-thinning, and shear localization. The combination of rheology and small-angle neutron scattering (rheo-SANS) has provided much insight into the microstructural mechanisms underlying complex flow phenomena in WLM dispersions, though many important questions remain about the effect of branched WLM morphologies on flow-induced structure and rheology. In this talk, we will discuss the results of rheo-SANS and flow-gradient (1-2) shear plane flow-SANS studies of WLMs composed of sodium laureth-1 sulfate, an anionic surfactant used as a detergent and foaming agent in the consumer products industry, in the presence of salt. By comparing the flow-induced structures of linear (low salt) and branched (high salt) WLMs over a range of shear rates and surfactant concentrations, we demonstrate the intriguing observation that while both morphologies exhibit shear-thinning rheology, flow-induced alignment occurs only at high salt concentration where WLMs are branched. This result is in contrast to previous reports on similar surfactant systems, which suggest that WLM branching hinders shear alignment. We will discuss possible mechanisms for this behavior in light of the local flow-induced structure extracted from spatially-resolved flow-SANS measurements in the 1-2 shear plane. The results of model fitting of the scattering data to determine the structural parameters of shear-aligned WLM structures will also be presented.

Monday 4:00 Commonwealth A

SC11

Orthogonal superposition rheology as a tool to study structural changes in ER fluidsCarlos A. Gracia-Fernández, Elmoumni Aadil, Franck Aly, and Rajaram Bharath*TA Instruments, New Castle, DE 19720, United States*

Many simultaneous techniques are being used to follow structural changes in materials as a result of an imposed shear deformation. Orthogonal superposition, first mentioned by Philippoff in 1934 is a mechanical technique and uses a small amplitude oscillation shear applied orthogonal to a shear flow. In contrast to parallel superposition, the flow fields are not coupled and the orthogonal storage and loss moduli only measure the effect of shear on the microstructure. OSP has been implemented in the ARES-G2 rheometer by modifying the transducer to apply a small oscillatory displacement in normal direction, while the actuator of the rheometer performs the transient or oscillatory rotational shear deformation. The normal force transducer in this case applies the orthogonal deformation and records the force. The dynamic moduli, complex viscosity and phase are determined using the embedded instrument correlation technique. The flow cell used to apply the rotational and linear axial shear simultaneously is a modified double wall cylinder with an opening at the bottom to avoid annular pumping and windows at the top to eliminate surface tension effects. With the OSP option the rheometer is capable to perform the following additional test modes: 1. Small linear strain orthogonal oscillation superposed on rotational steady shear; 2. Small strain orthogonal oscillation superposed on rotational oscillation at the same frequency with varying amplitude ratio between axial and rotational oscillation shear (2D-SAOS); 3. Standalone small axial displacement oscillations. Electrorheological fluids are suspensions of extremely fine non-conducting particles in an electrically insulating fluid, which show dramatic and reversible rheological changes when the electric field is applied. The ARES-G2 OSP functionality is used to characterize the structural changes of ER fluids when different voltages and shearing conditions are applied. Particularly, 2D-SAOS gives more insight in the structure formation and provides a tool to quantify it.

Monday 4:25 Commonwealth A

SC12

Orthogonal superposition rheometry of colloidal glassesAlan R. Jacob¹, Andreas S. Poulos¹, Sunhyung Kim², Jan Vermant², and George Petekidis¹¹IESL and Department of Material Science and Technology, FORTH and University of Crete, Heraklion, Crete 70013, Greece;²Chemical Engineering, KU Leuven, Leuven, Belgium

Colloidal glasses are out of equilibrium states due to caging of colloidal particles by their neighbors. In this state the system can partly relax through short time in cage diffusion while long time motion is largely suppressed. Small amplitude oscillatory shear (SAOS or dynamic frequency sweeps), probing the visco-elasticity at rest does not exhibit any terminal flow regime due to the ultraslow or frozen alpha relaxation. However upon application of steady shear out of shear induced out of cage motion is introduced as the sample yields and flows. Here we present orthogonal superposition rheometry^{[1][2]}, a novel experiment on colloidal glasses, on two systems of hard spheres and stars, where SAOS is superimposed orthogonally on the rotational steady shear. In this way we directly probe the shear induced cage breaking and relaxation and its dependence on the externally imposed steady shear rate. The orthogonal storage and loss modulus (G'_{orth} and G''_{orth}) provide interesting information of the viscoelastic spectrum of such systems under shear. Shifting of the orthogonal storage and loss modulus may provide a master curve, with the shifting factors as well as the crossover frequency scaling almost linearly with the shear rate for hard sphere glasses and sublinearly for softer interpenetrating star-like micelles. Converting the mean square displacement obtained from Brownian Dynamics Simulation of the hard spheres glasses into G' and G'' , using Generalized Stokes Einstein equation, seems to agree well with the experimental G'_{orth} and G''_{orth} .^[3]

[1] Orthogonal superposition measurements using a rheometer equipped with a force rebalanced transducer, Jan Vermant *et al.*, Rev. Sci. Instrum. 68, 4090 (1997). [2] Superposition rheometry of a wormlike micellar fluid, Sunhyung Kim *et al.*, Rheol Acta, 52, 727(2013). [3] Estimating the viscoelastic moduli of complex fluids using Generalized Stokes Einstein Equation, Thomas G. Mason, Rheol Acta, 39, 371(2000).

Monday 4:50 Commonwealth A

SC13

Mechanical anisotropy in colloidal gels: Superposition rheology and 2D-SAOS

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Colloidal gels constitute an important material class, with a variety of advanced technological and biological applications. The generic and technologically exploited behaviour, is linked to the solid like properties of the aggregated structures at rest and their ability to become liquefied under the action of a mechanical stress, with a thixotropic response on timescales much beyond the intrinsic material time scales. Different theoretical concepts, either based on fractal structure, percolation or glassy dynamics have been proposed, but fail as yet to explain the observed mechanical response. Microstructural studies reveal a complex, multi-length scale and highly anisotropic and flow sensitive structure. The present work shows, for the first time, how this anisotropy is reflected in the mechanical properties with moduli of a model aggregated suspensions, with the moduli differing by as much as two orders of magnitude depending on the straining direction. Therefore, in this work the relevance of the structural anisotropy is investigated by looking at the mechanical properties in different straining directions, using both superposition flows [1] to evaluate the response during flow, and 2D-SAOS upon cessation of flow [2]. As a system under investigation, we use a model thixotropic suspension of fumed silica's in a PIB/paraffin oil mixture [3].

[1] J. Vermant, P. Moldenaers, J. Mewis, M. Ellis and R. Garritano; Orthogonal superposition measurements using a rheometer equipped with a force rebalanced transducer, Review of Scientific Instruments, 68, 4090-4096 (1997). [2] Mobuchon C.M.C. Heuzey, Carreau P.J., Reddy Naveen K., Vermant J.; Anisotropy of non-aqueous layered silicate suspensions subjected to shear flow. Journal of Rheology, 53(3) 517-538 2009). [3] Dullaert, K., Mewis, J.; A model system for thixotropy studies. (2005). Rheologica acta, 45 (1), 23-32.

Monday 5:15 Commonwealth A

SC14

Rayleigh-Plateau instability of magnetorheological suspensions in toggled fieldsJonathan L. Bauer¹, James W. Swan², and Eric M. Furst¹¹Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States;²Department of Chemical Engineering, Massachusetts Institute of Technology, Boston, MA 02139, United States

In a direct magnetic field, paramagnetic colloids form system-spanning, kinetically arrested networks. It is possible to phase separate and condense the suspension by toggling the external field [1]. In its structural evolution, the suspension undergoes a Rayleigh-Plateau instability for a range of field strengths and toggle frequencies. The particles initially chain together to form a percolated network that coarsens diffusively. As time progresses, the surface of the columns in the network become unstable. When the amplitude of the waves reaches a critical value the columns pinch off and condense into ellipsoidal structures.

First, we study the effects of toggle frequency and field strength on the breakup dynamics. The frequency controls the fluid-like nature of the breakup. By measuring the wavelength of the instability, we use Tomotika's analysis of viscous thread breakup [2] to infer the apparent viscosity contrast of the colloidal columns. Second, we characterize the thinning of the strands as a function of time [3-4]. These point out contrasting dynamics of smooth phase separations at low frequencies versus rupturing mechanisms at high frequencies.

Second, we demonstrate that the field strength controls the surface energetics of the columns and thus the timing of the instability. At a given frequency, there is a critical field strength at which breakup occurs. Increasing the field strength causes the instability to proceed more quickly. The data scales onto a master curve that predicts the time necessary for breakup to occur as a function of field strength relative to the critical field strength. These results can be used to estimate the self-assembly kinetics of polarizable colloidal suspensions in a toggled field.

[1] J.W. Swan et al., *Soft Matter*, 10, 1102-1109, 2014. [2] S. Tomotika, *Proc. Royal Soc. London A*, 150, 332-337, 1935. [3] G.H. McKinley and A. Tripathi, *J. Rheol.*, 44, 653-670, 2000. [4] K. Niedzwiedz et al. *Rheol. Acta*, 49, 1103-1116, 2010.

Monday 5:40 Commonwealth A

SC15

Understanding yield stress enhancement in magnetorheological suspensions with nonmagnetizable particles

Benjamin T. Wilson and Daniel J. Klingenberg

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Magnetorheological (MR) fluids are suspensions of magnetizable particles which a magnetic field can alter their rheological properties. Active research areas consider ways to enhance these changes in rheological properties. One potential method for enhancing rheological properties in MR fluids is adding nonmagnetizable particles to the suspension. Experiments and simulations show that adding nonmagnetizable particles to an MR fluid can enhance the field-induced yield stress. The goal of this research is to better understand the mechanism behind this enhancement. Both monolayer and three dimensional particle level simulations show suspensions consisting of magnetizable and nonmagnetizable spheres have a larger yield stress than suspensions containing only magnetizable spheres. Observing visualizations of the suspensions, two potential mechanisms were identified: nonmagnetizable spheres directly contributing to stress transfer and nonmagnetizable spheres stabilizing clusters of magnetizable spheres. These mechanisms were probed in two ways: using Large Amplitude Oscillatory Shear (LAOS) and observing force chain visualizations for monolayers. LAOS shows an increase in the plateau storage modulus, suggesting nonmagnetizable spheres participate in stress transfer. Moreover, the critical strain is unchanged by the presence of nonmagnetizable spheres, indicating the magnetizable clusters are not more stable. Force chain visualization reveals repulsive forces between magnetizable and nonmagnetizable spheres transmit stress through the system. The magnitude of repulsive forces within force chains was larger for mixtures than suspensions containing only magnetizable spheres. This implies that at high concentrations, the field induces magnetizable spheres to form structures, and nonmagnetizable spheres directly participate in stress transfer through these structures via repulsive interactions.

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Monday 1:30 Commonwealth B

BB6

A multiaxial approach to shear rheology: opposite effects of axial loading on shear moduli of biopolymer networks and tissues

Anne S. van Oosten and Paul A. Janmey

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The mechanical properties of extracellular matrices (ECM) influence cell functions. Results supporting this conclusion have largely been generated using mechanically linear elastic substrates. Tissues, however, have a significant viscous component and nonlinear elastic responses to applied loads. Moreover, tissues *in vivo* are often subjected to multiaxial mechanical deformations. Therefore, characterizing the mechanical properties of the ECM and tissue over a wide range of strains and time scales is important in order to understand the mechanical stimuli that cells experience *in vivo*. We have measured the dynamic shear moduli of fibrin networks, the structural component of blood clots, and collagen type 1, the most abundant ECM protein, under static compression and stretch. In order to facilitate the extrapolation of these findings to soft tissue mechanics, we tested whole and contracted blood clots as simplified tissue systems. We find that reconstituted ECM networks stiffen both under tension and shear deformation, but that they soften under compression. When compression or tension is applied in concert with a shear deformation, the shear stiffening behavior is modified with respect to the magnitude of shear strain required to elicit the response and the amplitude of the change. Whole blood clots are stiffer than fibrin networks but respond similarly to mechanical loading. Inhibition of myosin II lowers the shear moduli of the blood clots to values similar to those of the fibrin alone. Contracted blood clots that have expelled enough serum to densely pack the cells within them behave differently from uncontracted clots and biopolymer networks; they show stiffening under compression and weakening under extension. These findings give new insights in both fundamental biopolymer physics and the understanding of tissues under physiologically realistic mechanical deformation.

Monday 1:55 Commonwealth B

BB7

Structure-function relations and rigidity percolation in bovine articular cartilage under shear

Jesse L. Silverberg¹, Aliyah R. Barrett², Moumita Das³, Poul B. Petersen², Lawrence J. Bonassar⁴, and Itai Cohen¹

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Studies of hierarchical structure in biological tissues are fundamental to identifying useful design principles that can be transferred to both biological and non-biological engineered systems. Among mammalian soft tissues, articular cartilage is particularly interesting, as it can endure 60+ years of daily mechanical loading despite having minimal regenerative capacity. This remarkable resilience may be due to the depth-dependent mechanical properties, which are known to localize strain and energy dissipation to the tissue's surface. Based on qualitative observations, it has

been proposed that these properties arise from the depth-dependent collagen fiber orientation. Nevertheless, this structure-function relationship has not yet been quantified. Here, we use confocal elastography, a technique that combines a rheometer with high speed confocal imaging, quantitative polarized light microscopy, and Fourier transform infrared imaging to look for constitutive relations between mechanical and structural quantities. Surprisingly, we find weak correlations between the shear modulus and the collagen fiber orientation. Instead, we find a much stronger correlation with the concentration of collagen fibers, which shows a 2-fold variation in collagen volume fraction correlates with a 100-fold variation in the modulus, and follows a scaling law relation. Such dependencies are observed in the rheology of other biopolymer networks whose structure exhibits rigidity percolation phase transitions. Along these lines, we propose that the collagen network is near a percolation threshold that gives rise to these large mechanical variations and strain-localization at the tissue's surface.

Monday 2:20 Commonwealth B

BB8

In situ imaging of rapid articular cartilage deformation

Lena R. Bartell¹, Lawrence J. Bonassar², and Itai Cohen³

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Recently there has been much interest in understanding semiflexible polymer networks, especially those reconstituted from biopolymers. Studies have addressed phenomenon such as yielding, nonlinear responses, and rigidity percolation. Though this is an active area of research, the field has only recently made progress to take these concepts beyond isolated or idealized networks and apply them to describe real complex materials, such as biological tissues. Here we present methods to continue this progress and investigate the nonlinear mechanical behavior of biological networks in situ. Specifically, we investigate articular cartilage (AC), a soft tissue in joints that protects bone from loading. AC is primarily composed of two entangled fiber networks that are anisotropic and heterogeneous with depth into the tissue. We designed a custom, spring-loaded impact device to interface with fast-camera imaging for testing the response of AC and other soft materials under rapid impact and high local strain. We fluorescently patterned AC samples and, using the fast camera, tracked their deformation with depth during rapid impact, achieving spatial and temporal resolutions of 60 μm and 1 ms, respectively. The concurrent motion of an aluminum backplate acted as a force sensor. Results show that most deformation occurs in the surface region of AC which recent studies have revealed to be more compliant. Overall, this is an effective method to study the deformation of soft materials, such as biological networks, under a range of loading. It is broadly applicable and can be easily tuned to change parameters such as the impact energy, impact geometry, and surrounding fluid environment. This method is poised to inform how to add useful complexity to current polymer network models and to more accurately describe real tissues. This knowledge is also directly applicable in fields such as tissue engineering which have not yet been able to reproduce a material that adequately mimics the mechanical properties of native AC.

Monday 2:45 Commonwealth B

BB9

Unraveling the nonlinear viscoelastic properties of fibrin using LAOS

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A blood clot forms to prevent blood loss after a vascular injury. Within the clot a network of fibrin fibers develops that provides strength and stability. This network exhibits remarkable, yet complex, nonlinear viscoelastic properties that are important for its functioning in both healthy and pathological circumstances. In this study a constitutive model is developed, based on results of large amplitude oscillatory shear (LAOS) experiments, that describes the nonlinear viscoelastic behavior. The data, analyzed in terms of Lissajous-Bowditch plots (strain versus stress) illustrates three nonlinear features. The model is based on a Kelvin-Voigt model that has been developed to describe the mechanical properties of a forming fibrin network. This model is extended by including the three nonlinear features. The observed strain stiffening, originating from fiber rearrangements and intrinsic nonlinearities of the fibers, is incorporated using a strain dependent shear modulus. The second nonlinear feature is a softening effect upon multiple deformation cycles. It has been hypothesized that fibers plastically elongate during successive deformation cycles, leading to this thixotropic behavior. By analyzing the transient LAOS data, this effect is quantified and incorporated using a network state parameter that governs the decrease of the shear modulus based on the deformation history. A third nonlinear feature is an increase of the viscous dissipation during a deformation cycle, incorporated using a strain dependent viscous contribution. The nonlinear features are extracted from the data consecutively and used to find parameter values. The model describes the rich nonlinear viscoelastic behavior of the fibrin network. The followed approach illustrates that LAOS, and its analysis in terms of Lissajous-Bowditch plots, is suitable for the development of relatively simple models for complex nonlinear viscoelastic behavior.

Monday 3:10 Commonwealth B

BB10

Interplay of platelets, fibrinogen, and erythrocytes on the viscoelastic properties of contracting clots

Valerie Tutwiler, Rustem Litvinov, Chandrasekaran Nagaswami, Tatiana Lebedeva, Doug Cines, and John Weisel
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Clot contraction is the final step of blood clotting in mammals and plays a key role in hemostasis and restoring blood flow past obstructive thrombi. Contracted clots consist of a fibrin network interspersed with platelets on the perimeter of the clot and a close-packed array of polyhedral erythrocytes (polyhedrocytes) in the core, making the clot impermeable. This study investigates the role of platelets, fibrinogen, and erythrocytes on the viscoelastic properties, microstructure, and kinetics of the clot contraction. Platelet, erythrocyte, and fibrinogen levels were varied through

the use of reconstituted blood. Samples were recalcified and activated with the enzyme thrombin. The viscoelastic properties and the force of contraction of the resultant clot were assessed using high precision rheology. Clot microstructure was assessed with scanning electron microscopy and the kinetics of contraction was analyzed using a Thromboimager, which allows for characterization of clot size over time. Together these results allowed for the development of a physical model of the clot contraction process. Rheological studies showed that at high hematocrit (erythrocyte volume fraction) the storage, loss and complex moduli of the clots were significantly decreased when compared to lower hematocrit or platelet rich plasma (no erythrocytes). The tand was significantly increased at the highest hematocrit levels and revealed a shift toward viscoelastic behavior. The contractile force generated by the fibrin-platelet meshwork was also significantly decreased at higher hematocrit levels. Varying erythrocyte levels also affected the final size and structure of the clot and the kinetics of contraction. These results along with those of varying platelet and fibrinogen levels reveal that the platelet-fibrin network on the outside of the clot can generate forces needed to reduce the clot size and to compact the erythrocytes in a manner fundamental to the formation of a stiff, dense hemostatic plug with low permeability.

Monday 4:00 Commonwealth B

BB11

Silk e-gel viscoelasticity

Alan P. Tabatabai¹, Daniel L. Blair¹, and David L. Kaplan²

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We present experimental results on the rheology of gels derived from aqueous solutions of reconstituted *Bombyx mori* silk fibroin protein. Through electrochemistry, the silk protein solution develops local pH changes resulting in the assembly of protein into a weak gel (e-gel). We determine the physical properties of the e-gels by performing rheology and observe that they exhibit the characteristics of a crosslinked biopolymer network. Interestingly, we find that these silk gels exhibit linear elasticity over a range of up to two orders of magnitude larger than most crosslinked biopolymer networks. Moreover, the nonlinear rheology exhibits a strain-stiffening behavior that is fundamentally different than the strain-stiffening observed in crosslinked biopolymers. By utilizing spectroscopic techniques, we find that these differences between e-gels and crosslinked biopolymer networks are rooted in shear induced protein interactions.

Monday 4:25 Commonwealth B

BB12

Correlation between viscoelastic properties of cystic fibrosis mucus and patient clinical status

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Mucus is a complex fluid that protects most surfaces of the body, especially the epithelial surfaces. It acts as a dynamic semipermeable barrier, trapping particles (such as bacteria and many pathogens) before they can attack epithelial cells. From the rheological point of view, mucus is a dense, viscoelastic gel-like material, characterized by the presence of a large number of entanglements between glycoproteins and other mucosal components, stabilized by hydrogen bonding and electrostatic and hydrophobic interactions [1]. In some pathological situations, such as Cystic Fibrosis, mucus shows different rheological properties and impaired clearance. CF is the most frequent life-limiting genetic disease in Caucasian populations, among whom it occurs in approximately 1 in 3000 birth [2]. In CF patients, airways mucus shows an increased viscoelasticity due to the concentration of high molecular weight components. Such mucus thickening leads to abnormal mucus clearance and, finally, to bacterial overgrowth [3]. The altered rheological behavior of mucus results in chronic lung infection and inflammation, which causes most of the cases of morbidity and mortality. Here, we present a quantitative study on the correlation between CF mucus viscoelasticity and patients clinical status. A new diagnostic parameter based on the correlation between CF mucus elastic modulus and the severity of the disease has been developed, with a high predictive efficiency (88%) estimated by principal component analysis. The data presented here show that the elastic modulus of airways mucus could be used as a new clinical parameter in the prognostic evaluation of cystic fibrosis [4].

[1] M. Dawson, D. Wirtz and J. Hanes, *J Biol Chem*, 2003, 278, 50393-50401. [2] B. P. O'Sullivan and S. D. Freedman, *Lancet*, 2009, 373, 1891-1904. [3] S. K. Lai, Y.-Y. Wang, D. Wirtz and J. Hanes, *Adv Drug Deliv Rev*, 2009, 61, 86-100. [4] G. Tomaiuolo, G. Rusciano, S. Caserta, A. Carciati, V. Carnovale, P. Abete, A. Sasso and S. Guido, *Plos One*, 2014, 9.

Monday 4:50 Commonwealth B

BB13

The gelation of oil using ethylcellulose

Alejandro G. Marangoni and Maya Davidovich-Pinhas

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Ethylcellulose-structured oleogels have been recently shown to have a wide range of applications in food, cosmetics and pharmaceuticals. The characterization of the thermo-gelation mechanism and properties of ethyl cellulose/canola oil oleogels was performed using rheology and thermal analysis. The effect of EC molecular weight and concentration on small deformation rheological behavior was characterized. Temperature sweep experiments using different cooling/heating rates were used to analyze the sol-gel transition. Hysteresis was detected in all samples where a higher cross-over temperature was detected during the heating compared to the cooling. Cooling and heating rates did not affect this cross-over temperature. The storage modulus (G') increased with increasing polymer molecular weight and concentration. In addition, an increase in G' with decreasing cooling/heating rate was detected for low molecular weight samples (13-18kDa). The effect of molecular weight and concentration on

the gelation temperature was determined using frequency sweep experiments at different temperatures. A decrease in gelation temperature with a decrease in polymer molecular weight was detected. No evidence for thermal transitions upon gel setting suggested the absence of any ordered secondary structure formation. These results provide a first insight into the ethylcellulose/canola oil gelation mechanism. Such understanding could potentially contribute to the development of novel products and applications, and to a better understanding of van der Waals gels.

Monday 5:15 Commonwealth B

BB14

Composite biopolymer hydrogels with a thermally-activated component

Joseph C. White¹ and Surita R. Bhatia²

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We present a thermo-responsive system consisting of alginate, a natural biopolymer derived from algae, and synthetic PEO-PPO-PEO triblock copolymers. Alginate forms hydrogels due to "ionic crosslinking" with divalent cations, such as calcium or barium, while PEO-PPO-PEO triblocks create thermo-reversible gels at a critical gelation temperature due to interactions between micelles. Creating a dual-component system with alginate and PEO-PPO-PEO allows for tunable control over hydrogel thermo-mechanical properties. Our results indicate the incorporation of PEO-PPO-PEO within an existing alginate network creates a composite hydrogel with unique temperature-dependent mechanical properties. Shear rheology and compression show a dramatic increase in modulus as the lower gelation temperature (LGT) is reached, demonstrating the "activation" of the secondary PEO-PPO-PEO gel structure within the alginate matrix. The temperature at which the systems gel is concentration-dependent. We show the effect of PEO-PPO-PEO incorporation on the compression behavior of the composite gel, where below the LGT the native elastic response is observed, and as the LGT is reached, the response transitions into plastic deformation behavior due to the cubically packed triblock micelles sliding. Fracture analysis shows increases of up to 200% in fracture stress (e.g., from 50 kPa to 250 kPa for 3 wt% alginate/20 wt% triblock) when comparing composite gels below and above the LGT, which corresponds to a nearly 600% increase over a neat alginate hydrogel. We also show that the thermo-mechanical response is tunable and similar results can be achieved using different types of triblocks.

Monday 5:40 Commonwealth B

BB15

Hybrid crosslink single polymer network hydrogels for tissue engineering and substance delivery

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Using molecular dynamics simulation, we investigated constant strain rate deformation behavior of a model hydrogel consisting of a single polymer network in which the ratio between the number of physical and chemical cross-links was varied. The physical cross-links were modeled as clusters of acrylic acid groups (AA) connected by hydrophilic macromolecular chains. Chemical cross-links were represented as permanent bonds between selected segments of neighboring chains and were added after constitution of the physical cross-links. We demonstrate that only a small amount of chemical cross-links leads to significant changes in the mechanical behavior of the hydrogel, thus, providing means to control its ability to adapt and self-heal. The strongest effect of chemical cross-links on the non-linear deformation response was obtained for physical and chemical cross-links set far apart. The molecular mechanism of the hydrogel network deformation consisted of (i) hopping of AA groups between neighboring clusters, (ii) cluster reorientation and (iii) combination of the two. The redistribution of the force between chemical cross-links was more efficient than that between purely physical cross-links. The proposed model was tested using series of hydrogels based on PLA-PGA-PEG block copolymers end-capped with ITA and cross-linked by light initiated reaction of ITA C=C bonds. These materials can be used in tissue engineering and controlled active substance delivery.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Monday 1:30 Commonwealth C

SM6

The effect of kappa-carrageenan and salts on gelation behavior of concentrated solution of hydroxypropyl methylcellulose

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Hydroxypropyl methylcellulose (HPMC) and kappa-carrageenan have been used as key film forming ingredients in pharmaceutical industry. This research is to study the interaction of salts and kappa-carrageenan with concentrated HPMC solutions. This will help optimize manufacturing process of hard and soft capsules and oral-film strips. Rheological measurements suggested gel structure changes as a function of kappa-carrageenan and salt. The gel elastic modulus of HPMC/kappa-carrageenan blends increased by two orders of magnitude compared with HPMC gel, while the gel elastic modulus of HPMC/kappa-carrageenan/KCl (low concentration) blends increased by three orders of magnitude compared with HPMC gel. Thermal analysis showed that the depression of melting temperature can be fitted linearly with salt concentrations independent of kappa-carrageenan. The free water and bound water content calculated using enthalpy data showed that free water content also decreased

increasing salt concentrations. The secondary peak appeared (bound water) in the mixture of HPMC and kappa-carrageenan in the presence of KCl. As the KCl salt concentrations increased, the bound water peak also increased and shifted to higher temperature.

Monday 1:55 Commonwealth C

SM7

Self healing and thermo responsive zwitterionic copolymers

Ya Zhao, Tao Bai, Shaoyi Jiang, and Amy Q. Shen

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Zwitterionic polymers are well known for their non-fouling properties due to their unique pendant side chain structures. In this work, we incorporated temperature-responsive N-isopropylacrylamide (NiPAm) with zwitterionic monomers (Carboxybetaine methacrylate (CBMA) and Sulfobetaine methacrylate (SBMA)), and synthesized statistical copolymers poly(NiPAm-co-CBMA) and poly(NiPAm-co-SBMA). The self-healing and thermal-responsive properties of these statistical copolymers under large strains and different temperatures were characterized by conducting UV-visible spectroscopy, dynamic light scattering, and rheological characterizations. We showed that poly(NiPAm-co-CBMA) copolymers consisted both mechanically and thermally reversible networks, favoring them as reusable and biocompatible elastic materials. As a comparison, introducing SBMA into NiPAm reduced the thermo-sensitive and viscoelastic features from the pure NiPAm based polymer, yielding a delayed low critical solution temperature (LCST) and weakened viscoelastic response in poly(NiPAm-co-SBMA) copolymers at both room and body temperatures. Our work demonstrates that CBMA monomers in NiPAm-co-CBMA copolymer act as stronger ionic bridges to form elastic networks when compared with NiPAm-co-SBMA copolymer. As a result, poly(NiPAm-co-CBMA) possess both non-fouling and thermo-sensitive features, without compromising its mechanical properties.

Monday 2:20 Commonwealth C

SM8

A rheological study on the role of molecular structure on interfacial self-adhesion of polyethylene films at elevated temperatures

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In this study, the influence of molecular architecture on interfacial self-adhesion above melting temperature of polyethylene films was examined. The adhesion occurred through diffusion of chains at the interface at temperatures high enough to allow chains to perform segmental motion through reptation. It was shown that the adhesion strength, while the interface is still molten, depends on the rheological behavior of the polymer melt in elongational deformation. For stereo regular and narrow molecular weight distribution metallocene catalyzed ethylene α -olefins containing equal amount of SCB, a linear dependence of adhesion strength with Mw was observed. The results also indicated that the presence of an even low amount of long chain branches hinders the reptation motion and diffusion, and results in lower adhesion strength in metallocene ethylene α -olefins. Moreover, the adhesion strength was found to reach a maximum at a certain temperature range, which is called temperature sealing window. Generally, a wide temperature window is desirable for applications such as flexible packaging. Our findings indicated that highly branched polymer chains with high relaxation time show a broad temperature window. The melt toughness, calculated from the area under the extensional flow stress-strain results, was used to estimate the energy dissipated by melt before rupture and correlated to temperature plateau broadness.

Monday 2:45 Commonwealth C

SM9

The effect of isomer type on the thermal and rheological properties of poly-(ether-imides)

Manojkumar Chellamuthu¹ and Deepak Doraiswamy²

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Thermal and rheological properties of poly-(ether-imides) homo-polymers with meta and para monomer isomer types were investigated using oscillatory rheology and thermal characterization techniques. The poly-(ether-imide) synthesized from para-based isomer showed an improved Tg with superior chemical resistance while effectively maintaining the flow properties. The observed shift in Tg and minimal differences in shear thinning index were most likely due to differences in entanglement density and segmental relaxation between the polymers. Additionally, we have attempted to show-case the predictive capabilities of non-linear oscillatory vs linear oscillatory rheology in differentiating the entanglement densities between isomer types. The effect of co-monomers in terms of entanglement density and glass transition will also be evaluated

Monday 3:10 Commonwealth C

SM10

Mobility of nanoparticles in semi-dilute polymer solutions

Firoozeh Babaye Khorasani, Ryan Poling-Skutvik, Ramanan Krishnamoorti, and Jacinta C. Conrad

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We measure the mobility of nanoparticles at low concentrations in non-Newtonian semi-dilute aqueous solutions of high-molecular-weight polymers. Using optical microscopy and particle tracking algorithms, we image and track hydrophilic polystyrene nanoparticles of diameter 400 nm moving in aqueous solutions of partially hydrolyzed polyacrylamide of molecular weight 8,000,000 Da and concentration of c^* to $100c^*$, where c^* is the overlap concentration. For all samples, the effective diffusivity of the nanoparticles, extracted from the long-time limit of the MSD using the Stokes-Einstein relation, is greater than that calculated from the zero-shear-rate viscosity measured using bulk rheology. For concentrations $c > 10c^*$, the mean-square displacements (MSD) of particles measured as a function of lag time revealed that the particle dynamics

are subdiffusive at short time scales and are Fickian on long time scales. The timescale for the crossover from subdiffusive to Fickian dynamics increases with increasing polymer concentration; moreover, it is longer than the relaxation time scale for polymer blobs and shorter than the Rouse time scale. Our results thus suggest that the nanoparticle dynamics are coupled to those of the polymers on a length scale intermediate between the blob size and the radius of gyration.

Monday 4:00 Commonwealth C

SM11

Understanding the relations between free volume and the temperature and pressure coefficients of viscosity for miscible polymer blends

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The viscosity of molten polymers depends on the processing conditions such as shear rate, temperature and pressure. The pressure dependency is often ignored, although it can be important in polymer processing operations such as injection moulding and extrusion. The main reason for the limited attention for pressure effects is the fact that viscosity measurements at high pressure are quite intricate. Thus, establishing alternative methods to assess the pressure dependency of the viscosity can facilitate and improve numerical simulations for the design and optimization of polymer processing equipment. It has been demonstrated in literature that variations in viscosity with either pressure or temperature can be related to changes in the polymer free volume. Nevertheless, more systematic investigations are needed to unambiguously correlate free volume on the one hand and pressure and temperature dependent viscosities on the other hand. In the present work, miscible PMMA/PVDF blends of different compositions have been prepared by melt extrusion to allow to vary systematically the free volume and temperature and pressure coefficients of viscosity. The melt viscosity at different temperatures and pressures was measured by means of a capillary rheometer equipped with a specially designed pressure chamber. Based on these data, temperature and pressure coefficients of viscosity at constant shear rate and at constant shear stress were determined. Pressure-volume-temperature data were collected by means of a high pressure mercury dilatometer. From the PVT data in the melt region, the free volume of the materials was extracted by means of fits with the Simha-Somcynski equation of state. Interestingly, unique linear relations were found between the temperature coefficients of viscosity and the pressure coefficients of viscosity as well as between the pressure coefficients obtained from PVT data and the rheologically determined pressure coefficients.

Monday 4:25 Commonwealth C

SM12

Dielectric relaxation of entangled monodisperse polyisoprene: Contribution of constraint release

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Cis-polyisoprene (PI) has the type-A dipole so that its slow dielectric relaxation detects the orientational memory (two-time correlation) of the end-to-end vector (for linear PI) and/or end-to-branching point vector (for star PI). In contrast, for both linear and star PI, viscoelastic relaxation detects decay of isochronal orientational anisotropy. Thus, comparison of dielectric and viscoelastic data can reveal some detailed aspects of entanglement dynamics. Indeed, the comparison had demonstrated success and failure of the molecular picture of constraint release (CR)-activated full dynamic tube dilation (DTD) for entangled monodisperse linear and star PI, respectively, and success of the partial-DTD picture for star PI. However, these pictures just specify a relationship(s) between the dielectric and viscoelastic relaxation functions, not the mechanism and time scale of relaxation. For this problem, we have conducted dielectric and viscoelastic tests for blends of a fairly dilute probe PI (either linear or star) in a matrix of much longer linear PI to detect the probe dynamics: The CR/DTD mechanism for the probe, working in its monodisperse bulk, is quenched on blending. The relaxation of linear probe was found to be moderately retarded on blending, but this retardation was considerably weaker than that expected for reptation along the fully dilated tube in monodisperse bulk. This result suggests that the linear probe in monodisperse bulk reptates along a partially (and longitudinally) dilated tube that wriggles in the fully dilated tube. In contrast, for the star probe, the retardation on blending was found to be exponentially enhanced with increasing probe arm molecular weight. The magnitude of this retardation suggested that the star arm retraction in monodisperse bulk occurs along the longitudinally dilated tube that wriggles in a wider, laterally dilated tube that is still thinner compared to the fully dilated tube.

Monday 4:50 Commonwealth C

SM13

Component relaxation times in entangled binary blends of linear chains: Reptation/CLF along partially or fully dilated tube

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Recent dielectric analysis suggested that entangled linear cis-polyisoprene (PI) chains in monodisperse bulk reptates, in the terminal relaxation regime, along a partially dilated tube with its diameter being determined by the constraint release (CR)-activated tension equilibration along the chain backbone. In relation to this finding, we have re-examined the terminal relaxation times of components in linear PI blends having various component molecular weights and volume fractions, M_i and v_i ($i = 1$ and 2 for the short and long components). In entangled blends with $M_2 \gg M_1$ and large v_2 , the relaxation time $t_{2,b}$ of the long chain decreases with decreasing v_2 but stayed considerably larger than $t_{2,soln}$ of the same long chain in a solution having the same v_2 . This result suggested that the CR-activated tension equilibration retards the reptation of the long chain in such blends. A simple "solution model" considering this retardation due to the CR relaxation of long-short entanglements was formulated.

Utilizing data for the CR relaxation time $\tau_{dil-2,CR}$ of dilute long chains, the model well described the $\tau_{2,b}$ data in the blends. Nevertheless, this model could not apply to the cases where M2 and M1 are rather narrowly separated and the short-long entanglements considerably survive in the time scale of the long chain relaxation. For this case, a "blend model" was formulated to consider self-consistently, though in an approximate way, the CR relaxation of all species of entanglements (short-short, short-long, long-short, and long-long entanglements) thereby mimicking coupled relaxation of the long and short chains. The component relaxation times deduced from this model were surprisingly close to the data, not only for the PI/PI blend but also for polystyrene blends. This result suggests that reptation of the components in the blends occurs along partially dilated tube with the diameter being determined by the CR-activated tension equilibration, which is in harmony with the result obtained for monodisperse bulk.

Monday 5:15 Commonwealth C

SM14

Constitutive equations, and maximum stretch, for entangled combs and randomly branched polymers

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In analogy with the pom-pom model, we introduce a simple constitutive model for entangled comb polymers with multiple side-arms attached to a linear backbone. This is obtained by considering a set of coupled equations describing the stretch in the individual inter-branch backbone segments. For a series of well characterized polyisoprene and polystyrene combs, we find good agreement with the experimentally determined transient stress growth coefficients in uniaxial extension. By examining the stretch dynamics in detail, we show that the equations predict a sudden onset of backbone stretch as the flow rate is increased. Drag-strain coupling smoothens this transition to some extent. Within a range of flow rates, the effective maximum stretch (priority) of the comb centre is dependent on the flow rate, whilst remaining influenced by branch-point withdrawal of the outer branchpoints. We discuss how insights from this model can be used to improve the maximum stretch condition in more approximate numerical schemes for constitutive modelling of randomly branched polymers.

Monday 5:40 Commonwealth C

SM15

Comparison of the single molecular dynamics of linear and circular DNAs in microfluidic planar extensional flows

Yanfei Li¹, Christopher A. Brockman², Daniel Y. Yates³, Kai-Wen Hsiao², Gregory B. McKenna¹, Charles M. Schroeder², Michael J. San Francisco³, Julia A. Kornfield⁴, and Rae M. Anderson⁵

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It was predicted by de Gennes in 1974 [1] that a coiled linear polymer undergoes a coil-stretch transition (CST) to adopt an open configuration above a critical Weissenberg number (Wi). This remarkable prediction has been verified for linear polymers [2]. However, it remains unknown how the elongational flow behaviors of ring-like or circular polymers compare with those of the linear counterparts.

In the present study, 45 and 115 kbp circular dsDNAs were synthesized and fluorescently labeled to be visualized at the stagnation point in a novel extensional flow device that has a cross-slot design [3]. We, for the first time, examine the elongation dynamics of large circular and linear DNA molecules with the goal of providing fundamental data in order to compare the CST [1] for the two types of macromolecules. In addition, we examine the molecular individualism (MI) of the circular DNAs and compare it to that of linear DNAs.

Our study has shown that the relaxation time of linear DNA is about 3.2 times of that of the circular DNA of the same molecular weight, and this is true for both 45 and 115 kbp materials. Also, both linear and circular DNAs exhibit a steady state CST at a Wi of about 0.4. However, for both 45 and 115 kbp circular DNA, upon comparison with the 48.5 kbp linear DNA, it is found that the transition is shallower. More interestingly, unlike linear DNA that tends to adopt folded configuration during a transient stretch [2], the 115 kbp circular DNA prefers forming a kink near the middle of the chain, while the 45 kbp circular DNA always shows a dumbbell configuration. Therefore, MI is a function of both size and topology. Overall, circular polymers, due to their unique structure, behave quite differently from their linear counterparts.

[1] P.G. de Gennes, J. Chem. Phys. 60, 5030-5042 (1974). [2] T.T. Perkins, D.E. Smith, and S. Chu, Science 276, 2016-2021 (1997). [3] M. Tanyeri, M. Ranka, N. Sittipolkul, and C.M. Schroeder, Lab on a Chip 11, 1786-1794 (2011).

Symposium CR Computational Rheology

Organizers: Mike Graham and Ravi Prakash Jagadeeshan

Monday 1:30 Washington A

CR6

Brownian dynamics of functionalized deformable nanocarriers

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Theoretical/numerical investigations have been carried out to understand the response of deformable nanocarriers (NCs) or nanogels under physiologically relevant flow conditions. Brownian dynamics simulations and theoretical models have been utilized based on the hypothesis that Brownian motion, polymer-melt reptations, and entanglement density dominate the nanogel structure and dynamics. We specify an entanglement density and use simulated annealing to mimic the initial structure of the nanogel (which are experimentally prepared through Maillard reaction). We compute equilibrium and steady shear rheological properties as functions of shear rate and entanglement density in the presence of hydrodynamic interactions. The long-time diffusivity of the assembly is consistent with the radius of gyration of the nanogel (i.e. corresponding to diffusion of the NC as a whole). Polymer prior to Maillard reaction behaves like a star polymer. In the assembled gel, the mixing of dextran brushes increases entropy, while the brush entanglement poses an entropic penalty. When the shear near the endothelial surface drives the system away from equilibrium, the entropic penalty due to entanglement causes the deformable gel to resist volume deformation, and this enhances their role as potential drug carriers. We also resolve internal and inhomogeneous / anisotropic stresses and strains, incorporating boundary effects. The computational approaches described here serve as powerful tools to fine-tune NC design by taking both the physiological as well as the hydrodynamic factors into consideration. Development of such models is essential to gain useful insights that can be translated into the optimal design of nanocarriers for targeted drug delivery.

We acknowledge support from NIH through grant NIH 1R01EB006818-05.

Monday 1:55 Washington A

CR7

Rheological model selection: Bayesian assessment of good fits versus credible models

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Rheological models with more parameters can generally better reproduce available data, though this does not mean they are necessarily better justified or preferred, since good fits are only part of model selection. We pursue a formal approach that balances goodness of fit against overfitting, i.e. against the undesired scenario of using more model calibration (fit) parameters than is justified. The approach is based upon Bayesian inference that simultaneously calibrates model parameters and quantifies overall model suitability. This metric favors closeness to data but consistently penalizes both the number of model parameters and their a priori uncertainty. The penalty depends upon prior-to-calibration expectation of the viable range of model parameter values, which we discuss as an essential aspect of the selection criterion. Models that are physically grounded are usually accompanied by tighter physical constraints on their respective parameters. A relatively narrow range of viable model parameter values increases the attractiveness in the model selection framework. It also reflects an important model attribute: models grounded in physics can be expected to enjoy greater generality and perform better away from where they are calibrated. In contrast, purely empirical models can provide comparable fits, but may be penalized due to both a large number of parameters and their a priori uncertainty, reflecting increased uncertainty away from a point of calibration. We demonstrate the approach by selecting the best-justified number of modes, subject to quantified assumptions, in a Multi-mode Maxwell model description of experimental linear viscoelastic oscillatory shear properties of a physically crosslinked polymeric hydrogel (PVA-Borax). We also quantify the relative merits of the Multi-mode Maxwell model relative to a powerlaw critical gel model and purely empirical fits for the PVA-Borax gel and a gluten gel network.

Monday 2:20 Washington A

CR8

Non-equilibrium fluctuations in “jammed” associative polymer networks under stress

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At low temperatures the viscosity of an associative polymer melt becomes infinite due to the formation of extremely long-lived aggregates. We explore this so-called “jammed” state in a hybrid MD/MC computer simulation of telechelic polymers, in which temporary bonds between chain end-groups constantly form and break. We investigate the behavior of the jammed state under small stress. Below a critical stress, slow creep is observed. The shear rate has positive and negative values - the mean being positive. These athermal nonequilibrium fluctuations obey the Gallavotti-Cohen steady-state fluctuation theorem. This allows us to calculate the effective temperature that characterizes the fluctuations. These nonequilibrium fluctuations might be a general property of a jammed state. They are observed in other systems driven far from equilibrium, such as wormlike micelles, as well. The fluctuation theorem expresses the fluctuations in terms of rates of entropy production and release. A negative shear rate is due to a temporary decrease in entropy and increase in elastic properties. We will report on the underlying microscopic changes in the polymer network structure, which cause the entropy to increase resp. decrease.

Monday 2:45 Washington A

CR9

Structural change and oscillating dynamics of colloidal gels under oscillatory shear flowJun Dong Park and Kyung Hyun Ahn*School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea*

Oscillating dynamics and rheological behavior of the colloidal gel under oscillatory shear flow have been studied in line with microstructural change by using the Brownian dynamics simulation method. Under oscillatory shear flow, depending on the flow conditions of various strain amplitude and frequency, colloidal gel showed various microstructural changes. As strain amplitude increased, the network structure of the colloidal gel broke into clusters and small flocs accompanying decrease of the average bond number. The microstructural change led to different oscillating dynamics and rheological behavior. They were studied in three flow regions of SAOS (Small Amplitude Oscillatory Shear), intermediate (between SAOS and LAOS), LAOS (Large Amplitude Oscillatory Shear) regions. In SAOS region, no remarkable structural fluctuation was observed. On the other hand, in intermediate region and LAOS region, the structural fluctuations represented by the fluctuation of the average bond number were observed during the oscillation cycle. The observed structural fluctuations at each region indicated different oscillating dynamics. At each region, different stress response was observed as well as the oscillating dynamics. The complex stress responses were analyzed through the stress decomposition method which decomposes the stress response into elastic and viscous components. Associating the oscillating dynamics and the stress response to the microstructure, characteristic behavior of colloidal gel at three different flow regions of SAOS, intermediate, LAOS was discussed.

Monday 3:10 Washington A

CR10

Application of non-uniform magnetic fields on ferrofluid colloidal dispersions using an iterative constraint method: A Brownian dynamics studyLewis E. Wedgewood and Sean H. Dubina*Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States*

Ferrofluids are steadily rising in applications across many fields, preferred for their ability to be remotely positioned and controlled via external magnetic fields. Currently, most ferrofluid simulation techniques are focused on uniformly applied magnetic fields. The behavior of particles in ferromagnetic clusters in uniformly applied magnetic fields has been simulated using Brownian dynamics, Stokesian dynamics, and Monte Carlo methods. However, little research has been developed to observe the influence of non-uniformly applied magnetic fields in these simulations, especially at the particulate level. A constraint method is developed to satisfy Maxwell's Equations when a non-uniform magnetic field is applied to ferrofluids in a heterogeneous Brownian dynamics simulation that examines the effects of ferromagnetic clusters in a mesoscale particle collection. The procedure ensures that essential laws of magnetostatics are met, namely Maxwell's Equations. This is accomplished by allowing the system to advance by a time-step under a non-uniformly applied magnetic field, then adjusting the particles via an iterative constraint method until Maxwell's Equations are satisfied. Results are compared to existing Brownian dynamics simulations as well as homogeneous models, which assume magnetization is a direct effect of the magnetic field. In conclusion, the resultant constraint model, employed with the Brownian dynamics technique, generates chain-like cluster formations and therefore, realistic ferrofluid behavior under a non-uniformly applied magnetic field while observing fundamental magnetostatic laws.

Monday 4:00 Washington A

CR11

Electrorheology of vesicle suspensionsShravan Veerapaneni*Mathematics, University of Michigan, Ann Arbor, MI 48104, United States*

We will present a new boundary integral equation formulation that describes the coupled electro- and hydro-dynamics of a vesicle suspended in a viscous fluid and subjected to external flow and electric fields. The dynamics of the vesicle are characterized by a competition between the elastic, electric and viscous forces on its membrane. The classical Taylor-Melcher leaky-dielectric model is employed for the electric response of the vesicle and the Helfrich energy model combined with local inextensibility is employed for its elastic response. The coupled governing equations for the vesicle position and its transmembrane electric potential are solved using a numerical method that is spectrally accurate in space and first-order in time. Using this method, we simulate, for the first time, the buckling process of vesicles under applied electric field in three dimensions. We will discuss the rheology of dilute vesicle suspensions in applied electric fields.

Monday 4:25 Washington A

CR12

Direct numerical simulations (DNS) of particles in spatially varying electric fieldsEdison C. Amah¹, Pushpendra Singh¹, and Mohammad Janjua²*¹Mechanical and Industrial Engineering, New Jersey Institute of Technology, Newark, NJ 07102, United States; ²Mechanical Engineering, American University in Dubai, Media City, Dubai, United Arab Emirates*

A numerical scheme is developed to simulate the motion of dielectric particles in uniform and nonuniform electric fields of a microfluidic device. The particles are moved using a direct simulation scheme in which the fundamental equations of motion of fluid and solid particles are solved without the use of models. The motions of particles are tracked using a distributed Lagrange multiplier method (DLM) and the electric force acting on the particles is calculated by integrating the Maxwell stress tensor (MST) over the particle surfaces. One of the key features of the DLM method is that the fluid-particle system is treated implicitly by using a combined weak formulation where the forces and moments between the particles and fluid cancel; as they are internal to the combined system. The MST is obtained from the electric potential, which, in turn, is obtained by

solving the electrostatic problem. In our numerical scheme the Marchuk-Yanenko operator-splitting technique is used to decouple the difficulties associated with the incompressibility constraint, the nonlinear convection term, the rigid-body motion constraint and the electric force term. A comparison of the DNS results with those from the point-dipole approximation shows that the accuracy of the latter diminishes when the distance between the particles becomes comparable to the particle diameter; the domain size is comparable to the diameter; and also when the dielectric mismatch between the fluid and particles is relatively large.

Monday 4:50 Washington A

CR13

Numerical simulation of forced droplet formation with complex fluids

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The controlled formation of droplets is of fundamental industrial and academic interest. The fluids of interest vary between industries and applications, and can include Newtonian and non-Newtonian homogeneous fluids, as well as complex fluid-particle suspensions. Although the break-up of fluid jets was first described in the late 19th century (Plateau, J. 1873, Gauthiers-Villars, Paris and Lord Rayleigh, 1879, Proc. R. Soc. 29:71), the field has continued to challenge researchers (Eggers, J. 1997 Rev. Mod. Phys., 69(3)). In order to accelerate our understanding of the forced generation of droplets of complex fluids, a numerical simulation study was initiated. The simulation describes the jetting mechanism for highly viscous complex fluids that utilizes a helical viscous micropump to transfer fluid into a jetting chamber and ejects a volume through the actuation of a voltage-controlled piezo mechanism. The simulations are performed with IBOFlow (2011), a multi-phase flow solver developed at the Fraunhofer-Chalmers Centre. The granular suspension is modeled as a mixed single phase suspension with all properties determined from the specific mixing of the carrier fluid and solid particles. The rheology of the suspension is modeled by a Carreau-Maxwell model. The surface tension between the two phases is included and modeled with the Brackbill model. The structural dynamics solver is coupled with the fluid flow solver through an immersed boundary condition and the resulting fluid forces are added as surface sources in the structural dynamics solver. The coupling is either made explicit or Gauss-Seidel iterations will be employed. The ejected fluid body has been studied with respect to the utilised piezo signal, geometric configuration of the nozzle chamber and filling of the jetting chamber. Relationships between piezo actuation signal and nozzle geometry are presented with respect to droplet volume and speed.

Monday 5:15 Washington A

CR14

Flows in irregular geometries simulated by Dissipative Particle Dynamics have improved convergence when guided by tailored body forces

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Fluid flows simulated by Dissipative Particle Dynamics (DPD) have been achieved mainly in regular geometries, such as rectilinear channel flow driven by a spatially uniform body force applied to each DPD particle. For particle models a body force can function as a local guide to drive the fluctuating particles in the general direction defined by the boundaries. Here the guiding force is derived from the pressure gradient of the Navier-Stokes (N-S) system. The flows of complex fluids in irregular geometries are generally troublesome to solve for by particle models such as DPD, SPH, etc.. A complex fluid driven by N-S derived body forces will yield disturbed V-P fields differing from their N-S counterparts. In this work we demonstrate this concept in the DPD simulation of two flows. The first is a square lattice of counter-rotating line vortices which can be viewed as a periodic square containing four vortices bounded by streamlines. This potential flow satisfies the N-S equation, and its periodicity avoids the need to model real-wall boundary conditions. For a Newtonian fluid of standard DPD particles excellent agreement is found between the analytical and the simulated stagnation-point velocity fields and stresses. A bead-spring molecular model with bending stiffness is introduced into the stagnation region, and its response is compared to experiments on actin molecules suspended in a stretching flow. The second example is flow in a plane channel with a rectangular indentation on one wall. The N-S pressure field is calculated from the Nektar code, and its gradient becomes the body force to guide deposition of platelets suspended in plasma flowing in the same channel.

Monday 5:40 Washington A

CR15

3D finite element formulation for flows with nonlinear partial slip condition on curved geometries

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For many classes of fluid flows, the behavior of the fluid doesn't adhere to the traditional no-slip condition or perfect slip law at the physical boundaries. For real geometries of interest, such physical boundaries are composed of arbitrary 3D curved surfaces (as defined using the CAD/geometric modeling system). This creates a need for an analysis tool that supports non-linear partial-slip boundary condition and not only provides required accuracy in a consistent way but also attains scalable performance. In this talk we will focus on a finite-element formulation that includes 3D non-linear partial-slip condition on general curved surfaces. We will present convergence studies on canonical problems and also demonstrate the current formulation on cases with complex curved surfaces. We will further show that the current formulation is amenable to high-order analysis and massive parallel computing.

Symposium FR Food Rheology

Organizers: Rakesh Gupta and Mahesh Padmanabhan

Monday 1:30 Washington B

FR1

A critical gel fluid with high extensibility: The rheology of chewing gum

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Chewing gum provides an excellent everyday example of viscoelastic behavior, and understanding its rheological properties is important for application purposes. Despite the fact that chewing involves large, complex, and unsteady deformations, little has been published concerning these deformation regimes. Here, we compare both the linear and nonlinear rheological behavior of selected commercial chewing gums and bubble gums.

Small amplitude oscillatory shear, shear creep, and steady shear demonstrated that both chewing and bubble gums behave like power-law critical gels in the linear regime. Nonlinear viscoelastic behavior was investigated using large amplitude oscillatory shear, shear creep, and start-up flows (in shear and uniaxial extension). Transient viscosity and creep compliance reveal nonlinear shear network destruction of the gums studied, and LAOS confirms this is due to a decrease in both the normalized elastic stored energy and viscous dissipated energy represented by G_1' and G_1'' . In start-up of steady uniaxial extension, all gums demonstrated high extensibility, while bubble gums showed more pronounced strain hardening and greater stresses to break than chewing gums. We argue that this combination of rheological signatures is sufficient to provide a new robust definition of chewing gum that is independent of specific molecular composition. There are potentially many different formulations and design routes that can achieve this distinctive rheological fingerprint.

For this work Randy H. Ewoldt are affiliated with both the University of Minnesota and the University of Illinois at Urbana-Champaign.

Monday 1:55 Washington B

FR2

Gel point determination thanks to microrheology

Roland Ramsch¹ and Jonathan Denis²

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This work presents a new technique of passive microrheology for the study of the microstructure viscoelastic properties and the gel point transition for polymers and hydrogels. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from the thermal energy, that is to say the Brownian motion. Our technique is based on Diffusing Wave Spectroscopy. It consists of Dynamic Light Scattering (DLS) extended to an opaque media. In a DWS experiment (more precisely Multi Speckle-DWS in our case), a coherent laser beam is applied to the sample containing scatterers (particles, droplets, fibers...). The light is multi-scattered by these scatterers, which leads to interfering backscattering waves. An interference image is detected by a multi-pixel detector. In dynamic mode, the scatterers motion (resulting from thermal energy) induces spot movements of the speckle image. A patented algorithm enables the treatment of this speckle image in order to determine the scatterers mobility in terms of speed and displacement which are directly related to the samples viscoelastic properties. The determination of the Mean Square Displacement (MSD) curve enables to characterize completely the viscoelastic properties of a sample. The technique allows to measure particles displacement in a spatial range between 0,1 and 100 nm and a time scale between 10⁻³ and 10⁵ seconds. This work presents a rescaling data processing known in rheology as time cure superposition [1], [2] to determine the gel point transition and gel strength parameters. Results will show the automatic determination of the gel point versus time for gelling systems, gel point versus concentration for xanthan polymer, cross-linker concentration effect on the gel point.

[1] T. H. Larsen, E. M. Furst, Physical Review Letters, 2008, 100, 14600. [2] K. M. Schultz, E. M. Furst, Soft Matter, 2012, 8, 6198.

Monday 2:20 Washington B

FR3

Microrheology of yoghurt formation

Jonathan Denis¹, Roland Ramsch², and Giovanni Brambilla²

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This work presents studies on yoghurt preparation using microrheology. Passive microrheology studies the mobility and displacement of micron sized particles which results from Brownian motion [1]. The motion of particles induces local deformations of the sample, which are directly related to its viscoelastic properties. Our technique is based on Multi Speckle Diffusing Wave Spectroscopy (MS-DWS), which consists of Dynamic Light Scattering (DLS) extended to an opaque media. With a patented algorithm, the backscattered interfering light can be analysed in terms of Mean Square Displacement (MSD), which is directly related to the viscoelastic properties of a sample. Moreover, the optical method allows to study especially weak gels without any applied shear, which avoids perturbation of the sample. This work shows how passive microrheology can be used to follow up yoghurt preparation. On the example of different types of milk (fat content, fresh milk or UHT) and acidifying agent (GDL, bacteria) different parameters were studied such as gel time, final elasticity and viscosity. It was shown, amongst other,

that increasing GDL concentration reduces gel time, but increases elasticity of the yoghurt. Gel time was determined by a new rescaling method, namely Time-Cure Superposition (TCS) [2,3]. This data processing determines the gel point according to the Winter-Chambon criterion [4].

[1] D. A. Weitz, D. J. Pine, in: *Dynamic Light Scattering*, W. Brown (Ed.) (Oxford Univ. Press, New York, 1993), Chap. 16. [2] T. H. Larsen, E. M. Furst, *Phys. Rev. Letters*, 2008, 100, 14600. [3] K. M. Schultz, E. M. Furst, *Soft Matter*, 2012, 8, 6198. [4] H. H. Winter, F. Chambon, *J. Rheology* 1986, 30, 364-382.

Monday 2:45 Washington B

FR4

Advanced rheometric tools for food applications

Joerg Laeuger

Anton Paar Germany, Ostfildern, Germany

Food products are rather complex multicomponent systems. Rheometric techniques have been used for gaining a better understanding of the structure but also of the behavior during the oral processing of food samples. The aim of this paper is to highlight some new techniques which further extend the rheometric tool box available for the food scientist. Due to stability reasons a structure is often highly desirable in food samples. On the other hand, since a good mouth feeling is required, these structures are mostly very weak and are influenced at already very small stresses and strains. The measurement of a small elasticity in samples with low viscosity is therefore quite challenging. A new rheometer concept based on two air bearing supported electronically commutated (EC) synchronous motors provides an increased sensitivity. With one motor as the drive and one motor kept at a fixed position and operated solely as a torque transducer the device is turned into an enhanced separate-motor-transducer rheometer (SMT) for rotational and oscillatory tests at a wide measuring range down to extremely low torques and normal forces. By selecting a measuring geometry which reduces the influence of fluid inertia and surface tension measurements of weakly elastic samples are possible. In the counter-rotation test mode the motors are set to rotate in opposite directions. The pre-set speed is divided and shared by the two motors, whereas the torque and normal force are measured at the upper motor unit. This mode is an invaluable option for microscopy applications by creating a stagnation plane allowing the observation of the structure elements of the sample during shear. Research in the last years showed that not just rheological but also tribological parameters are important for the mouth feeling. Special accessories turn the rheometer into a tribometer. Examples of tribological measurements and their correlation to the perception of certain attributes are presented.

Monday 3:10 Washington B

FR5

Revealing the role of starch in a hydrating snack food bolus: Combining α -amylase mediated starch digestion with transient rheology

Michael W. Boehm¹, Jason R. Stokes¹, Frederick J. Warren², Moore E. Jackson¹, Stefan K. Baier³, and Michael J. Gidley⁴

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Oral processing transforms a brittle snack food (e.g., potato chips) into a hydrated food bolus that has characteristics of a viscoelastic soft solid. This transformation comprises mechanical breakage and crushing, hydration by saliva, enzymatic degradation of starch by α -amylase and high shear deformation, all of which impact digestion-with implications for nutrition and health-and elicit sensory percepts that influence consumer acceptance. Thus, a key challenge when designing next generation snack foods is to emulate the temporal rheological properties of the food bolus during oral processing while maintaining consumer acceptability. We present our *in vitro* approach for capturing the transient rheology of a food bolus during hydration and enzymatic degradation using potato chips as a relatively simple model snack food. We have shown that the storage modulus of an *in vitro* bolus in physiological buffer increases over time according to first-order hydration kinetics; we have established that the storage and loss moduli are critically dependent on solids content and that the oil from the chips, which disperses as individual droplets within the solids matrix, reduces the moduli. We will demonstrate that α -amylase significantly reduces the elasticity of the bolus due to degradation of the potato starch. However, the bolus maintains its solid-like character, which we assign to the structuring properties of the residual plant cellular material. We discuss the implications of our findings and rheological approach on oral processing and digestion of foods.

Monday 4:00 Washington B

FR6

Extensional flow to formulate micron-scale oil-in-water emulsions

Daoyun Song¹, Johnny Casanovas², Sushant Agarwal³, Rakesh Gupta³, and Mahesh Padmanabhan⁴

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The inherent advantage of extensional flow over shear flow was exploited to formulate oil-in-water emulsions that have a controlled droplet size and size distribution. The roles of total extensional strain, strain rate, relative amount of extensional strain to shear strain, multiple stretching episodes and mixer geometry were examined. An extensional-flow mixing-device, consisting of a "cone" and containing inserts of different shapes and sizes was fabricated to subject liquids to large total extensional strains. Using a turbine impeller, several coarse soy bean oil-in-water emulsions, containing 50% by volume soybean oil, were formulated using polysorbate 60 and whey protein concentrate as emulsifiers. A phase-contrast optical microscope equipped with a digital camera was used to capture images of these emulsions. Droplet sizes were computed using ScionImage image analysis software, and the volume-averaged initial droplet size ranged between 20 μm and 30 μm . The coarse emulsions were pumped through the cone at different flow rates. It was found that neither a single episode of extension followed by relaxation of a coarse emulsion in the cone nor high shear flow through a fine capillary resulted in significant size reduction. By increasing the number of consecutive stretching

episodes and by multiple passages through the mixing device the average droplet size could be reduced to almost 1 μm . For these fine emulsions, a Shimadzu laser diffraction particle size analyzer was employed to give the complete droplet size distribution. The behavior of the different emulsions was observed as a function of time to see if ripening or phase-separation took place. For stable emulsions, the flow properties were measured using a Carri-Med CSL 100 rotational viscometer. In general, it was found that there was a clear relationship between the gap between the insert and the cone wall and the emulsion droplet size. Narrowing the gap resulted in a progressively finer emulsion. The value of the maximum extension rate could also be raised by increasing the flow rate, and this too led to progressively smaller dispersed phase sizes. These results were very repeatable, and there was virtually no temperature rise in the process. The fine emulsions produced using extensional flow seemed to possess a yield stress and were remarkably stable. Consequently, no phase separation was observed even after several months of storage. In addition, the shear viscosity of the fine emulsion could be as much as two orders of magnitude larger than that of the coarse emulsion, especially when the emulsion was forced to flow through clearances of the order of 25 μm . Increasing the amount of emulsifier used resulted in a finer emulsion but one whose viscosity, especially at low shear rates, was substantially higher. A key result of this work is that different stretch rate profiles, obtained by changing the insert geometry, had a major influence on both the size and size distribution of the final emulsion.

Monday 4:25 Washington B

FR7

Steady state rheology of HPMC solutions with a polyol plasticizer

Carlos A. Pinzon and Aldo Acevedo

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Rheological measurements were used to evaluate the plasticizer effect on the viscosity and yield stress of aqueous hydroxypropyl methylcellulose (HPMC) solutions for formulation and development of edible films for the oral delivery of active pharmaceutical products. Processing and structural properties of the polymer film provides an understanding of the molecular and component interactions necessary to optimize processes and develop new formulations. Typically, plasticizers can improve processing but cause undesirable effects on the performance, for example strength or dissolution. In this study HPMC aqueous solutions were prepared using glycerol as plasticizer in concentration from 0 to 40 wt%, shear rates from 0.01 to 100 s^{-1} , and constant 25 $^{\circ}\text{C}$ were used to evaluate the effect on the steady-state viscosity. The viscosity can be adjusted to a Bingham fluid model. Both the yield stress and plateau viscosity increased smoothly with increasing glycerol concentration up to 28%. Nevertheless, above this concentration a discontinuity on the trends suggested phase separation. Agreement with predictions of the phase behavior was observed. Results are discussed in the context of drying of casted films and their mechanical properties.

Symposium SF Self-assembly and Flow-induced Systems/Gels

Organizers: Eric Furst and Anne Grillet

Monday 1:30 Washington C

SF6

Peptide-based systems as equilibrium gels of valence-limited particles

Nikola A. Dudukovic and Charles F. Zukoski

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Solutions of short peptide derivative molecules can form rigid gels ($G' > 10,000 \text{ Pa}$) at very low volume fractions ($< 1\%$) due to highly specific anisotropic interactions. Increasing attractions in these systems results in self-assembly of molecules into space-filling fibrous networks that exhibit characteristic gel-like rheological properties. We explore a typical representative molecule, Fmoc-diphenylalanine (Fmoc-FF), which forms fibrous gels when dissolved in dimethyl sulfoxide (DMSO) and mixed with water. Using rheology measurements, confocal fluorescence microscopy, and static and dynamic X-ray scattering, we study the kinetics and dynamics of gel formation and aging. We find that the aging process of these gels is associated with a tendency of the system to reach a steady state through the structure evolving into an increasingly uniform network (correlated with growth to a plateau value of the elastic modulus), as opposed to coarsening seen in typical particulate gels. Further, we demonstrate that the gels are mechanically and thermally reversible, and hypothesize that the system is in equilibrium in its fibrous network state. The observations provide experimental evidence for simulations of aggregation of valence-limited "patchy" particles published in the literature, which suggest that upon increasing attractions, gelation can occur at low volume fractions without an intervening phase separation, resulting in an equilibrium gel.

Monday 1:55 Washington C

SF7

Capillary-induced gelation in ternary blends of immiscible polymers and silica particles

Trystan E. Domenech and Sachin S. Velankar

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We investigate capillary-induced gelation phenomena in ternary fluid-fluid-solid particles suspensions. The systems are composed of spherical silica particles dispersed in PIB, and a small to moderate quantity of PEO (which wets the particles almost completely) is added. The morphologies resulting from melt blending are examined by confocal microscopy, electron microscopy and rheometry. Increasing the amount of wetting fluid in the ternary system induces a morphological transition from a pendular network to compact capillary aggregates, with an intermediate funicular state. These transitions are similar to those found in wet granular materials, but remarkably, the capillary aggregates are themselves percolated into a network. To our knowledge, such a structure has not been seen previously and seems to result from arrested coalescence of the capillary aggregates due to a balance between their bulk solid-like properties and Laplace pressure. The yield stress increases at first, and then decreases as

the amount of wetting fluid increases, with a maximum value reached for a wetting fluid-to-particle volume ratio of roughly 0.2. For pendular systems, linear viscoelastic properties display soft glassy rheological behavior above the percolation threshold (~5 vol% particles) and complex viscosity data can be scaled using the high frequency plateau value, as well as a single characteristic relaxation time which decreases when the particle concentration is augmented. Additionally, particle concentration dependence of the yielding transition in the pendular regime appears to be very well described by two parameters extracted from the steady state flow curves: the yield stress and a critical shear rate value. Although these non-colloidal structures result from flow-driven assembly, the scaling laws for our pendular gels are reminiscent of silica-based colloidal gels with fractal geometry. Our studies suggest new pathways to create physical gels, where interparticle attraction strength is determined by capillary interactions.

Monday 2:20 Washington C

SF8

A green solar paint from precrystallized components

Ngoc A. Nguyen, Roddel Remy, and Michael E. Mackay

Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States

The morphology of poly (3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) based photovoltaic devices is a critical aspect to the solar cell performance. Many processing parameters have been studied to control the structure of this composite film including: variation of the semiconducting polymer molecular weight, thermal annealing and changing solvent systems. Particularly, halogenated solvents such as dichlorobenzene have been used to reach an optimal efficiency in P3HT based solar cell systems. However, thermal treatments at high temperatures and solvent toxicity raise concerns since the processing cost is high and there are environmental problems. Moreover, spin-coating is a common processing technique utilized to manufacture solar cells which is not appropriate for mass production. In this study, we use flow induced crystallization of P3HT/PCBM blends in a non-solvent at room temperature to make a liquid with the consistency of paint. Since the solvent does not have to dissolve the components it can be less aggressive and non-carcinogenic than those presently used. We found that shear not only removes defects from P3HT crystals it also leads to nanophase agglomeration of PCBM. Percolated network of P3HT fibrils and the PCBM phase separated domains apparently present better pathways for transporting electrons and holes. Thus, better performance of the solar cells from a pre-crystallized semiconducting polymer solution is found which also do not require thermal annealing.

Monday 2:45 Washington C

SF9

Mechanisms of shear thickening in transient guar networks

Yuntao T. Hu

Production Enhancement, Halliburton, Houston, TX, United States

The shear thickening behavior of reversibly cross-linked guar networks is studied using rheological and particle imaging velocity measurements. It is demonstrated that the elastic modulus of the shear thickening state and its relaxation time can be used to discriminate between non-Gaussian chain stretching and shear-induced crosslinking mechanisms. The detection of a linear strain regime where the measured modulus does not change with the strain amplitude indicates absence of non-Gaussian chain stretch. When chains are stretched into the non-Gaussian regime, the relaxation time becomes smaller whereas it remains unchanged (or can potentially increase) if only crosslink density increases. Strong evidence is presented for both non-Gaussian chain stretching and shear-induced increase in crosslink density being the mechanisms for shear thickening in cross-linked guar. Which mechanism(s) plays a predominant role for shear thickening depends on the applied shear rate and shear time. At shear rates not too much larger than $1/t$, where t is the network relaxation time, shear thickening is mainly caused by the increase in crosslink density. At higher shear rates, shear thickening is initiated by the increase in chain density at short times, and non-Gaussian chain stretching further enhances the magnitude of shear thickening at longer times. At high shear rates, flow may become unstable with bulk fracture, shear banding, and continuous flow occurring randomly as revealed by the velocity profile across the flow cell gap.

Monday 3:10 Washington C

SF10

Water sensitive self-assembly of gelators in oil: A bioinspired strategy for sealing oil leaks from submerged tubes

Hyuntaek Oh, Nicholas A. Yaraghi, and Srinivasa R. Raghavan

Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States

Molecular organogelators are known for their ability to convert a liquid into an elastic gel by the formation of a self-assembled fibrous network in three dimensions. This ability enables a variety of applications such as oil spill treatment, art conservation, and plasma and serum separation. Protein-based molecular gelators also play a critical role in biology. In particular, gelators in our blood stream perform the vital function of sealing wounds. At the wound site, an inactive form of the gelator (fibrinogen) is transformed by thrombin into an active gelator (fibrin), and a fibrin network forms to seal the wound. This process is highly sensitive to the environment: under normal conditions, the gelator remains inactive and does not hinder the blood flow. In this study, we put forward a scheme that mimics the environment-sensitive gelation of blood. A well-known organogelator, dibenzylidene sorbitol (DBS), was selected as a counterpart of fibrin and a mixture of non-polar solvent and DMSO was used as a model fluid. DBS solubilized in this solvent mixture remains as discrete molecules (inactive) and does not form a gel in the container or when flowed through a tube. However, when the tube springs a leak in an aqueous environment, DBS undergoes gelation at the site of the leak, thus sealing the leak. The diffusion of DMSO (good solvent for DBS) from the oil phase to the aqueous phase gives rise to a phase-sensitive gelation of DBS. We hope that our work will stimulate the study and application of phase-sensitive gelation.

Monday 4:00 Washington C

SF11

Computational studies of flow-induced structural changes in self-associating polymer networksMark Wilson¹ and Arlette R. Baljon²¹*Computational Science, San Diego State University, San Diego, CA 92182, United States;* ²*Physics, San Diego State University, San Diego, CA 92182, United States*

Solutions of associating polymers possess the ability to span a large spectrum of material properties, from fluid-like viscosity to near solid-like elastic dynamics. These viscoelastic materials are commonly studied by quantifying the stress response imposed through oscillatory shear deformation. Relatively small changes in external parameters, such as temperature, concentration, or frequency and amplitude of oscillation, can result in large transitions in the viscoelastic behavior. In the following, numerical simulations of associating polymers are utilized to study viscoelastic behavior. A hybrid molecular dynamics, Monte Carlo algorithm is employed. Polymer chains are modeled as a coarse grained bead-spring system. Functionalized end groups, at both ends of the polymer chains, can form reversible bonds according to MC rules. At high temperatures the system is shown to behave as a fluid. Decreasing the temperature below the micelle transition results in a self-assembly of the system, forming a network that is transient in time. The nodes of this network consist of aggregates of end groups, while links between aggregates are formed by one or more bridging polymer chains. We report on the macro-structural changes in such a polymer network that arise in response to an oscillatory shear. The stress response has been obtained as a function of the oscillatory frequency and amplitude in both the linear and nonlinear regimes. Data are correlated with observed changes in the flow-induced structure and dynamics of the transient networks. For instance, a decrease in the elastic modulus is usually due to an increase in the number of loops (chains that have both ends connected to the same aggregate) or dangles. A secondary cause is a tendency of the chains to form additional bridges between the same sets of aggregates, thereby increasing the mesh size of the network.

Monday 4:25 Washington C

SF12

Mesoscopic modeling and simulation of transiently networked fluids/gelsLin Zhou¹ and L.Pamela Cook²¹*Mathematics Department, New York City College of Technology, CUNY, Brooklyn, NY 11201, United States;* ²*Department of Mathematical Sciences, University of Delaware, Newark, DE 19716, United States*

Wormlike micellar solutions have been studied primarily through macroscopic models and their numerical simulation. Most such models predict an exponential decay in time in the (small amplitude) stress relaxation response. However, experiments show that as the concentration of the micelles increases, micellar solutions exhibit a stretched exponential or a power-law stress relaxation. These slow relaxation processes are similar to that of many biopolymer networks and physically cross-linked gels.

To understand the behavior of wormlike micellar solutions in both (exponential relaxation and slower/power-law relaxation) regimes, we consider the mesoscopic simulation of transient networks in which the connecting chains can break free and can reconnect to the network at randomly distributed sticky nodes (van den Brule and Hoogerbrugge, JNNFM 1995). The motion of the beads and junctions (nodes with beads) are governed by a Langevin equation. We explore the effect of the attachment/detachment rate of the sticky nodes and the effect that the number of beads that are allowed to connect to the sticky node has on the shear stress response of the networked system. The inclusion of the topology of the network in the simulations allows the entire system to reorganize in response to localized breakages. Stochastic simulations based on different probability distribution functions will be analyzed to understand the slow relaxation processes.

Monday 4:50 Washington C

SF13

Spatial mapping of flow-induced molecular alignment in a non-crystalline biopolymer fluid using double quantum filtered (DQF)²³Na MRIGalina E. Pavlovskaya and Thomas Meersmann*Sir Peter Mansfield Magnetic Resonance Centre, University of Nottingham, Nottingham, Nottingham NG7 2RD, United Kingdom*

Flow induced molecular alignment was observed experimentally in a non-liquid crystalline biopolymeric fluid during fully developed pipe flow. The fluid was comprised of rigid rods of the polysaccharide xanthan and exhibited shear-thinning behavior. Without requirement for optical transparency or the need for an added tracer, ²³Na magic angle (MA) double quantum filtered (DQF) magnetic resonance imaging (MRI) enabled the mapping of the anisotropic molecular arrangement under flow conditions. A regional net molecular alignment was found to be located in areas of high shear values in the vicinity of the tube wall. Furthermore, the xanthan molecules resumed a random orientation after the secession of flow. A flow induced net molecular alignment was observed previously in liquid crystalline phase but little experimental evidence exists for an alignment in non-liquid crystalline polymeric fluids that exhibit shear-thinning behavior. Shear-thinning behavior manifests itself in the decrease of the fluid viscosity as flow intensifies. A direct link of this rheological property to molecular behaviour (i.e. the molecular-mechanical link) is demonstrated in this work using magic angle (MA) double quantum filtered (DQF) ²³Na NMR spectroscopy. Adapted for MRI, the *in situ* MA DQF method highlighted the molecular alignment in regions with elevated spatial velocity gradients (i.e. areas of high shear) located near the wall during developed tubular flow. The 0.5 g of xanthan was dissolved in 100 g of 0.1M phosphate buffer, pH=7.0 to ensure rigid rod conformation of xanthan molecules in this non-crystalline fluid. It is important to note that no additional sodium tracer was added for the MRI experiments. All data in this study were obtained under lower than physiological sodium concentration.

Monday 5:15 Washington C

SF14

A Janus particle viscometerIlona Kretzschmar*Chemical Engineering, City College of the City University of New York, New York, NY, United States*

Gold-capped Janus particles have been shown to assemble into staggered chains upon exposure to an AC electric field. The AC electric field causes the polarization of the metal caps resulting in a dipole that is positioned at the base of the cap and is aligned with the external electric field. The particles assume an orientation within the staggered chain in which the caps of two adjacent particles touch. Simulations show that this configuration allows for the energetically most favorable dipole-dipole interaction. Recently, we have prepared Janus particles with varying iron oxide caps. One of the iron oxides, Fe_3O_4 , exhibits both conducting and magnetic properties. Exposure of the Fe_3O_4 Janus particles to a magnetic field leads to close-packed double chains, while staggered chains are formed in an AC electric field. This finding opens up the possibility to study chain dynamics, if conditions can be found in which the relative stability of the two minima can be varied through the external field strength. In this talk, we will report on the behavior of Fe_3O_4 -capped Janus particles in the presence of combined electric and magnetic fields and present a simple model that explains it. Using the model, we are able to predict conditions at which the Janus viscometer can be converted into a Janus rheometer.

Monday 5:40 Washington C

SF15

Microstructural origins of yield, strain hardening and hysteresis in thermoplastic elastomers under uniaxial deformation: An in-situ tensile-SANS studyCarlos R. López-Barrón¹ and Aaron P. Eberle²*¹ExxonMobil Chemical Company, Baytown, TX, United States; ²ExxonMobil, Annandale, NJ, United States*

In-situ morphological characterization of elastomeric materials under periodic deformation is crucial to understand the structural origin of equilibrium mechanical properties and time dependent properties like hysteresis and fatigue. We present unique measurements that combine the power of small-angle neutron scattering (SANS) and precision mechanical measurements to measure the morphology on the nanoscale and the mechanical properties simultaneously. To this end a new instrument was developed at the NIST Center for Neutron Research (NCNR), consisting of a Sentmanat extensional rheometer (SER) to measure the uniaxial stress response during SANS measurements. The first in-situ tensile-SANS (tenSANS) measurements were performed on two commercial thermoplastic elastomers (TPEs) consisting on styrene-isoprene-styrene (SIS) triblock copolymers with two styrene contents: 14 wt% (SIS14) and 22 wt% (SIS22). Under quiescent conditions, SIS14 forms a bcc lattice with glassy (polystyrene) spheres, whereas SIS22 forms glassy rods arranged in hexagonal structures. The glassy domains are connected by (polyisoprene) amorphous tie chains. By using advanced SANS nano-metrology techniques, we were able to quantify the special arrangement of the glassy domains and thereby determine affine deformation at low strains (in the linear regime), and cluster formation at high strains where yield and strain hardening is measured. Remnant nano-deformation is observed after loading-unloading cycles, which is directly correlated to the macroscopic permanent set and deformation hysteresis. In addition, the orientation angle of the clusters associated to yield and the alignment of the rods in the SIS22 system were quantified. Complementary techniques (in-situ WAXS and SALS and birefringence measurements during extension) are being used to quantify cavitation, strain-induced crystallization, and molecular alignment during uniaxial extension, and ultimately correlate these microstructural features with the measured stress.

Tuesday Morning

Symposium PL Plenary Lectures

Bingham Lecture

Tuesday 8:30 Millennium Hall

PL2

Rheology revealed - Measuring the atomistic-to-micron scale structure and dynamics of complex fluids and soft matter under flow with neutrons

Norman J. Wagner

Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States

The development of structure-property relationships for rheologically interesting fluids and soft materials is a common goal among rheologists and as a consequence, numerous methods have been developed to measure material structure under controlled flows - with the use of visible light being the most well known in the form of rheo-optics, light scattering, and direct microscopic observation under flow. In this presentation I will discuss the use of neutrons as a relatively new means of quantitatively investigating the structure, from the atomistic to the 10s of micron in scale, of rheologically complex fluids and soft materials under flow, as well as the nano- to micron scale dynamics in such materials. Methods to reveal the microstructure responsible for a broad range of rheologically interesting behaviors will be illustrated with examples including: shear thinning and thickening colloidal suspensions, shear banding polymer-like micelles, multilamellar vesicles, polymer blends, block copolymers, self-assembled surfactants, thixotropic gels, proteins and biopharmaceuticals. Methods to study the nanoscale internal dynamics of these fluids are also introduced and shown to reveal relationships between nanostructure and rheological properties. I will also discuss opportunities for further advances in this approach and connections to nonequilibrium thermodynamics and materials discovery, design, and development.

Symposium SC Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Tuesday 10:00 Commonwealth A

SC16

Rheology of non-Brownian particles suspended in a colloidal shear thickening fluid

Colin D. Cwalina and Norman J. Wagner

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Suspensions of non-Brownian particles in non-Newtonian fluids show a varied and rich flow behavior that often reflects the rheological properties of the suspending fluid. To date, such investigations have largely focused on matrices consisting of shear thinning and Boger fluids. Of significant interest is the link between the rheological properties of the suspension and non-trivial microstructures that develop as a consequence of hydrodynamic interactions between particles in the non-Newtonian suspending fluid [Van Loon et al. (2013)]. In the current work, we investigate the rheological consequences of adding non-Brownian spheres to moderately concentrated colloidal dispersions under shear flow. This particular choice of suspending fluid is novel in that it exhibits both shear thinning and shear thickening. In the range of non-Brownian particle volume fractions investigated, we find that the critical stress for the onset of shear thickening in these suspensions is identical to that of the pure colloidal dispersion, while the critical shear rate is a decreasing function of the volume fraction. These findings are of practical significance as many industrial processes and materials (e.g. cement) consist of suspensions of mixtures of colloidal and non-Brownian particles.

Tuesday 10:25 Commonwealth A

SC17

FT-rheology and MITLAOS analyses of concentrated fumed silica dispersions

Gale A. Holmes¹, Jonathan E. Seppala¹, Manojkumar Chellamuthu², and Kirk D. Rice³

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Fumed silica/oglioether dispersions at concentration levels below 18 mass % have been extensively studied and shown to be stable dispersions that exhibit continuous shear thickening (CST) behavior. Recent investigations have targeted greater than 20 mass % fumed silica/oglioether dispersions for use as performance enhancement additives in soft body armor. The large amplitude oscillatory shear (LAOS) study of 20 and 25 mass % dispersions showed a change from CST behavior to discrete shear thickening (DST). In the 25 mass % dispersion, the agglomerates were found to undergo non-reversible breakdown during the onset of shear thickening. The LAOS response of these dispersions were further investigated using the FT-Rheology and MITLAOS frameworks. From the FT-Rheology approach, the third (Φ_3) and fifth (Φ_5) harmonic phase

angles were found to trend, as predicted by Neidhöfer and Wilhelm, toward the expected shear thickening response (360°). In the post-transition region, however, the responses of Φ_3 and Φ_5 bifurcate with Φ_3 generally exhibiting shear thickening behavior, while Φ_5 trends toward a shear thinning response (180°). Following a suggestion by Ewoldt, MITLAOS analyses of the data indicate that there is a finite interval during shear thickening where the instantaneous stored energy exceeds the dissipated energy. This elastic dominated region is bracketed at low and high maximum strain rates by viscous dominated regions. The implications of these findings on the potential of STFs as liquid armor will be discussed.

Tuesday 10:50 Commonwealth A

SC18

Large amplitude oscillatory shear rheology study of shear-thickening dispersions

Sunilkumar Khandavalli and Jonathan Rothstein

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Shear-thickening fluids are an intriguing class of particle dispersions and are of an enormous amount of interest in both academia and industry. Significant research has been dedicated to understanding the origins of shear-thickening behavior of various shear-thickening fluids and the mechanisms have been accepted to be well understood. However, non-linear viscoelastic behavior of shear-thickening fluids is very less explored, which can offer significant insights of the underlying mechanisms. We present our study on the large amplitude oscillatory shear rheology (LAOS) behavior of shear-thickening dispersions. The study was conducted on three types of dispersions, which shear-thicken by three commonly known mechanisms. The first is a sterically stabilized nanoparticle dispersion which shear-thickens due to the formation of anisotropic hydroclusters driven by short range lubrication hydrodynamic forces. The second is a partially stabilized dispersion by the adsorption of a high molecular polymer onto the nanoparticles surface. This dispersion shear thickens by the formation of nanoparticle clusters bridged polymer chains facilitated by shear forces. The third is non-Brownian dense suspensions of corn starch in water and shear-thickens by shear-induced jamming of the particles, where particle contact/frictional forces are primarily the cause for the strong rise in the viscosity. In this talk, the LAOS characterization of the three shear-thickening systems will be presented. The inter-cycle as well as intra cycle viscoelastic nonlinearities will be examined for a range strain amplitude and frequency space through the observation of Lissajous-Bowditch plots and non-linear material quantities. The viscous nonlinearities of each fluid were found to agree well with the steady-shear thickening measurements. The elastic nonlinearities associated with each fluid were found to be quite different from each other. In this talk, they will be compared and the physical origins of their differences discussed.

Tuesday 11:15 Commonwealth A

SC19

Particle-scale simulation of shear thickening in dense colloidal suspensions

Ryohei Seto, Romain Mari, Jeffrey F. Morris, and Morton M. Denn

Levich Institute, City College of New York, New York, NY 10031, United States

Sheared suspensions are inherently out of equilibrium, so the rheology is determined by shear-induced microstructures. The shear-induced microstructures of colloidal suspensions are moderated by Brownian forces, causing the rheological response to depend on the Péclet number. Shear thickening in colloidal suspensions is a high Péclet number phenomenon, and here we address the shear thickening for concentrated colloidal suspensions. The unique feature introduced here is to regularize the lubrication singularity to allow direct contact between particles and introducing a tangential contact (frictional) force, as in our previous work on non-Brownian suspensions [1, 2]. Hence, we are able to elucidate the Péclet number dependence of dense colloidal suspensions and quantify the approach to the high Péclet number limit, which can be understood as a frustrated state resulting from contact friction. We compare the simulation results of shear thickening with experimental data from the literature.

[1] R. Seto, R. Mari, J. F. Morris, and M. M. Denn. Discontinuous shear thickening of frictional hard-sphere suspensions. *Phys. Rev. Lett.*, 111:218301, 2013. [2] R. Mari, R. Seto, J. F. Morris, and M. M. Denn. Shear thickening, frictionless and frictional rheologies. arXiv:1403.6793, 2014.

Tuesday 11:40 Commonwealth A

SC20

Modified DPD method for simulation of colloidal suspensions

Safa Jamali, Arman Boromand, and Joao Maia

Macromolecular Science and Engineering, Cleveland, OH 44106-7038, United States

Dissipative Particle Dynamics as a mesoscale method was originally introduced to scientific community as a tool to study dynamics of suspensions under flow condition. However the proposed method failed to mimic properties of suspensions mainly due to lack of (1st) a potential to reproduce lubrication forces and (2nd) a clear definition for the colloid surface. Thus in the past decade different groups have modified the original DPD model in order to explain different aspects of suspension behavior. Recently we reported a modified DPD method which defines colloidal particles as particles with hard core and a dissipative coat. An additional lubrication force was introduced to include the short-range hydrodynamics that are not captured in original DPD. The model was found to be able to reproduce shear properties of suspensions for a wide range of different systems, from monodisperse to bimodal with different volume fractions, compositions and size ratios. In this work, we evaluate performance of our modified DPD method to study equilibrium properties of colloidal suspensions. To do this, zero shear viscosity of suspensions with different characteristics are measured (via Green-Kubo expressions) and compared to theoretical predictions. Furthermore, structure formation under shear, with special emphasis on the role of contact forces in shear thickening behavior of a suspension will be studied.

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Tuesday 10:00 Commonwealth B

BB16

Interfacial rheological properties of vibrio cholerae biofilms

Emily C. Hollenbeck¹, Ji Youn Lim², Jiunn Fong³, Fitnat H. Yildiz³, Lynette Cegelski², and Gerald G. Fuller¹

¹Chemical Engineering, Stanford University, Stanford, CA 94305, United States; ²Chemistry, Stanford University, Stanford, CA 94305, United States; ³Microbiology and Environmental Toxicology, UC Santa Cruz, Santa Cruz, CA 95064, United States

Vibrio cholerae-the causative agent of cholera-is a gram-negative bacterium capable of forming biofilms, which are interface-associated communities of microorganisms surrounded by a self-secreted biopolymer matrix. *V. cholerae* forms biofilms in its natural aquatic habitat and potentially *in vivo*, which likely contributes to its survival and infectivity, and the overall severity of cholera outbreaks. To ultimately interfere with the formation of *V. cholerae* biofilms we require a better understanding of *V. cholerae* biofilm growth and function. In this study we used interfacial rheology to investigate the elasticity of biofilms growing at the air-liquid interface, called pellicles, to deduce the contribution of different matrix proteins to the biofilm structure. Measurements were performed during pellicle formation on a rugose strain of *V. cholerae* and its matrix protein mutants. We also used macroscale imaging, electron microscopy, and contact angle measurements to further define pellicle properties and structure. Rheology measurements revealed that the matrix protein Bap1 is uniquely required for maintaining pellicle strength over time, while scanning electron microscopy images show that the Bap1 mutant pellicle microstructure is distinctly different from the rugose pellicle. Additionally, based on contact angle measurements, the Bap1 mutant pellicle is more hydrophilic than the wild-type pellicle. Taken together our results show a connection between the mechanical strength, appearance, and microscale architecture of wild-type and mutant *V. cholerae* pellicles and suggests that Bap1 may be a critical matrix component to target in biofilm prevention and dispersal.

Tuesday 10:25 Commonwealth B

BB17

Rheological properties of Pseudomonas aeruginosa biofilm formation in the presence of quorum sensing inhibitors

Uranbileg Daalkhaijav and Travis W. Walker

School of Chemical, Biological, & Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States

Pseudomonas aeruginosa is an environmental opportunistic pathogen that is the main cause of morbidity in cystic fibrosis (CF) patients. One of its main virulence factors is its ability to form viscous, alginate-encased biofilms within the pulmonary mucus. The viscoelastic properties of this biofilm contributes to its ability to evade phagocytic activities, to reduce the effectiveness of antibiotics, to develop antibiotic resistant strains, and to persist or reoccur in CF patients. The quorum sensing property of *P. aeruginosa* is well documented, and its contribution to its virulence is being extensively studied. The goal of this study is to investigate the effects of certain natural quorum sensing inhibitors on biofilm formation. The disruption of biofilm formation would have a beneficial impact on the treatment of diseased CF patient as it will make the infection more susceptible to antibiotics and host phagocytosis. This study correlates the activity of the quorum sensing inhibitors with viscoelastic changes in the *P. aeruginosa* biofilm on the air-medium interface.

Tuesday 10:50 Commonwealth B

BB18

Rheology of extracellular matrices of swarming colonies of Pseudomonas aeruginosa

Raf De Dier¹, Wouter Sempels², Johan Hofkens², and Jan Vermant¹

¹Chemical Engineering, KU Leuven, Leuven, Belgium; ²Chemistry, KU Leuven, Leuven B-3001, Belgium

Bacterial colonies of *Pseudomonas Aeruginosa* exhibit complex swarming and spreading phenomena, used by these microorganisms when invading and colonising solid surfaces. The bacteria live in an extracellular matrix composed polysaccharides, DNA fragments and other secreted products. The rheology of this matrix plays an important role for both the motion of the individual bacteria as well as for the collective swarming behaviour. In the present work we characterise the rheological response of this matrix, using both macroscopic bulk rheology and microrheology using magnetic tweezers. The results demonstrate an important viscoelastic response, with relaxation times extending up to several seconds. The relevance of the rheological properties on both the local scale motion and the macroscopic swarming behaviour will be discussed, in light of results of ultra-fast confocal experiments.

Tuesday 11:15 Commonwealth B

BB19

Interfacial rheology's role on the measurement of the bulk rheology of biological solutions

Zhenhuan Zhang, Sourav Barman, and Gordon F. Christopher

Mechanical Engineering, Texas Tech University, Lubbock, TX 79409-1021, United States

Recent studies of biological solutions have noted behaviors such as yield, high elasticity, and rheopexy even at extremely low concentrations of biological molecules. In particular, bovine serum albumin solutions and synovial fluid, a multi-component viscoelastic solution which acts as a joint lubricant, have been found to exhibit these potentially useful properties. The behaviors in both materials have been attributed to bulk

interactions between molecules; however, recent evidence suggests that the bulk behavior is in fact a measurement artifact caused by interfacial rheology.

We have characterized both the interfacial rheology and bulk rheology of bovine serum albumin solutions, hyaluronic acid solutions and a model synovial fluids composed of hyaluronic acid, bovine serum albumin and globulin. Using an interfacial rheometer and multiple bulk geometries on a rotational rheometer, results prove that previously observed yield, elasticity and rheopexy of these solutions is entirely due to interfacial rheology affecting bulk measurements on rotational rheometers. For bovine serum albumin solutions, we observe significant interfacial viscosities and moduli. When these interfacial effects are removed from bulk measurements through experimental procedure, bulk viscoelastic moduli decrease by more than an order of magnitude. Hyaluronic acid exhibits significant interfacial viscosity and small viscoelastic moduli, which contribute to the observed bulk response of pure hyaluronic acid solutions and synovial fluid. When interfacial effects are removed from synovial fluid and pure hyaluronic acid, we observe no difference between the systems in steady shear. In oscillation, synovial fluid exhibits slight increases in elasticity at low strains and frequencies, which may indicate some minimal bulk interaction. In general, bulk interaction in all of these solutions is negligible, and previous results can be attributed to interfacial response affecting bulk measurements.

Tuesday 11:40 Commonwealth B

BB20

Rheology of bacterial adhesion layers at air/water and oil/water interfaces

Patrick A. Rühls¹, Lukas Böni¹, Lukas Böcker¹, Fredrik Inglis², Christoph Jans¹, Tomás de Wouter¹, and Peter Fischer¹

¹IFNH, ETH Zurich, Zurich 8092, Switzerland; ²Department of Environmental Sciences, ETH Zurich, Zurich 8092, Switzerland

Bacteria adhesion layers are highly complex biological assemblies composed of bacterial cells embedded in an extracellular polymeric matrix. Such biofilms are ubiquitous and, on one hand may cause severe environmental and health problems but on the other hand protect and support the gut flora during digestion. Therefore it is intriguing to understand the influence factors on the formation and the destruction of bacteria biofilms [1, 2]. In this contribution, we study the initial kinetics of bacterial attachment as well as the transient layer formation of model bacteria at both the air/water and oil/water interface through interfacial rheology and tensiometry. Electrophoretic mobility measurements and bacterial adhesion to hydrocarbons (BATH) tests were performed to characterize selected bacteria. To validate interfacial rheology and tensiometry measurements, we monitored biofilm formation utilizing both confocal laser scanning microscopy and light microscopy. Using this combination of techniques, we were able to observe the interfacial tension and elasticity development over time, from the first bacterial attachment up to biofilm formation. Interfacial rheology proved to be a valuable tool for studying biofilms as the influence of temperature, media type, bacterial strain, pH and surfactant concentration could be observed successfully during biofilm formation [1, 3].

[1] Rühls PA, Böni L, Fuller GG, Inglis RF, Fischer P: PLOS One 8 (2013) e78524. [2] Wu C, Lim JY, Fuller GG, Cegelski L: Biophysical Journal 103 (2012) 464-471. [3] Rühls PA, Böcker L, Inglis RF, Fischer P: Colloids Surf. B 117 (2014) 174-184.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Tuesday 10:00 Commonwealth C

SM16

Dynamics of non-concatenated entangled cyclic polymers

Michael Rubinstein¹ and Sergey V. Panyukov²

¹Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, United States; ²P. N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow 117924, Russia

Scaling model of fractal conformations and self-similar dynamics of non-concatenated entangled rings is developed. It is based on the conjecture that the overlap parameter of loops on all length scales is the same $O \sim 20$. Topological interactions force these cyclic polymers into fractal globular structure with fractal dimension $D=3$ that we call loopy globule. It is shown that dynamics of entangled polymers with fractal dimensions $D=2$ (linear chains), $D=3$ (loopy globules), and $D=4$ (lattice animal conformations of rings in an array of fixed obstacles) are universal with diffusion coefficient reciprocally proportional to square of the degree of polymerization independent of fractal dimension D . The length of primitive paths of these entangled polymers is proportional to $2/D$ power of the degree of polymerization, which is $2/3$ power for rings in a melt. The longest relaxation time of these entangled polymers is proportional to $D+1$ power of the primitive path length or $2+2/D$ power of the degree of polymerization. For linear chains this reproduces the reptation result, while for melt of rings it predicts relaxation time proportional to $8/3$ power of the degree of polymerization. In addition for the melt of rings the model predicts the mean square displacement of a monomer proportional to $1/4$ power of time, the mean square displacement of the center of mass proportional to $5/8$ power of time, and the stress relaxation function $G(t)$ decreasing as $-3/8$ power of time without any rubbery plateau. These theoretical predictions are in excellent agreement with recent computer simulations and experiments.

Tuesday 10:25 Commonwealth C

SM17

Rheological study of crystallization behavior of PLA and PLA-reinforced flax fiber biocompositesAndrea M. Arias¹, Marie-Claude Heuzey¹, and Paula M. Wood-Adams²¹*Chemical Engineering Department, Polytechnique Montreal, Montreal, Quebec H3N2N2, Canada;* ²*Department of Mechanical and Industrial Engineering, Concordia University, Montreal, QC, Canada*

In this work, the behavior of compounded polylactide (PLA) and polylactide-based flax fiber biocomposites under quiescent crystallization was investigated by means of small amplitude oscillatory shear experiments under isothermal conditions. In addition, the effect of shear flow on PLA crystallization was studied by performing a shearing step prior to SAOS tests. The rheological results, carried out in parallel plate flow geometry, were performed at temperatures varying from 110 to 140 °C in the case of quiescent conditions, and at 140 °C for shear flow-induced crystallization studies. Rheological measurements began one minute after reaching the set crystallization temperature. Time-temperature superposition principle and Arrhenius equation were employed to predict the initial viscosity for all systems; results were found to be very accurate to experimental values, particularly at lower crystallization rates. A simple empirical model was used to determine the induction time of experiments in a wide range of supercooling degrees. Experimental issues associated to such measurements are pointed out and the key parameters ensuring reproducible and accurate data are discussed. The complete understanding of crystallization for PLA systems by means of rheometry for both, quiescent and flow-induced conditions, remains challenging with the current state of art.

Tuesday 10:50 Commonwealth C

SM18

Flow-induced crystallization of polyethylene as probed by Raman spectroscopyKalman B. Migler¹, Angela Hight Walker², and Anthony P. Kotula³¹*Materials Science & Engineering, NIST, Gaithersburg, MD 20899, United States;* ²*Physics Laboratory, NIST, Gaithersburg, MD, United States;* ³*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

The presence of flow is known to enhance the nucleation rate in semi-crystalline polyolefins by as much as five orders of magnitude, but the underlying molecular mechanism is still under debate. Here we describe Raman spectroscopy experiments on a linear polyethylene that are supplemented by turbidity, birefringence and polarized optical microscopy measurements. Following a temperature quench into a regime of low undercooling, we observe the growth of a liquid-crystalline phase that precedes the occurrence of crystallinity. This phase is characterized by consecutive trans sequences that induce local chain straightening. We examine the interaction between this phase and the flow field that causes the dramatic acceleration of the crystallization rate.

Tuesday 11:15 Commonwealth C

SM19

SAXS/WAXS studies on the temperature and flow rate dependence of uniaxial extensional flow-induced crystallization of poly(1-butene)Erica M. McCready and Wesley Burghardt*Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, United States*

We report studies of flow-induced crystallization of poly(1-butene) following uniaxial extensional flow. Flow was applied using an SER extensional fixture housed in a custom built oven designed to facilitate in situ synchrotron x-ray experiments. Samples were loaded onto the fixture, heated to well above the melting temperature, and then cooled to the desired crystallization temperature. Three different temperatures were chosen for experiments based on their sufficiently slow rate of quiescent crystallization. A short term uniaxial extensional flow was applied and both extent of crystallization and degree of orientation were observed afterward using simultaneous small- and wide-angle x-ray scattering (SAXS and WAXS) patterns. SAXS and WAXS exhibit generally consistent results for extent of crystallization, although the SAXS invariant shows a decrease at longer times that is not seen in WAXS. The WAXS patterns have a higher degree of orientation than the SAXS, and both show time dependence throughout the experiment. The effect of different crystallization temperatures and extension rates are analyzed.

Tuesday 11:40 Commonwealth C

SM20

The influence of concentration on extensional rheology of polymer solutionsQian Huang, Ludovica Hengeller, Nicolas J. Alvarez, and Ole Hassager*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby 2800, Denmark*

Recent experiments by Huang et al. [1] have shown that polystyrene (PS) melts and concentrated PS solutions with the same number of entanglements per chain (Z) have different nonlinear rheological properties. Furthermore, Huang et al. [2] also showed that when the solvents are different, even concentrated PS solutions with the same number of entanglements and tube diameter behave differently in nonlinear extensional flow. The authors proposed a hypothesis that this difference is due to nematic interactions between polymer/polymer and polymer/solvent.

In this work, we show that the effect of solvent is negligible when the volume fraction of the polymer is significantly low. We prepared four PS solutions with the same Z in the same solvent (oligomeric styrene), but with different concentrations. With a proper scaling of the time constant and the plateau modulus, all the solutions show identical linear viscoelastic properties. The solutions with the lowest two concentrations also behave similarly in the nonlinear region, while the other two solutions with higher concentrations behave differently. The results support the hypothesis of nematic interactions in polymer solutions, since the response is a function of polymer concentration. In other words, the nematic interactions can be shielded when the concentration of polymer is low. The results for the lowest two concentrations also agree with literature data [3, 4] for PS solutions in different solvents.

[1] Q. Huang et al., *Macromol.* 46: 5026-5035 (2013). [2] Q. Huang et al., *ACS Macro Lett.* 2: 741-744 (2013). [3] P. K. Bhattacharjee et al., *Macromol.* 35: 10131-10148 (2002). [4] T. Sridhar et al., *Macromol.* 47: 379-386 (2014).

Symposium NF Non-Newtonian Fluid Mechanics and Stability

Organizers: Bamin Khomani and Sarah Hormozi

Tuesday 10:00 Washington A

NF1

Jetting and jet break-up of complex fluids in inkjet printing

Oliver G. Harlen, Neil F. Morrison, and Claire McIlroy

School of Mathematics, University of Leeds, Leeds, United Kingdom

Inkjet printing is rapidly emerging as a manufacturing technology with applications in areas beyond graphical printing. However, the speed of printing and the range of fluids that can be printed are limited by the requirement to have well controlled drop production. Modern printing applications involve extremely high shear and extension rates, as the fluid is typically ejected at speeds of order 10 m/s through nozzles of order 50 microns in diameter. Under these extreme conditions many fluids, such as those containing polymeric or colloidal components show complex rheological behaviour that can strongly affect jet break-up and drop speed. However, relating this to rheological measurements, even apparently related experiments such as capillary thinning, is challenging. We have used a combination of numerical simulations with simple constitutive equations (FENE-CR, Giesekus and Carreau) and simplified models which we compare with experimental measurements on "model inks" to identify the rheological characteristics that determine inkjet performance. For dilute polymer solutions we show that there are three different regimes of jetting characterised by the jet Weissenberg numbers and for high Weissenberg numbers that the extensional viscosity (determined from the extensibility) determines the jet speed and break-off time. We also show how shear rheology can be exploited to eliminate satellite drop formation.

Tuesday 10:25 Washington A

NF2

Fiber spinning under filament pull-out conditions: A stability analysis

Patrick Anderson¹, Carina Walt, van der¹, Martien Hulsen¹, and Arjen Bogaerds²

¹*Materials Technology, Eindhoven University of Technology, Eindhoven 5600MB, The Netherlands;* ²*DSM, Geleen, The Netherlands*

In wet-spinning, a polymeric fluid is pushed through a spinneret die. Subsequently, the extruded filament is taken up downstream at a higher velocity than the average extrusion velocity and cooled (e.g. in a water bath) to form a solidified fiber. As the take up velocity increases, a periodic variation of the filament diameter can occur beyond a critical draw ratio which is generally referred to as the draw resonance instability. Also, if the fluid strength is sufficiently high, upon increasing the take up velocity or, with an increase of the stretching force, the filament may be pulled out from the extrusion die. At a high Trouton ratio, filament pull-out is the phenomenon where the upstream fluid detaches from the die wall which is known to occur in isothermal solution spinning of silk by spiders as well as solution spinning high performance polymers. This pull-out condition complicates the dynamic stability analysis in the sense that the upstream boundary conditions are no longer constant but depend on the deformation history of the polymeric fluid in the spinning die. Moreover, the upstream boundary conditions depend on the position of the detachment point as the filament length can vary in time. In this work we determine, and obtain an understanding of, the stability limits in fiber spinning under pull-out conditions. This includes the stability analysis depending on the upstream conditions in the die, i.e. the dynamic contact point when pull-out of the filament occurs. The approach incorporates the full viscoelastic computational analysis of the fiber spinning dynamics where also possible slip phenomena of the melt/solution with the extrusion die wall are taken into account. In addition, we perform experimental validation of our analysis using a well-defined IUPAC-A polymer melt.

Tuesday 10:50 Washington A

NF3

Modeling the polymer wet spinning process

Hasan Zerze and Anthony J. McHugh

Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Wet spinning is used in the production of fibers from systems such as polyacrylonitrile, cellulosic, and vinyl-based polymers, as well as for fabrication of hollow fibers for membrane applications. In this process, a homogeneous solution is extruded into a liquid bath where mass, momentum, and heat transfer take place, resulting in liquid demixing, gelation, and formation of a solid, structured fiber. Modeling involves coupling the transport and phase separation processes with constitutive models to account for viscoelastic effects. Critical features to be captured include prediction of the locking-in of fiber diameter, stresses, and internal structure along the spin line, since these generally fix the as-spun fiber properties. The text by Ziabicki (1) reviews wet spin modeling up to about 1976; however, since then, there have been relatively few new studies reported. The most complete recent studies we are aware of are those of Kalabin et al. (2) that combine a Newtonian constitutive model with a binary diffusion model that incorporates thermally-induced gelation along the spinline. Our approach is built on our previous dry-spin model (3) and incorporates a two-component constitutive model based on parallel combination of Newtonian and Giesekus equations, coupled with a 2-d pseudo-ternary diffusion formalism with separate equations for the fiber gel and solution phases. These are combined with mass transfer boundary conditions at the fiber-bath interface and incorporation of the ternary phase diagram based on Flory-Huggins theory to quantify the gelation

dynamics along the spinline. Model results illustrating spinline fiber profiles and structuring for several systems and processing conditions will be discussed along with comparisons of literature data for the wet spinning of PAN fibers.

[1] A. Ziabicki, *Fundamentals of Fiber Formation*, John Wiley and Sons, NY, 1976. [2] A.L. Kalabin, *Fibre Chemistry*, 37, 141 (2005). [3] Z. Gou and A.J. McHugh, *J. Non-Newt. Fl. Mech.* 118, 121 (2004).

Tuesday 11:15 Washington A

NF4

A regularized thin-fiber model for nanofiber formation by centrifugal spinning

Seyed Mohammad Taghavi¹ and Ronald G. Larson²

¹*Chemical Engineering Department, McGill University, Montreal, Quebec H3A 0C5, Canada;* ²*Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109, United States*

We develop a regularized thin-fiber model to study nanofiber formation by centrifugal spinning and determine the steady velocity of the fiber, its diameter and its trajectory. In centrifugal spinning, the fiber with initial radius a_0 emerges from a nozzle rotating at a radial distance r_0 from the axis in the presence of centrifugal, inertial, viscous, surface-tension, and gravitational forces. The results are controlled by four dimensionless groups, namely, the Rossby number Rb expressing the ratio of inertial to centrifugal forces, the Reynolds number Re , the ratio of inertial to viscous forces, the Weber number, the ratio of inertial to surface-tension forces, and the Froude number Fr , the ratio of inertial to gravitational forces. Although the dimensionless fiber thinness parameter $e = a_0/r_0$ can be taken to be very small, surprisingly, the thin-fiber equations that arise at the lowest order in e (i.e., the "string" equations) fail to have physically relevant solutions at values of $ReRb^2$ less than around unity, i.e., for the most interesting regime of viscous fibers at high spinning speeds. Arne et al. 2011 showed that this behavior results from a non-removable singularity in the string equations, which is avoided in a theory that is higher order in e , namely the Cosserat rod theory. We show that the singularity is also avoided by simply adding to the string theory the highest order derivative in the fiber curvature that appears in Cosserat rod theory (i.e., the third derivative) with an arbitrarily small pre-factor as a regularization term. This "regularized string theory" reproduces the results of the higher order Cosserat rod theory for slender fibers. We find that for small Rb (fast spinning), at large distances along the fiber the inviscid solution for both the trajectory and fiber diameter are recovered, regardless of how high the fiber viscosity is. We also show that our regularized string theory is easily adapted to consider the effects of surface-tension, gravity, and non-Newtonian viscosity.

Tuesday 11:40 Washington A

NF5

Fabrication of polymer nanofibers using centrifugal jet spinning

Liyun Ren¹, Rahmi Ozisik¹, Shiva P. Kotha², and Patrick T. Underhill³

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Polymer micro-fibers and nanofibers have been used in a wide range of applications. The cost-yield efficiency can limit the areas in which they can be used. Centrifugal jet spinning is a method that has been used for a long time to produce fibers at high production rate and low cost, but it suffers from a lack of control of product quality. In this talk, we will discuss a new configuration of centrifugal jet spinning in which we have quantified the fiber size and morphology as a function of the key dimensionless groups that govern the process. During the filament thinning, the key dimensionless groups are the Weissenberg number, the Deborah number, and the Ohnesorge number. By systematically varying the fluid properties and processing conditions, we have been able to map the response as a function of these parameters. Specifically, as the dimensionless groups increase, the system transitions from no fiber formation to a beads-on-a-string morphology to a cylindrical fiber morphology. The final fiber diameter is also a function of the evaporation of the solvent during spinning, and is therefore also a function of the "processability parameter."

Symposium BC Blends, Composites and Multiphase Systems

Organizers: Arezoo Adekani and Florian Nettesheim

Tuesday 10:00 Washington B

BC6

Advances in characterization of rheology at high strain rates related to paint atomization

Eric C. Houze¹, Michael R. Koerner², John R. Moore¹, Gareth H. McKinley³, and Bavand Keshavarz³

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Paint atomization is a nonlinear time-dependent process that involves very high shear and strain rates. Historically, industry researchers have used high shear viscosity as a predictor for atomization quality because there were no commercially available instruments capable of measuring extensional viscosity of ready-to-spray paints under realistic conditions. This sometimes leads to poor predictions of the suitability of formulations for spray application. Studies using the Capillary Breakup Extensional Rheometer (CaBER) have been previously used to assess capillary thinning and filament formation dynamics. This can often be related to the droplet formation process during paint spraying but is often limited as a result of relatively low relaxation times observed in commercial paints. More recently we have developed a jet-based approach to measure extensional rheology. Stroboscopic recordings of the thinning dynamics in a periodically forced free-stream paint jet can be analyzed to reveal local domains

of visco-capillary and elasto-capillary behavior. Fitting these models to time-resolved measurements of the jet diameter provides characteristic measures of the paint rheology (specifically the viscosity and fluid relaxation time) at high deformation rates. Characteristic relaxation times of waterborne paints can be successfully determined down to less than 60 μ s using this jet rheometry approach. We explain the test methodology used to characterize the paint rheology and share data collected from both model fluids and commercial coatings. To relate these measurements to heuristic assessments of paint 'sprayability' we use strobed shadowgraphy methods to collect droplet particle size distributions in a spraying process. We show that the droplet size distribution in our paint sprays is well described by a single gamma distribution as described by Villermaux et al for Newtonian fluids.

Tuesday 10:25 Washington B

BC7

Ion transport in porous battery electrodes

Anne M. Grillet, Scott A. Roberts, Daniel E. Wesolowski, Christine C. Roberts, Ashley N. Allen, Lisa A. Mondy, Richard P. Grant, Bonnie McKenzie, Bion Shelden, Mario J. Martinez, and Jonathan Clausen
Sandia National Laboratories, Albuquerque, NM 87185, United States

Battery electrodes are complex multiphase systems which must provide efficient bicontinuous networks for transport of electrons (through the particle phase) and positive lithium ions (through the electrolyte filled pores of the electrode). We will examine several methods for measuring the permeability and ion transport in molten salt batteries. Because the electrolyte is solid at room temperature, we are able to perform quantitative microprobe analysis to measure transport of bromine tracers between the electrodes of the battery with a series of single cells quenched at various times. We are able to elucidate the process of electrolyte transport from the separator into the electrodes and also probe the ionic permeability within the battery. Computational models for the partially-saturated porous flow of the electrolyte in the active molten salt battery will also be presented. We will examine the relative influence of porosity, degree of flooding and wetting properties of the electrodes on the final distribution of the electrolyte and discuss the expected impact on battery performance.

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Tuesday 10:50 Washington B

BC8

Dissipative particle dynamics studies on the controlled assembly of polymer grafted nanorods

Shaghayegh Khani¹, Joao Maia¹, and Stuart Rowan²

¹*Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States;* ²*Case Western Reserve University, Cleveland, OH 44106, United States*

Nanorods due to their attractive properties involve a major class of nanoparticles that can improve the mechanical properties of the system by forming a percolated network when added to a homopolymer matrix. Controlling the dispersion and aggregation of nanorods in the polymer matrix will advance the technology in the field of nanoparticle-based devices. Recently, composites of polymer-grafted nanorods with stimuli-responsive behavior have been fabricated in which assembly of nanorods in the polymer matrix is controlled by grafting a polymer brush on the surface of the rod. Depending on the interaction between the brush polymer and the matrix a percolated network can be achieved which results in a significant improvement in mechanical properties. Dispersion of the nanorods grafted with polymer brush in a homopolymer matrix is influenced by different enthalpic and entropic variables. Flory-Huggins parameter (which determines the relative repulsion/attraction between the matrix and the brush), geometry of the rod, concentration, thickness of the brush and the degree of polymerization of the matrix are the most important factors in determining the final properties. In this study, Dissipative Particle Dynamics (DPD) is employed in order to investigate the phase behavior of polymer grafted nanorods in a homopolymer medium and to understand the physical changes in the material that lead to its stimuli-responsive behavior. DPD is a coarse-grained mesoscale method which has been found very promising in simulating multi component systems. The interaction parameter between the components of the systems can be mapped onto the Flory-Huggins parameter via well-known Groot-Warren expression. Also, the repulsion parameter is set based on the compressibility of a real fluid. In the present work, we investigate the abovementioned parameters and their effect on morphology/properties of composites. The main goal is to provide a phase diagram which can be used as a guide for designing stimuli-responsive polymer-nanorod systems.

Tuesday 11:15 Washington B

BC9

Magnetic microdisks in a rotating magnetic field

Han Song¹, Travis W. Walker², Albrecht Jander¹, and Pallavi Dhagat¹

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Composites made from embedding fine metallic magnetic particles in an insulating matrix are promising materials for high frequency inductor and antennae applications. Recently, composite materials consisting of magnetic particles with high aspect ratios (i.e., rod-shaped or disk-shaped particles) are gaining increased attention as they exhibit enhanced high frequency permeability in comparison to composites with spherical particles. Moreover, magnetic alignment of these high aspect ratio particles further increases the high frequency permeability and ferromagnetic resonance frequency. Typically, the alignment is achieved by applying an external magnetic field during curing of the matrix. With rod-shaped particles, this constant field results in a composite material with uniaxial anisotropy. In this study, we show that curing a composite of disk-shaped particles in a rotating magnetic field produces a composite with planar anisotropy. We investigate the dynamics of the alignment process to determine the conditions for achieving a high degree of alignment while avoiding inhomogeneous distribution of particles due to sedimentation

or agglomeration. We use Ni and NiFe microdisks in a UV curable binder as the study system and report the effect of alignment time on the microstructural and magnetic properties of the composite. The physical orientations of the embedded Ni and NiFe microdisks inside the composites are investigated by dark field optical microscopy. The cross sections of microdisk composites with varying alignment time are observed in planes orthogonal and parallel to the axis of rotation. Theoretical models, based on Stokes flow of a single magnetic oblate ellipsoidal particle in a rotating magnetic field, are developed to enable understanding and control of the observed alignment dynamics process. Comparisons of times scales are made to controlled single particle experiments.

Tuesday 11:40 Washington B

BC10

A preliminary investigation into fiber length effects on the transient rheology of long glass fiber suspensions

Mark J. Cieslinski, Gregory M. Lambert, and Donald G. Baird

Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States

Long fiber (lengths > 1mm) composites are of interest for improved creep and impact properties when compared to short fiber (lengths < 1mm) reinforcement. However, increasing fiber length may also cause fibers to bend when subjected to flow which would influence orientation kinetics. Models used to predict the fiber orientation created during the molding process require phenomenological parameters to be determined to accurately reflect the experimental fiber orientation. The premise of this work is to use a rheological approach to determine the material parameters independently of the molding process. A sliding plate rheometer is used to measure the transient response caused by fiber orientation during the startup of shear flow. Measured values of fiber orientation are also obtained as a function of shear strain in order to further understand the relationship between stress and fiber orientation. Preliminary results obtained from the planar elongation of the fiber suspension using lubricated squeeze flow will also be discussed. Model parameters determined from the simple shear flow experiments will be used to compare with measured fiber orientation from extensional flow. In addition, the rheological response, measured fiber orientation and model predictions will be presented as fiber lengths transition from short to long.

Symposium CC Confined and Coupled Systems

Organizers: Patrick Anderson and Cari Dutcher

Tuesday 10:00 Washington C

CC1

Probing colloidal flocculation during solvent removal in microscale droplet reactors

Sharon M. Vuong¹, Blake M. Bleier¹, Shelley L. Anna², and Lynn M. Walker¹

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Microscale droplet reactors offer a convenient method of probing the stability and macroscopic behavior of colloidal suspensions. Highly uniform pL droplets containing an aqueous suspension of nanoparticles are generated in a microfluidic device. Dehydration of the droplet and a corresponding increase in the suspension concentration result from slight solubility of the water in the outer oil phase and permeability through the device materials. Charge stabilized suspensions of silica nanoparticles dehydrate to a finite droplet size. Regardless of the conditions driving the dehydration process, the final droplet reactor volume achieved is expected for a suspension of hard spheres. With the addition of salt, the droplet reactor stops shrinking at a lower final volume fraction. We rationalize through the evolving composition of the droplet reactors. Varying the initial salt concentration allows us to probe flocculation rates and the critical flocculation concentration. Probing the microrheology of the suspension reveals that the viscosity increases dramatically at timescales consistent with expected flocculation timescales. The observed timescales are rapid enough at high added salt concentrations that flocculation should occur rapidly at later stages of the dehydration experiments. These observations suggest that compressive stresses developing in a flocculated network may be large enough to arrest droplet dehydration at lower volume fractions, and that the loose networks of particles may also permit salt crystals to form within the interstitial spaces. Thus, microfluidic droplet reactors provide a useful means of probing both fundamental stabilization mechanisms for colloidal suspensions and the mechanics of highly concentrated suspensions not easily accessible macroscopically.

Tuesday 10:25 Washington C

CC2

Probing aerosol particle interfaces with biphasic microfluidics

Cari S. Dutcher and Andrew R. Metcalf

Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States

Atmospheric aerosols are one of the major contributing factors to our climate, yet are the largest source of uncertainty in climate modeling. This uncertainty arises from the intricate nature of aerosol particles. As complex microenvironments, these particles can contain multiple interfaces due to internal liquid - liquid phase partitioning and the external vapor - liquid surface. These aerosol interfaces have profound effects on particle morphology, species uptake, equilibrium partitioning, activation to cloud condensation or ice nuclei, and optical properties. Many factors play a role in determining a particle's internal structure, resulting in many possible particle configurations. For example, the aqueous and organic phases in a single aerosol particle may align in a side-by-side nodule morphology, whereas in other cases, the organic phase may form a film that can completely surround the aqueous phase. In order to fully predict a particle's internal structure at a given temperature, relative humidity, and chemical composition, fundamental studies of interfaces observed in atmospheric aerosol particles are essential. In this talk, a method using

biphasic microscale flows will be introduced for generating, trapping, and perturbing complex interfaces at atmospherically relevant conditions. These microfluidic experiments are conducted using phase contrast and fluorescence microscopy on a temperature-controlled inverted microscope stage with high-speed imaging to monitor interfacial phenomena at the microscale. Chemical compositions of the aqueous and organic phases studied here include electrolyte and water soluble organic acid species often observed in the atmosphere, such as mixtures containing ammonium salts and dicarboxylic acids. From these measurements and others, important rheological, thermodynamic, and kinetic properties of the atmospheric aerosol mimics can be explored, yielding insight into multiphase aerosol particle dynamics.

Tuesday 10:50 Washington C

CC3

Rheological behavior of unfilled and filled, uncrosslinked and ionically crosslinked guar solutions

Alexander C. Barbati¹, Agathe Robisson², and Gareth H. McKinley¹

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²*Schlumberger-Doll Research Center, Schlumberger, Cambridge, MA 02139, United States*

Guar-based materials are used in a variety of foodstuffs and industrial applications. Notably, crosslinked guar solutions are used to support proppant particles for hydraulic fracturing. In this process, solids must remain suspended throughout the flow. Thus, fracture engineering is sensitive to the rheology of the crosslinked guar material. A polysaccharide, guar consists of a mannose backbone with galactose side units in a ratio of approximately 2:1. On the addition of a crosslinker, the galactose side units are bridged creating an entangled ionic network. These physical crosslinks impart increased viscosity and elasticity to the guar solutions, and help sustain suspensions of sand and fibers that build additional structure and load-bearing stresses into this complex highly-filled viscoelastic material. Here, we perform a series of linear and nonlinear measurements to probe the rheological behavior of borate crosslinked and uncrosslinked guar solutions with and without dispersed particles. Small amplitude oscillatory shear (SAOS) tests reveal a rheological response reminiscent of the Green and Tobolsky temporary network model at low frequencies although this model does not capture the moderate and high frequency response. We demonstrate that a fractional Maxwell model with an additional Rouse-like element more accurately captures these data. SAOS data collected at elevated temperature and decreased crosslinker concentration reveal a systematic softening in G' , G'' , and a decrease in the SAOS relaxation (crossover) time of the material. Loading of spherical particles in the crosslinked guar up to 20 wt% appears not to affect the relaxation time, while the loss modulus increases with particle loading. Additionally, we perform steady shear experiments for loaded and unloaded guar and show that the material shear thins for low crosslinker concentrations. As the crosslinker concentration is increased, a pronounced shear thickening region is encountered beyond the initial shear thinning region.

Tuesday 11:15 Washington C

CC4

Validation via rheological experiments of theories for the flow through porous media

Mario Minale¹, Claudia Carotenuto¹, Anja Vananroye², and Jan Vermant²

¹*Dept. of Industrial and Information Engineering, Seconda Università di Napoli, Aversa, Ce 81031, Italy;* ²*Chemical Engineering, KU Leuven, Leuven, Belgium*

The momentum balance on the solid skeleton of a porous medium like porous rocks, foam metals or porous brushes is here theoretically derived with the volume averaging method. The equation holds in the whole porous medium and contains volume averaged stresses and velocity. For homogeneous porous media, the momentum balance on the solid skeleton is coupled with the momentum balance on the fluid within the porous medium, i.e. Darcy's equation with the first and the second Brinkman's correction, through a geometrically rescaled Darcy's term. This approach gives the opportunity to derive a new stress boundary condition at the interface between a porous medium and a homogeneous fluid stating that the stress is transferred both to the fluid within the porous medium and to the solid skeleton. A negligible stress jump is obtained that is proven to be exactly zero in simple shear flow. The theory is validated with rheological tests where the porous medium is mimicked either with a cross-hatched geometry on a ARES (TA) strain controlled rheometer, or by gluing some sandpapers on a plate-plate device of a NOVA (Reologica) stress controlled rheometer. The experiments are conducted by measuring the viscosity of Newtonian oils at different imposed gaps, in correspondence of the same applied stress in the NOVA rheometer, and at an imposed shear rate corresponding to a stress invariant with the gap, for the ARES rheometer. The viscosity always decreases with the gap and an "extrapolation length" can be inferred. This is due to the shear-induced flow through the slender porous media and the velocity at the interface is explicitly related to the extrapolation length. This velocity is used as validation parameter in the comparison with the theoretical predictions and the agreement is very good.

Tuesday 11:40 Washington C

CC5

Viscoelastic focusing down to the nanoscale

Ilaria De Santo¹, Gaetano D'Avino², Francesco Greco³, Paolo Antonio Netti¹, and Pier Luca Maffettone²

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We show that nanoparticles suspended in dilute polymer solution in Poiseuille flow can be trapped in the central region of a microtube. The trap force is due to the viscoelasticity of the suspending fluid, and can be modulated by selecting liquids with specific rheology. We propose a simple theoretical argument that supports the experimental evidence, and links the trapping force to a dimensionless parameter that compares normal forces and Brownian forces. These arguments distill into a simple equation, which could be used to downscale flow cytometers, or to design microfluidic devices for counting, coding or separating nanoparticles.

Tuesday Afternoon

Symposium SC Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Tuesday 1:30 Commonwealth A

SC21

Rheology and morphology of lyotropic nanocylinder dispersions

Virginia A. Davis

Department of Chemical Engineering, Auburn University, Auburn University, AL 36849, United States

Inorganic and organic nanocylinders including nanorods, nanotubes, and nanowires are an emerging class of "rod-like" dispersions. Much of their self-assembly and rheological behaviors can be explained based on the behavior of lyotropic liquid crystalline polymer solutions. However, there are several key distinctions. Nanocylinders can have significantly larger aspect ratios, persistence lengths, polydispersities, attractive interactions, and densities than their polymeric cousins. We compare the rheology and morphology of five distinct nanocylinder systems: cellulose nanocrystals in water, carbon nanotubes in aqueous DNA, mixtures of silver nanowires and spheres in ethylene glycol, and silica nanorods in dimethyl sulfoxide [Urena-Benavides et al. (*Macromolecules*, 2011), Ao et al (*ACS Nano*, 2011), Murali et al (*Langmuir*, 2010), and Xu et al (*Langmuir* 2014)]. These systems span a broad range of structural and chemical characteristics and include dispersions that form nematic, cholesteric and smectic, phases. Comparison of these systems to each other and lyotropic liquid crystalline polymers highlights opportunities for new insights into the fundamental behavior of colloidal rods.

Tuesday 1:55 Commonwealth A

SC22

The concentration instability of a sedimenting suspension of weakly flexible fibers

Harishankar Manikantan¹, Lei Li², Saverio E. Spagnolie², and David Saintillan¹

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A dilute suspension of sedimenting rigid rods is itself unstable to density fluctuations as a result of hydrodynamic interactions. We develop a theory for the role of fiber flexibility in sedimenting suspensions in the asymptotic regime of weakly-flexible bodies. Individual elastic filaments reorient as they sediment, leading to an anisotropic base-state distribution of orientations in an otherwise homogeneous suspension. A Smoluchowski equation is written down to describe the evolution of the concentration field, and we explore the stability of the base state to concentration perturbations. Fiber compliance is shown to have two distinct and opposing effects on suspension stability. First, the base state is anisotropic - more acutely so for more flexible fibers - and favors an orientation perpendicular to gravity. We elucidate a mechanism by which such an orientation distribution could be more prone to be destabilized by density perturbations than an isotropic distribution of rigid rods, and indeed our analysis concurs with this. And second, the propensity of particles to orient perpendicular to gravity hinders horizontal migration, thereby suppressing the instability. In the presence of thermal noise, the dominant effect depends critically upon the relative scales of flexibility-induced reorientation and rotational Brownian motion.

Tuesday 2:20 Commonwealth A

SC23

Rheo-optical response of carbon nanotube suspensions

Gioviannantonio Natale¹, Naveen K. Reddy², Gilles Ausias³, Julien Ferec³, Marie-Claude Heuzey¹, and Pierre J. Carreau¹

¹*Chemical Engineering, École Polytechnique de Montréal, Montréal, Québec, Canada;* ²*Chemical Engineering, KU Leuven, Heverlee, Belgium;* ³*Mechanical Engineering, Université de Bretagne du Sud, Lorient, France*

Carbon nanotubes (CNTs) hold remarkable promises for the next generation of materials, with potential applications in organic electronics, reinforced and electrically conducting composites and even new types of biological sensors and devices. Despite these potentialities, CNT suspensions in polymer melts are inherently difficult to process and in order to design efficient processing schemes, it is necessary to fully understand and predict their rheological behavior. In this work, we analyze the rheo-optical response of carbon nanotube suspensions, more specifically dichroism obtained in parallel plates and for the first time in a Couette flow geometry. CNTs were dispersed in a model Newtonian epoxy matrix, at different concentrations covering the dilute and semi-dilute regimes. Surprisingly, the average orientation angle with respect to the flow direction is far from zero degree even at high Péclet (Pe) numbers in very dilute suspensions. To explain this unique behavior, a new model for flexible rods, valid in the dilute regime, is proposed. It is based on the development proposed by Latz and Strautins (2007) considering flexible rods made of beads and connectors. We modified their bending potential that allows only straight rods at equilibrium with a harmonic cosine expression. This simple modification changes drastically the behavior of these flexible particles that exhibits a non negligible orientation component in the vorticity direction, even under steady state.

Strautins U, Latz A. Flow-driven orientation dynamics of semiflexible fiber systems. *Rheologica Acta*. 2007/10/01 2007;46(8):1057-1064.

Tuesday 2:45 Commonwealth A

SC24

On the negative magneto-rheological effect of a rod-like hematite particle suspension by means of Brownian dynamics simulationsAkira Satoh*Department of Machine Intelligence and System Engineering, Akita Prefectural University, Yuri-Honjo 015-0055, Japan*

We have investigated the behavior of the rod-like hematite particles, of which a magnetic suspension is composed, in a simple shear flow in order to clarify the dependence of the negative magneto-rheological effect on the particle aggregation and orientational distribution of the particles. The present Brownian dynamics method has a significant advantage that it takes into account the spin rotational Brownian motion about the particle axis in addition to the ordinary translational and rotational Brownian motion. The net viscosity is decomposed into three components and discussed at a deeper level and in more detail: these three viscosity components arise from (a) the torque due to the magnetic particle-field interaction and (b) the torque and (c) the force due to the interaction between particles. The orientational distribution does not change significantly for the change in the field strength, the volumetric fraction and the magnetic particle-particle interaction, but the peak position and the whole shape of the distribution are slightly shifted to a certain direction. This slightly reformed distribution makes a significant influence on the negative magneto-rheological effect. In a dilute suspension, the effect of the magnetic field strength on this negative magneto-rheological effect is both qualitatively and quantitatively in good agreement with that obtained by the previous theory and Brownian dynamics simulations without translational Brownian motion. The negative magneto-rheological effect decreases and finally disappears with increasing volumetric fraction. This is because although the viscosity due to the torque arising from the particle-field interaction shows a negative value, the viscosity due to the magnetic particle-particle interaction comes to dominate and surpass this effect, resulting into a positive net viscosity. The change in the Peclet number does not induce rapid formation or collapse of raft-like clusters, leading to a monotonic change in the viscosity.

Tuesday 3:10 Commonwealth A

SC25

Using rheology to characterize graphene oxideIssam M. Ismail¹, Ahmed A. Abdala², and Christopher W. Macosko¹*¹Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455-0132, United States; ²Chemical Engineering, The Petroleum Institute, Abu Dhabi, Abu Dhabi 2533, United Arab Emirates*

We are studying the potential of rheology as a characterization tool for estimating average aspect ratio of graphene oxide (GO). Rheological measurements are made using both shear rotational rheometry and a glass capillary viscometer. The intrinsic viscosity at both the low and high shear limit (determined by the Peclet number) are correlated and used to estimate the aspect ratio by applying models for hard, plate-like colloids. The polydispersity of GO is accounted for using distribution functions. We compare these rheological results with measurements of particle size obtained from dynamic light-scattering, fluorescence quenching microscopy and atomic force microscopy. This study covers a range in aspect ratio, Peclet number and GO samples synthesized by different methods, thus assessing the objective limits within which rheology can be accurately used to estimate aspect ratio of GO and, by extension, similar nanoparticle systems.

Tuesday 4:00 Commonwealth A

SC26

Patterning surfaces with colloid-bottlebrush polymer suspensionsCharlotte Pellet¹, Jean-Marc Suau², and Michel Cloitre¹*¹Matière Molle et Chimie, ESPCI ParisTech, Paris 75005, France; ²Coatex SAS, Genay 69730, France*

The deposition of colloidal particles from liquid droplets on solid substrates is an attractive surface patterning technology for fabricating biological, electronic or optical devices. One current limitation is the difficulty to achieve uniform patterns during solvent evaporation because the particles tend to deposit along the droplet periphery resulting in a ring-like morphology, known as the coffee-ring effect. Recently the origin and the modeling of the coffee ring effect have stimulated a lot of research but its suppression remains an important challenge for applications. Here we describe a new method for inhibiting the coffee ring effect in colloidal suspensions using bottlebrush polymers as additives. The bottlebrush polymers we use consist of a highly charged polyelectrolyte backbone and hydrophilic pendant chains densely tethered to it. This specific architecture confers remarkable rheological properties to bottlebrush solutions. They have a low viscosity up to high concentrations and are nearly insensitive to variations of pH and ionic strength. When added at extremely low concentrations to colloidal calcium carbonate suspensions, bottlebrush polymers totally suppress the coffee ring effect and produce very uniform defect-free patterns. We will present the new mechanism which is at the origin of coffee ring inhibition by bottle brush polymers and discuss the generality of our results for other colloidal suspensions.

Tuesday 4:25 Commonwealth A

SC27

Oscillatory rheology of colloidal near hard-sphere suspensions with ASDStephanie Marenne and Jeffrey F. Morris*Levich Institute, City College of New York, New York, NY 10031, United States*

The viscoelastic response of near hard-sphere colloidal dispersions is studied using the discrete-particle simulation method Accelerated Stokesian Dynamics. At steady state for a constant shear rate, the structure and rheology of this complex fluid are defined by two dimensionless parameters: Pe , which is the ratio of hydrodynamic to thermal forces and the solid volume fraction, ϕ . For dynamic oscillatory shear flows, there is an additional variable for the amplitude of oscillations: γ_0 . The viscoelastic character of the dispersion is studied by examining the evolution of the shear stress and the normal stress differences. The pair distribution function, $g(\mathbf{r})$ with \mathbf{r} the pair separation vector, describes the microstructure. Comparisons

are made with experiments and theory in literature. The main focus is on suspensions far from equilibrium ($Pe \gg 1$) and high volume fraction ($0.3 < \phi < 0.5$). By varying the parameters over a wide range of Pe and γ_0 , the transition from linear to non-linear viscoelasticity can be observed independently for the hydrodynamic and Brownian contributions to the stress. The startup of shear flow also leads to a transient evolution from an initial linear response to the steady-state regime, observable in the microstructure as well as the rheological measurements.

Tuesday 4:50 Commonwealth A SC28

The Medium Amplitude Oscillatory Shear (MAOS) of semi-dilute colloid dispersions - Third harmonic of the suspension stress

James W. Swan¹, Kate Gurnon², and Norman J. Wagner³

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We study the response of semi-dilute colloidal dispersions under Medium Amplitude Oscillatory Shear (MAOS). Using an excluded annulus model of the hard-core repulsion and hydrodynamic interactions among the particles, we determine the third harmonic of the stress response of a colloidal dispersion in the pair limit. Importantly, the influence of hydrodynamic forces, both in magnitude and in character, on the MAOS of semi-dilute dispersions is made explicit through comparison of such nonlinear rheological properties while varying the ratio of the hard-core to hydrodynamic radius. We show through comparison with experiments that hydrodynamic forces have a considerable effect on the microstructure of dispersions undergoing MAOS. Consequently, the nonlinear, oscillatory rheology of semi-dilute suspensions is quite sensitive to non-conservative, hydrodynamic, forces.

Tuesday 5:15 Commonwealth A SC29

Modeling thixotropic colloidal dispersions in Large Amplitude Oscillatory Shear (LAOS) experiments

Matthew J. Armstrong, Antony N. Beris, and Norman J. Wagner

Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States

Applying large amplitude oscillatory shear (LAOS) to complex fluids induces nonlinear rheological responses that, with proper modeling, can be used to sensitively probe the underlying microstructure and its dynamics. We demonstrate this for prototype concentrated colloidal suspensions using three semi-empirical thixotropic models from the literature [1,2], and one that we developed as an evolution of the model described in [3], all based on a scalar internal structural parameter. In addition to experimental data from literature we also used our own data. A 2.9vol% fumed silica in paraffin oil and poly-isobutylene (31wt%) [4] was formulated and its rheological response to steady shear, transient step-up and step-down, and LAOS, deformations measured. The experiments were performed on a strain-controlled TA Instruments ARES-G2 rheometer. Modeling of this stress response with several different thixotropic models described above, enables extracting also information about the structural order parameter [1,2,3]. The respective model parameters were found using a recently developed robust least squares stochastic global optimization. While all the models were found to be able to quantitatively fit the steady state experimental data, important quantitative and qualitative differences were observed regarding the transient LAOS data. A critical comparison of the predictions of selected LAOS data is made based on model parameters obtained from steady state and other LAOS data or, alternatively step-up and step-down experiments. The results are used to identify areas for improvement in thixotropic suspension modeling.

[1] J. Mewis and N.J. Wagner, *Colloidal Suspension Rheology*, Cambridge Univ. Press, 2012. [2] P. de Souza Mendes and R. Thompson. *Rheol. Acta* (2013) 52:673-694. [3] A. Mujumdar, A.N. Beris and A.B. Metzner. *J. Non-Newtonian Fluid Mech.* (2002) 102:157-178. [4] K. Dullaert and J. Mewis. *Rheol. Acta* (2005) 45:23-32.

Tuesday 5:40 Commonwealth A SC30

Study of nonlinear behavior in oscillatory shear of dense colloidal suspensions using asymptotically nonlinear material functions

Mansi Agarwal¹, Randy H. Ewoldt², and Charles F. Zukoski³

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Nonlinear rheological properties of dense colloidal suspensions were studied using asymptotically nonlinear material functions in oscillatory shear as introduced in [1]. Silica nanoparticles of diameter 40 nm were dispersed in low molecular weight polyethyleneglycol (PEG) to mimic a hard-sphere colloidal suspension with volume fractions ranging from 0.4 to 0.46. The asymptotically nonlinear properties provide robust definitions of critical strain as a function of frequency, and can be used to infer changes in structure as the suspension enters the non-linear regime. These material functions therefore provide a better understanding of the yielding process in colloidal systems.

[1] Ewoldt et al, *Rheologica Acta*, 2013.

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Tuesday 1:30 Commonwealth B

BB21

Using a live cell monolayer rheometer to probe the mechanics of the cytoskeleton

Claire M. Elkins¹, Wen-Jun Shen², Victor K. Khor², Fredric B. Kraemer², and Gerald G. Fuller¹

¹*Chemical Engineering, Stanford University, Stanford, CA, United States;* ²*Stanford Medical School, Palo Alto, CA, United States*

The mechanical properties of adherent cells are predominantly determined by the cytoskeleton, a filamentous network consisting primarily of three components: actin microfilaments, intermediate filaments, and microtubules. A growing body of evidence suggests that these three major cytoskeletal components play distinct but complementary roles in determining the overall mechanics of the cell. Our lab has developed a linear cell monolayer rheometer to measure the average mechanical properties of live, adherent cell monolayers in order to gain a more quantitative understanding of how each cytoskeletal component contributes to whole-cell stiffness. In the linear cell monolayer rheometer, a live monolayer of cells is gently compressed from above by a collagen-coated plate. A waiting period then provides the cells an opportunity to form adhesions to the top plate. Following this, the top plate executes a series of lateral step strain motions, thereby inducing shearing deformations of the cell layer. A force transducer attached to the top plate simultaneously collects stress data for each step strain. The entire apparatus is mounted on an inverted microscope, enabling live cell imaging to be performed throughout the experiment. We have utilized this technique to provide quantitative evidence for the contributions of actin microfilaments, vimentin intermediate filaments, and microtubules to the mechanics of a live monolayer of stromal vascular cells. This was accomplished through systematic inhibition of each cytoskeletal component (via drug-induced inhibition for actin and tubulin, genetic mutation for vimentin), followed by live cell imaging and measurement of the shear relaxation modulus of the cell monolayer. Relaxation moduli were acquired for confluent monolayers in which cells maintained their adherent geometry and cell-cell contacts throughout testing, a unique advantage of employing a linear cell monolayer rheometer for these measurements.

Tuesday 1:55 Commonwealth B

BB22

In vitro live-cell imaging to determine how spatial gradients in shear stress affect migratory response of endothelial cells

Vinay N. Surya, Maggie A. Ostrowski, Eva Huang, Alexander R. Dunn, and Gerald G. Fuller

Chemical Engineering, Stanford University, Stanford, CA, United States

Fluid flow plays an important role in regulating the physiological function of endothelial cells (ECs), which line our blood vessels. The adaptive response of ECs to fluid shear stress is necessary for proper vascular function and has been implicated in the development of cardiovascular disease. How ECs sense fluid flow is a central and unanswered question in cardiovascular biology. We have developed a high-throughput live-cell fluid flow chamber which models the physiological shear stress gradients experienced by ECs in vessel branches and bifurcations. Live-cell, time-lapse imaging allows us to probe important cellular response to flow, most notably EC migration, which has a key role in vessel development. We find that human lymphatic microvascular ECs collectively migrate against flow and up spatial gradients in wall shear stress, a markedly different response from other EC subtypes, which migrate with flow direction. In addition, lymphatic ECs display varied responses to different flow fields, sensing both magnitude and direction to control collective monolayer response. In efforts to probe how ECs sense flow, we made the unexpected discovery that the membrane-bound G-protein coupled receptor (GPCR) sphingosine 1-phosphate receptor 1 (S1PR1) is required for directed, flow-induced migration. Ongoing work aims to connect the physical stimulus of flow to a host of other morphological changes such as alignment and shape.

Tuesday 2:20 Commonwealth B

BB23

High resolution mapping of intracellular fluctuations using carbon nanotubes

Nikta Fakhri¹, Alok Wessel¹, Charlotte Willms¹, Dieter Klopfenstein¹, Matteo Pasquali², Fred MacKintosh³, and Christoph F. Schmidt¹

¹*III. Physikalisches Institut - Biophysik, Georg-August-Universität, Göttingen, Germany;* ²*Rice University, Houston, TX, United States;* ³*Department of Physics & Astronomy, Vrije Universiteit, Amsterdam, The Netherlands*

Cells are active systems with molecular force generation that drives complex dynamics at the supramolecular scale. Here we present a quantitative study of molecular motions in cells over times from milliseconds to hours. We observe a regime of active random "stirring" that constitutes an intermediate mode of transport, different from both thermal diffusion and directed motor activity. We image highly stable, near-infrared luminescence of single-walled carbon nanotubes (SWNTs) targeted to kinesin-1 motor proteins in COS-7 cells for non-invasive tracking. High-frequency motion is thermally driven. At times >100 ms, non-equilibrium dynamics dominate. In addition to directed transport along microtubules, we observe strong random dynamics driven by myosins that result in enhanced non-specific transport. We present a quantitative model connecting molecular mechanisms to mesoscopic fluctuations.

Tuesday 2:45 Commonwealth B

BB24

Rheology of concentrated algae suspensionsVictor Breedveld, Vikram Prasad, and Steven Edgar*School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, United States*

We report on the rheological behavior of suspensions of the synechocystis cyanobacterium. The flow behavior of these systems is of practical significance because of their use in algae-based biofuel production processes. In particular, the algae species in this study is being explored for large scale bioethanol production. The economic feasibility of that process strongly depends on the ability to separate biomass from the ethanol containing medium in which they are suspended; the transport of concentrated suspensions is a critical element of the proposed process.

We found that the rheology of algae suspensions in their natural environment is dominated by the presence of freely dissolved exopolysaccharides, which are excreted by the algae into the suspending medium during the growth phase. When the exopolysaccharides are removed from the suspension, the rheological properties are dominated by interactions between the grafted polysaccharide coatings on the algae. We report the shear viscosity of suspensions as a function of algae concentration and show that the strongly shear-thinning behavior is well described by the Carreau-Yasuda model. Confocal microscopy and local particle tracking microrheology measurements of concentrated suspensions confirmed the dominant effect of the brush-like extracellular polysaccharide coat on the suspension rheology.

Tuesday 3:10 Commonwealth B

BB25

Rheological properties of fire ant aggregationsMichael Tennenbaum¹, Zhongyang Liu², Alberto Fernandez-Nieves¹, and David L. Hu³*¹School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, United States; ²School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States; ³School of Mechanical Engineering and Biology, Georgia Institute of Technology, Atlanta, GA 30332, United States*

Fire ants, *Solenopsis invicta*, form aggregations that are able to float, drip, spread like simple liquids but are also able to store energy and maintain a shape like an elastic solid. They are an active material which constantly converts chemical energy into work. We examine how the active nature of the individuals affects the properties of the aggregation through comparison of aggregations of live and dead ants. In oscillatory tests, live ants exhibit a storage modulus (G') and loss modulus (G'') that have comparable values over three orders of magnitude of frequency and two orders of magnitude of strain, indicating that both elasticity and dissipation are equally important. In comparison, dead ants are more solid-like with a larger storage modulus than loss modulus.

Tuesday 4:00 Commonwealth B

BB26

Characterization of aqueous alginate solutions at high concentrations with neutron scattering and rheologyHuseyin B. Eral¹, Keshavarz Bavand², Gareth H. McKinley², and Patrick S. Doyle¹*¹Massachusetts Institute of Technology, Cambridge, MA 02139, United States; ²Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Alginate (ALG) is a polysaccharide that is commonly used in the food and pharmaceutical industry as a filling material. Due its ability to ionically crosslink with divalent ions, it also finds applications in biomedical industry as a biocompatible hydrogel in wound dressings, for encapsulating active ingredients for controlled release and most recently in pharmaceutical production. Therefore, characterization of its rheological characteristics is critical for developing optimal continuous manufacturing processes. Combining neutron scattering and rheological measurement, we have investigated both uncrosslinked ALG solutions and crosslinked gels at varying ALG concentrations. At low ALG concentrations (i.e. less than 4% weight/ volume), small amplitude oscillatory shear tests of uncrosslinked aqueous ALG solutions show Maxwell-like behavior with one dominant timescale for both loss and storage modulus. However, at high concentrations (>4% weight/ volume), power law behavior is observed for both moduli which is a signature of the existence of a weak fractal network. We investigated the underlying physical mechanism responsible for the power law behavior at high ALG concentrations. Our preliminary results indicate that the existence of Hydrogen-bonding groups along the alginate backbone are important in the formation of this weak elastic network. Understanding and controlling the strength of this percolated network facilitates the design of more efficient flow-based manufacturing processes for ALG-containing biomaterials of interest to the pharmaceutical industry.

Tuesday 4:25 Commonwealth B

BB27

Viscosity and short time dynamics of concentrated solutions of proteins interacting with a short range attractive and long range repulsive interactionPaul D. Godfrin¹, Kunlun Hong², Lionel Porcar³, Peter Falus⁴, Norman J. Wagner¹, and Yun Liu⁵*¹Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States; ²Center for Nanophase Materials and Sciences, ORNL, Oak Ridge, TN, United States; ³Large Scale Structures Group, ILL, Grenoble, France; ⁴Time of Flight and High Resolution Group, ILL, Grenoble, France; ⁵NIST Center for Neutron Research, NIST, Gaithersburg, MD, United States*

Concentrated colloidal dispersions interacting with a short range attractive and long range repulsive interaction are currently of significant scientific and technological interest as they can exhibit intermediate range order as well as significant viscosities. Such systems are capable of producing clustered fluid phases in which reversible, thermodynamically stable aggregates of finite size exist in equilibrium with monomers.

Clustered fluids are formed by the balance of the competing potential features and are thought to be especially prevalent in concentrated protein solutions. Of particular importance in biotechnology is the effect of this fluid structure on the viscosity and diffusivity of proteins in solution. Recent studies have linked the formation of clusters in solutions of lysozyme and monoclonal antibodies to a substantial increase in solution viscosity (Biophys. J. 105:720, 2013). The goal of our work is to quantify the effect of intermediate range order and cluster formation on the viscosity of model protein solutions. Here we present experimental results for lysozyme, which is selected because of its availability, stability, and globular structure, the latter enabling quantitative comparison to models. Zero shear viscosity is obtained by microrheological measurements to avoid artifacts of interfacial rheological effects. A strong divergence of zero shear viscosity is observed for volume fractions well below that for hard sphere dispersions. The fluid microstructure and protein short time-self diffusion are measured across a broad range of conditions by small angle neutron scattering (SANS) and neutron spin echo (NSE), respectively. Previously validated models that include explicit hydrodynamic, Brownian, and interaction contributions to the viscosity fail to account for the large viscosity rise with concentration. However, this excessive viscosity rise can be semi-quantitatively predicted when protein clustering is properly accounted for and effective cluster-cluster interactions properly included.

Tuesday 4:50 Commonwealth B

BB28

Rheology and thermodynamics/scattering of concentrated protein solutions: pH-dependent viscoelasticity of solutions of bovine serum albumin and monoclonal antibodies

Prasad Sarangapani¹, Steven D. Hudson², Arun Parupudi³, Prakash Manikwar¹, Justin Weaver⁴, Ronald Jones², Kalman B. Migler², and Jai A. Pathak¹

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We elucidate how conformation and inter-molecular interactions influence transport properties in BSA and monoclonal antibody solutions. The observation that chain conformation is another critical driver of solution viscoelasticity, in addition to inter-molecular interactions, is an important contribution to current discussions in the field of concentrated protein solution rheology. We report biophysical characterization, solution rheology and thermodynamic interaction potential, $u(r)$, for these systems across broad pH and concentration ranges of $3.0 < \text{pH} < 8.9$ and $2 \text{ mg/mL} < c < 500 \text{ mg/mL}$, respectively. Near-UV circular dichroism (n-UV CD) and intrinsic viscosity data demonstrate that conformation (tertiary structure) of BSA clearly changes with concentration and pH. The measured BSA intrinsic viscosity does not equal the classical hydrodynamic hard-sphere result (2.5) at any pH between 3.0 and 7.4. Size-exclusion chromatography (SEC) measurements reveal that these BSA solutions are polydisperse: containing monomers and higher order soluble clusters. In investigations of solution thermodynamics using Small-Angle Neutron Scattering (SANS), we account for this polydispersity using the model of Gregory Beaucage combined with our own Random Phase Approximation (RPA), which accounts for short- and long-range attraction and also long-range repulsion. We find that BSA is not a thermodynamic hard sphere either, and $u(r)$ changes with pH and concentration. The concentration and pH dependent conformation and solution polydispersity influence the complex rheology of BSA solutions. We also contrast the solution behavior of a self-associating monoclonal antibody ("mAb1") and a non-self-associating mAb (mAb2). CD reveals that the tertiary structure of mAb2 changes appreciably with concentration. Conversely, mAb1 shows weak conformational changes. SANS data revealed that the wavevector (q)-dependent mAb-specific form factor, $P(q)$, and $u(r)$ clearly change with concentration and pH. At low pH conditions we prove that both mAbs exist in an expanded conformation. For $\text{pH} > 3.0$, mAb2 shows evidence of conformational transitions with concentration, while mAb1 shows comparatively weaker conformational transitions. These conformational transitions are important contributors to the concentration-dependent viscoelasticity, which increases steeply at pH 3.0 for both mAbs: mab1 gels at 100 mg/mL.

Tuesday 5:15 Commonwealth B

BB29

High temperature rheometry of lignocellulosic biomass

Daniel J. Klingenberg¹, Thatcher W. Root¹, C. T. Scott², Carl Houtman², Keith J. Bourne², and Vish Subramaniam³

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Knowledge of the rheological properties of lignocellulosic biomass is important for the design and operation of processes for converting these materials to fuels and chemicals. At high solids content, lignocellulosic biomass is a yield stress material whose yield stress increases rapidly with solid content. A critical element that is missing in our understanding of the rheological properties of biomass is the behavior of the biomass under the relatively extreme reaction conditions often employed (e.g., low pH, $170 < T < 230^\circ\text{C}$). In this presentation, we describe a new device that can be used to measure the rheological properties of biomass at high temperature, high pressure, and low pH.

At ambient conditions, rheological properties measured with this device are consistent with those measured with other instruments. The yield stress and apparent viscosity decrease significantly with increasing temperature. Changes in the apparent rheological properties with temperature are reversible for small temperature changes, and are irreversible for large temperature changes, or when a sufficient amount of mineral acid is present. Irreversible changes in rheological properties appear to arise from the acid-catalyzed hydrolysis of the biomass solids. Experimental results with model systems are presented to provide insight into the mechanisms of the observed behavior.

Tuesday 5:40 Commonwealth B

BB30

Pressure-driven flow of lignocellulosic biomass: A compressible Bingham fluidJoshua C. Duncan¹, Anaram Shahravan¹, Michael D. Graham¹, Daniel J. Klingenberg¹, C. T. Scott², Keith J. Bourne², and Roland Fleisner²¹Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States; ²US Forest Service Forest Products Lab, Madison, WI 53726, United States

Lignocellulosic biomass can be used in the production of liquid fuels, chemicals and materials. One proposed method for reducing the cost is to increase the concentration of insoluble solids. However, concentrated biomass is a viscous, non-Newtonian fluid, which makes mixing reactants and conveying the biomass challenging. Understanding the flow of these non-Newtonian materials is thus important for designing and optimizing processes. We have examined the pressure-driven flow of lignocellulosic biomass experimentally, using an extruder to pump concentrated biomass through a tube fitted with pressure transducers. Heterogeneities and pressure fluctuations are observed. We have also measured large yield stresses, a nonlinear dependence of pressure drop on pipe length, and expansion of the biomass in the pipe after the extruder was stopped. All experimental observations suggest that the biomass is a compressible viscoplastic fluid whose yield stress is a function of density. The pressure and velocity profiles for compressible Bingham fluids in pressure-drive tube flow were also determined by numerical solution of the mass and momentum balances. If the yield stress is allowed to increase with density, the experimentally observed pressure profiles can be reproduced. Expansion of the biomass after cessation is also sensitive to the dependence of yield stress on density. Model features required to reproduce these and other observed phenomena will be discussed.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Tuesday 1:30 Commonwealth C

SM21

The influence of hydrogen bonding on nonlinear extensional rheology of supramolecular poly(n-butyl acrylate)Aamir Shabbir¹, Seyedhadi Goldansaz², Nicolas J. Alvarez¹, Evelyne V. Ruymbeke², and Ole Hassager¹¹Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby 2800, Denmark; ²Institut De La Matière Condensée Et Des Nanosciences, Université Catholique De Louvain, Louvain-la-Neuve 1348, Belgium

Supramolecular polymers are used in many fields as adhesives, coatings, cosmetics and in printing. Understanding the dynamics of such transient systems is essential for tailoring user defined properties. Unlike linear viscoelasticity, only few extensional rheology data exists for supramolecular polymers. They indicate that they are very promising for tailoring the appearance of strain hardening. On the other hand, such data is also needed to develop sophisticated multi-scale models that can later be used for predicting the flow behavior and molecular dynamics of supramolecular networks. We investigate rheological properties of well-defined linear supramolecular polymers based on Poly (n-butyl acrylate) (PBA). Systems with varying hydrogen bonding made via hydrolysis of PBA were studied. While systems with moderate degree of hydrolyzation exhibit pure reptation based relaxation in the linear regime, they exhibit significant strain hardening behavior compared to the untreated PBA. Furthermore, at a critical percentage of hydrolyzation, the supramolecular PBA exhibits rubber like characteristics. For such rubbery like material, thermo-rheologically complex behavior is observed, elucidating the presence of two mechanisms i.e., association/disassociation kinetics in addition to the reptation based disentanglement mechanism. The extensional rheology experiments were performed on an updated filament stretching rheometer.

Tuesday 1:55 Commonwealth C

SM22

Slip of polydisperse polymers: Molecular weight distribution above and below the plane of slipS. Mostafa Sabzevari¹, Satu Strandman², and Paula M. Wood-Adams¹¹Department of Mechanical and Industrial Engineering, Concordia University, Montreal, QC, Canada; ²Departement de Chimie, Université de Montreal, Montreal, QC, Canada

When strong slip occurs, during the drag flow of highly entangled polybutadienes (PBD) in a sliding plate rheometer equipped with stainless steel parallel plates, a thin film of polymer remains on the substrate after the slip. This debris layer is assumed to be formed by the disentanglement process that occurs in strong slip at a distance of about one molecular size from the plate. In order to evaluate the composition of the debris we collected it with tetrahydrofuran and subjected it to gel permeation chromatography. It was found that the molecular weight distribution (MWD) of the debris is significantly different from that of the bulk while the composition of bulk before and after shear is unchanged. Moreover, in binary and ternary mixtures prepared from monodisperse PBDs with distinctly different molecular weights, the MWD of the debris was found to be richer in low molecular weight components and leaner in the high molecular weight component compared to the bulk. This information is important since it reveals the compositional difference between the bulk and interfacial layer above and below the plane of slip. The difference in MWD is likely a consequence of the strong slip in which some of long chains are pulled away from the surface-adsorbed chains by the flow leaving a debris lean in the high molecular weight component.

Tuesday 2:20 Commonwealth C

SM23

Molecular scale simulations of rheological behavior – Understanding slip of molten polymersJohn R. Dorgan and Nicholas A. Rorrer*Colorado School of Mines, Golden, CO 80401, United States*

New simulation results of slip phenomena at the molecular level shed new fundamental insight into this important phenomena. While most experimental studies of homopolymer slip treat drag and pressure driven flows as equivalent, simulations show this is not the case. In particular, molecular weight fractionation means that slip in pressure driven flows (Poiseuille flow) are distinct from drag flows (Couette). For monodisperse melts in shear flow, slip is not observed at low shear rates, however, a cascade of wall slip followed by cohesive failure is observed with increasing shear rates. In comparison, parabolic flow exhibits slip at all apparent wall shear rates, in agreement with the theories originally proposed by Brochard and deGennes. The slip velocity at the wall is found to scale with molecular weight and shear rate. When polydisperse melts are simulated there is a small preference for lower molecular weight chains at the wall under quiescent conditions which is not enhanced in planar Couette flow. However, at all flow rates there are gradients in shear rate for parabolic flow, and thus there are always migration effects present. The cascade of molecular events in rectilinear shear is thus distinct from parabolic flow. Interestingly, early experiments recognized this difference but more recent work has not. Polydispersity serves to alleviate slip in both cases; higher shear rates can be reached prior to the onset of slip. Reduction of slip is observed in the shear stress response and in the chain end density for shear flow, and is observed in a reduction of the slip velocity in parabolic flow. These simulations shed light onto the fundamental microscopic and molecular origins of slip, and are in post facto agreement with experimental and theoretical investigations.

Tuesday 2:45 Commonwealth C

SM24

Shear banding in entangled polymers in micron scale gap: A confocal-rheoscopic studyPouyan Boukany¹ and Shi-Qing Wang²¹*Chemical Engineering Department, Delft University of Technology, Delft 2628 BL, The Netherlands;* ²*University of Akron, Akron, OH, United States*

Based on simultaneous rheometric and particle-tracking velocimetric measurements, this work characterizes the deformation fields of two identically entangled polybutadiene (PBD) solutions in a small gap distance of $H \sim 50 \mu\text{m}$. At a concentration of 13 wt % of PBD with $M_w = 1.0 \times 10^6 \text{ g/mol}$, there are 54 entanglements per chain in these solutions. We use two different polymeric butadiene solvents to prepare two 13 % solutions that have different intrinsic capacities to undergo wall slip. For the PBD solution made with a low molecular-weight PBD solvent of 1.5 kg/mol, wall slip is the dominant response within the accessible range of the shear rate, i.e., up to a nominal Weissenberg number Wi as high as 290. Wall slip is minimized in solution made with a high molecular-weight PBD solvent of 10 kg/mol. Severe shear banding is observed in this second solution. These results are consistent with the published phase diagram (*Macromolecules* 2011, 44, 183) depicting the relation between homogeneous shear, wall slip and shear banding.

Tuesday 3:10 Commonwealth C

SM25

Chain conformation, entanglements, and the origin of stress overshoot during startup shear of entangled polymer meltsYuyuan Lu¹, Lijia An¹, Shi-Qing Wang², and Zhen-Gang Wang³¹*Changchun Institute of Applied Chemistry, Changchun, China;* ²*University of Akron, Akron, OH, United States;* ³*California Institute of Technology, Pasadena, CA, United States*

Using Brownian Dynamics simulation, we determine the chain orientation and stretching and their connection to stress overshoot in an entangled polymer melt undergoing startup shear at rates lower than the reciprocal of the Rouse time yet higher than the reciprocal reptation time. In this regime, the prevailing tube theory envisions little chain stretching, so that the coil size (as characterized by the radius of gyration) and shear stress are determined primarily by chain orientation. In contrast, our results reveal that there is significant chain stretching which persists well beyond the Rouse time and contributes substantially to both the initial stress growth and the evolution in the radius of gyration. In particular, stress overshoot is found to be primarily due to chain retraction after considerable stretching rather than chain orientation. The coil size shows a pronounced peak as a function of the strain. Furthermore, up to many Rouse times, the relaxation of the initial entanglements is slower than that under the quiescent condition. These results point to fundamental deficiencies in the molecular picture of the tube model for startup shear.

Tuesday 4:00 Commonwealth C

SM26

Finite cohesion due to chain entanglement in polymer meltsShiwang Cheng¹, Yuyuan Lu², Lijia An², Zhen-Gang Wang³, and Shi-Qing Wang¹¹*Department of Polymer Science, University of Akron, Akron, OH, United States;* ²*Changchun Institute of Applied Chemistry, Changchun, China;* ³*California Institute of Technology, Pasadena, CA, United States*

Stress relaxation and delayed rate-switching during stress relaxation from step-wise deformation are carried out using a SER fixture to elucidate the existence of a finite entropic barrier against chain retraction. The stress relaxation experiment reveals identical relaxation modulus as a function of time below a threshold strain, where the relaxation is quiescent. Specifically, there is little hastened stress relaxation for step shear up to amplitude of $\gamma = 0.7$ and for step extension up to a stretching ratio $\lambda = 1.5$. This contrasts sharply with the theoretical description based on the most sophisticated tube theory (GLaMM). A sudden application of startup extension during different stages of the stress relaxation after a

step-wise extension, i.e., the delayed-rate-switching experiment, suggests that the effect of chain stretching, leading to a transverse geometric condensation of entanglement strands, survives well beyond the Rouse time t_R . In contrast, the GLaMM calculation shows that chain retraction takes place right away at any amplitude of the step-wise extension and the effect of geometric condensation decays from the onset of the relaxation.

Tuesday 4:25 Commonwealth C

SM27

Strain hardening in startup shear

Gengxin Liu¹, Mengchen Wang¹, and Shi-Qing Wang²

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The idea to treat entangled polymer solutions and melts as transient solids has allowed us to unify shear and extensional rheology that is often worked on by different sub-communities. Yielding of the entanglement network is a common thread because it occurs in both shear and extension, rheometrically manifested as shear stress and engineering stress overshoots respectively. Shear and extension are also sometimes different: at the same rate, shear produces yielding through chain disentanglement, signified a stress overshoot (strain softening); but extension can produce true strain hardening [1]. On the other hand, we already know that it is not true for polymers with long chain branching [2]. This work examines whether it is always true that strain hardening never occurs in startup shear. This work is supported, in part, by NSF (DMR-1105135).

[1] Shear and extensional rheology of entangled polymer melts: Similarities and differences, *Sci. China - Chem.* 55, 779 (2012). [2] Strain hardening in startup shear of long-chain branched polymer solution, *Phys. Rev. Lett.* 111, 068302 (2013).

Tuesday 4:50 Commonwealth C

SM28

The behavior of strongly entangled polymers in strong shearing startup flows

Peter D. Olmsted¹, Richard S. Graham², and Ewan P. Henry³

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Entangled polymers have a long and colorful history, as befits the challenges in both measuring their properties and constructing suitable theories. With the advent of flow visualization methods and new rheological devices that can help reduce the probability of instabilities, the community is now able to probe more deeply into the behaviour of entangled polymers in strong flows. I will discuss recent experiments, and our attempts to model them, on various types of startup flows (primarily shear), including fluid relaxation after step strain, elastic recovery after startup, and double step shear rate experiments. We use variants of the Rolie-Poly and GLaMM models, and in some cases include the possibility of inhomogeneous flows.

Tuesday 5:15 Commonwealth C

SM29

Microscopic theory of tube constraints and elasticity in isotropic, anisotropic, confined and deformed entangled polymer liquids

Ken Schweizer¹, Daniel Sussman², W.-S. Tung², Karen Winey², and Rob Riggleman²

¹*University of Illinois, Urbana, IL, United States;* ²*University of Pennsylvania, Philadelphia, PA, United States*

A microscopic, force-level, self-consistent theory for the transverse dynamic confinement potential of entangled chain liquids has been constructed based on modeling polymers as freely jointed chains of infinitely thin and uncrossable rigid primitive path steps [1]. The approach allows a unified description of tube localization in isotropic fluids and in systems subject to liquid crystalline orientational order, geometric confinement or deformation. For isotropic melts the tube diameter is predicted to scale with the packing length, and the full confinement potential is anharmonic and softens for large enough transverse displacements. Quantitative calculations agree well with MD and primitive path simulations and experiment [1]. Importantly, tube softening beyond the harmonic regime implies the entanglement network has a finite strength and can be destroyed by a large enough applied stress or strain, in qualitative agreement with the force imbalance and microscopic yielding ideas of S.Q. Wang and coworkers. Additional theoretical analysis suggests the single chain primitive path orientation and correlated interchain stress contributions to the entanglement plateau modulus are comparable in magnitude and proportional to the thermal energy divided by the packing length cubed [2]. Distinctive tube dilation emerges for conformationally anisotropic bulk liquids (e.g., nematics) and under thin film and cylindrical confinement; good agreement between simulation and theory is found for the latter [3]. Under shear deformation, tube dilation is predicted assuming rapid equilibration of chain stretch, and the corresponding reduction of the number of entanglements agrees well with steady state shear simulations.

[1] D.M.Sussman and K.S.Schweizer, *PRL*, 109, 168306 (2012). [2] D.M.Sussman and K.S.Schweizer, *JCP*, 139, 234904 (2013). [3] D.M.Sussman, W.S.Tung, K.I.Winey, K.S.Schweizer and R.A.Riggleman, submitted, 2014.

Tuesday 5:40 Commonwealth C

SM30

Almost ab initio multi-level slip-link modeling

Marat Andreev¹ and Jay D. Schieber²

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It is widely accepted that dynamics of entangled polymers can be described by the tube model. Here we advocate for an alternative approach to entanglement modeling known as slip-links. Recently, slip-links were shown to possess important advantages over tube models, namely they have

strong connections to atomistic, multichain levels of description, agree with non-equilibrium thermodynamics, are applicable to any chain architecture and can be used in linear or non-linear rheology. We present a hierarchy of slip-link models that are connected to each other through successive coarse graining. Models in the hierarchy are consistent in their overlapping domains of applicability in order to allow a straightforward mapping of parameters. One might choose a particular member of the hierarchy depending on the problem at hand, in order to minimize computational effort. In particular, the most-detailed level of description has four parameters, three of which can be determined directly from atomistic simulations. The last parameter, the only dynamic parameter, corresponds to the characteristic relaxation time of an elementary chain segment—the Kuhn step. Since this timescale is accessible to atomistic simulations, we believe we are closing in on fully *ab initio* rheology predictions. We will show how using the hierarchy of slip-link models, we can make predictions about the nonlinear rheology of monodisperse homopolymer melts, polydisperse melts, or blends of different architectures.

Symposium NF Non-Newtonian Fluid Mechanics and Stability

Organizers: Bamin Khomani and Sarah Hormozi

Tuesday 1:30 Washington A

NF6

Analysis of steady and transient shear banding in the flow of polymer solutions

Michael Cromer¹, Glenn H. Fredrickson², and Gary Leal²

¹NIST, Gaithersburg, MD, United States; ²University of California Santa Barbara, Santa Barbara, CA, United States

We have recently revealed, through a two-fluid formalism based upon the Rolie-Poly constitutive model, that shear banding is possible in the flow of polymer solutions driven by polymer migration up stress gradients via the Helfand-Fredrickson coupling mechanism. In this talk we delve further into the analysis of this phenomenon, focusing on both steady and transient behavior. We compare and contrast linear stability analysis with numerical simulations to better understand the various phenomena that arise. For example, we look more closely at the development of multi-banded (> 2 bands) velocity profiles that occur at steady state and evolve in time. Furthermore, we use a "transient linear stability analysis" to help provide a better understanding for the observed multiple steady state behavior. As an extension of this work we consider flows beyond the simplest case of planar shear. In particular we will look at the introduction of curved streamlines and their effect on the shear-rate driven flow. We consider the case of a circular Taylor-Couette cell in which a geometric bias now exists to determine the location and number of bands. A particularly interesting question is whether elastic recoil (negative velocity) due to the stress overshoot is predicted for our model fluid as has been observed in experiment

Tuesday 1:55 Washington A

NF7

Hi-Fidelity simulation of flow-induced inhomogeneous disentanglement and shear banding in polymeric melts

Mouge Mohagheghi and Bamin Khomami

Chemical and Biomolecular Engineering, University of Tennessee-Knoxville, Knoxville, TN, United States

Development of hi-fidelity atomistic or coarse-grained simulation models are essential in paving the way for determining the critical condition for onset of shear banding as well as developing a mechanistic understanding of this phenomenon in highly entangled polymeric liquids. To this end, we have performed hi-fidelity dissipative particle dynamics (DPD) simulations in a broad range of entanglement densities and system sizes to determine the critical conditions for occurrence of both transient and steady shear banding. Overall, our aim is to pave the way for a mechanistic understanding of shear banding in entangled polymeric fluids via detailed analysis of flow-microstructure coupling. In this presentation, we report, for the first time, hi-fidelity DPD simulation results that clearly demonstrate the inter-connection between spatially inhomogeneous entanglement densities and shear banding in this class of flows. Finally, based on these observations a simple mechanism for shear banding in entangled polymeric fluids will be discussed.

Tuesday 2:20 Washington A

NF8

Intriguing nonlinear instability phenomena occurring in film blowing process

Joo Sung Lee¹, Hyun Wook Jung², and Jae C. Hyun²

¹Battery R&D, LG Chem, Daejeon, Republic of Korea; ²Dept. of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea

SOR Annual Meeting, Philadelphia, Oct. 5-9, 2014 "Intriguing nonlinear instability phenomena in film blowing process" Joo Sung Lee 1, Hyun Wook Jung 2, and Jae Chun Hyun 2 1 Battery R&D, LG Chem, Daejeon, Korea 2 Dept. of Chemical and Biological Engineering Korea University, Seoul, Korea The film blowing is one of the most important polymer processing operations widely used for producing bi-axially oriented film products in a single-step process. It has been in operation over 40 years and many researchers around the world have been seeking ways how to enhance the productivity and product film quality of this convenient process even further. All these efforts have been possible ever since the seminal work by Pearson and Petrie in 1970 which established the theoretical framework for modeling and simulation of the process. While two fundamentally different instabilities have been found in film blowing during the last four decades by various research groups, i.e., draw resonance and helical instability, transient simulation of these instabilities have been rather elusive due to the highly nonlinear character of the process dynamics generated by the complicated set of governing equations comprising hyperbolic partial differential equations. It is rather recent that we have successfully produced the first transient simulation results of film blowing (Hyun et al. 2004 and Lee et al. 2011) which closely portray the

experimentally observed draw resonance instability. Now, we are in the process of simulating the other nonlinear instability of film blowing, i.e., helical instability, and hereby report the first transient simulation results which agree well with the experimental data, obtained by incorporating the buckling instability analogy into the modeling of the helical instability.

Tuesday 2:45 Washington A

NF9

Nonlinear elastic instability in channel flows at low Reynolds numbers

Paulo E. Arratia¹, Alexander Morozov², and Christian Wagner³

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It is presently believed that flows of viscoelastic polymer solutions in geometries such as a straight pipe or channel are linearly stable. In this talk, we present experimental evidence that such flows can be nonlinearly unstable and can exhibit a sub-critical bifurcation. Velocimetry measurements are performed in a long, straight microchannel; flow disturbances are introduced at the entrance of the channel system by placing a variable number of obstacles. Above a critical flow rate and a critical size of the perturbation, a sudden onset of large velocity fluctuations indicates the presence of a nonlinear sub-critical instability. Together with the previous observations of hydrodynamic instabilities in curved geometries, our results suggest that any flow of polymer solutions becomes unstable at sufficiently high flow rates.

Tuesday 3:10 Washington A

NF10

Elastic instabilities in the flow of complex fluids

Laura Casanellas¹, Sandra Lerouge², and Anke Lindner¹

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Elastic instabilities may occur at vanishing Reynolds number in the flow of viscoelastic fluids and a general criterion for the onset of such instabilities can be established based on the curvature of flow streamlines and fluid elasticity (Pakdel & McKinley, PRL 1996). Our goal is to study experimentally the onset of elastic flow instabilities in viscoelastic (polymeric or wormlike micellar) solutions of various rheologies in different flow geometries, from microfluidic to macroscopic devices. Experiments realized in microfluidic serpentine channels using diluted polymeric solutions showed that indeed the onset of elastic instabilities strongly depends on the channel curvature, which could be easily tuned in such devices (Zilz et al, JFM 2012). Besides, we recently found that an increase of the polymer concentration tends to stabilize the flow, shifting the elastic instability onset towards larger applied flows. The onset of elastic instabilities was also experimentally reported for the Taylor-Couette flow of shear-banding wormlike micellar solutions (Fardin et al, PRL 2010). We observed that the transition from a laminar to an elastically-driven turbulent flow regime exhibits significant hysteresis, which makes us presume that the bifurcation is subcritical.

Tuesday 4:00 Washington A

NF11

Using yield stress fluids for shaped multi-layer flow configurations

Ian Frigaard¹, Sarah Hormozi², and Geoff Dunbrack³

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Visco-plastic lubrication (VPL) has been established as a method for reliably suppressing interfacial instabilities and enhancing flow stability for multi-layer systems. Here we extend this methodology to the formation of shaped interfaces in multi-fluid core-annular configurations. We report both experimental and computational results. The experiments are performed using Carbopol and either xanthan or PEO, over a range of flow rates. We show that single pulsed changes in the imposed inflow rates can result in small interface indentations that remain frozen into the interface as it propagates downstream. Repeated pulses produce periodically patterned interfaces. We are able to control the frequency and amplitude of the interfacial patterns, but not directly the shape. Inelastic core fluids have been observed to produce rounded bulges whereas elastic core fluids have produced diamond shapes. Computational studies reveal more of the structure of the flows and help in focusing our interest at the all-important forming sections of the flow tube.

Tuesday 4:25 Washington A

NF12

Macro-scale drop encapsulation in yield stress fluids

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Yield stress fluids have the property that they do not deform unless a given yield stress is exceeded. While in some flows this leads to unwanted features, this property can also be exploited in order to produce novel flow features. For example, stable multi-layer flows can be achieved at high Reynolds numbers by using a yield stress fluids as a lubricating outer layer, far beyond what might be expected for a typical viscous-viscous interface. These flows have been demonstrated to be linearly and nonlinearly stable. Here we extend this idea to investigate the feasibility of

encapsulating droplets within a visco-plastic fluid. By encapsulation we mean the drop is "frozen-into" the bulk carrier fluid. Other methods of encapsulation utilized capillary forces in order to dampen the instabilities, which is most effective at small length-scales. However, in our proposed method, length scale is governed by the yield stress and macroscopic flow geometry. This means that we may encapsulate significantly larger droplets, which in turn, could open up possibilities for the applications in industries that do not operate on the micro-scale, as in most large scale industrial processing. We study this method both theoretically (asymptotic analysis) for slender droplets and computationally for general size of droplets in two different geometries: 2D channel and pipe. We show that sufficiently small droplets can be held in the unyielded plug of the Poiseuille flow without breaking the plug. As the size of the droplets increases the carrier fluid eventually yields, which potentially breaks the encapsulation. We identify that the plug breaks in two different fashions depending on the size and aspect ratio in both pipe and channel geometries. Theory and computation show that larger drop can be encapsulated in pipe geometry. Finally the effect of density difference is studied, which results in larger drop encapsulation when the droplet is heavier than the carrier fluid and the flow is in the opposite direction of gravity.

Tuesday 4:50 Washington A

NF13

Yield stress fluid droplet impact on coated surfaces

Brendan C. Blackwell, Marc E. Deetjen, and Randy H. Ewoldt

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Yield stress fluids, including gels and pastes, are effectively fluid at high stress and solid at low stress. In liquid-solid impacts, these fluids can stick and accumulate where they impact, motivating several applications of these rheologically-complex materials. Here we use high-speed imaging to experimentally study liquid-solid impact of yield stress fluids on dry and precoated surfaces. With a precoating of the same material, we can observe large, long-lifetime ejection sheets with redirected momentum that extend away from the impact location. Under critical splash conditions, sheet breakup occurs and ejected droplets can be nonspherical and threadlike due to the inability of capillary stresses to deform material above a certain lengthscale. By varying the droplet size, impact velocity, surface coating thickness, and rheological material properties, we develop appropriate dimensionless parameters, quantify splash characteristics including height and radial extent of deposition, and present a regime map of impact behaviors.

Tuesday 5:15 Washington A

NF14

Viscoplastic dip-coating

Mathilde Maillard¹, Anne-Laure Andrieu¹, Jérémy Bleyer¹, Jalila Boujlel², and Philippe Coussot¹

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Many industrial techniques rely on interactions between yield stress fluids and solids. This is in particular the case for the coating of objects, a process widely used in painting, food or building industries. Here, we are interested in characterizing in detail the specific technique of dip-coating of a vertical plate from a bath of yield stress fluid. This experiment concerns the study of the Landau-Levich flow with soft-jammed systems [1]. The key issue is to understand the formation process of the layer coated on the plate in particular to predict its thickness. We carried out such tests with Carbopol gels. Our data show that during withdrawal, in our range of fluid yield stresses and velocities, the layer coated on the plate has a uniform thickness and there is no drainage of the fluid along the plate. This thickness increases slightly with the plate velocity and strongly with the material yield stress. In particular, we observe the existence of a critical value for this thickness at vanishing velocities. Thanks to PIV we show that in order to be coated, the fluid is strongly sheared by the plate and becomes liquid in a layer of uniform thickness along the plate while the rest of the fluid stays solid. A close analysis of the velocity fields suggests that the liquid layer separates into two parts: one remaining in the bath while the other is stuck solid on the plate. We determined the thickness of the liquid layer and its fraction eventually coated on the plate as a function of the Carbopol yield stress. Then, we performed numerical simulations of the material flow inside the bath. The velocity fields obtained fit very well our experimental data and predicts the evolution of the liquid layer thickness with the plate velocity and the material properties.

[1] Maillard, M., Boujlel, J., & Coussot, P. (2014). *Phys. Rev. Lett.*, 112(6), 068304.

Tuesday 5:40 Washington A

NF15

Flow of elasto-viscoplastic materials past a flat plate

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Recent experimental observations reported in the recent literature describe a material behavior that deviates qualitatively from the one predicted by the classical viscoplastic models usually employed in simulations of flows of yield-stress materials. These observations (e.g. de Souza Mendes et al., 2007) demonstrate that the presence of elasticity leads to striking effects in the flow pattern and on the size and shape of the unyielded regions. To better understand these phenomena, in this article we selected a recently proposed elasto-viscoplastic constitutive model (de Souza Mendes, 2011) and performed a numerical investigation of the external flow of materials with this behavior past a finite flat plate. This physical situation is akin to the motion of a blade into a gel or a paste during a cutting process.

The elasto-viscoplastic constitutive model is based on the Oldroyd-B model, modified to allow the dependence of the viscosity, relaxation and retardation times on the structuring level of the microstructure. The constitutive and conservation equations are approximated by a three-field Galerkin least-squares method in terms of the extra-stress tensor, pressure and velocity. The GLS methodology was employed to allow the use of equal-order combinations of Lagrangian finite elements. This methodology is capable of approximating in a stable manner flows at quite high

Deborah number values. The results focus on determining the influence of elasticity and yield stress on the topology of the yield surfaces, on the elastic deformation field, and on the drag force at the plate.

[1] P. R. de Souza Mendes, M. F. Naccache, P. R. Vargas, F. H. Marchesini, Flow of viscoplastic liquids through axisymmetric expansions contractions, 2007, *J. Non-Newtonian Fluid Mech.*, 142, 207-217. [2] P. R. de Souza Mendes, Thixotropic elasto-viscoplastic model for structured fluids, 2011, *Soft Matter*, 7, 2471-2483.

Symposium BC Blends, Composites and Multiphase Systems

Organizers: Arezoo Adekani and Florian Nettesheim

Tuesday 1:30 Washington B

BC11

High pressure- and temperature-dependent viscous anomalies in polymer oil mixtures

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Machine elements such as rolling element bearings and gears operate under elasto-hydrodynamic (EHD) conditions. The temperatures and pressures of lubricants in the contact areas of these machine elements can be very high. The rheological properties of the lubricant determine the film thickness through a pressure viscosity coefficient considering a power law fluid. In this study, high (up to 400 MPa) and ultra-high (to 1.2 GPa) pressure falling body viscometers have been used to measure the viscosities of commercial engine oils and laboratory mixed lubricants at 40, 75 and 100 °C. The commercial lubricant containing polymeric viscosity index (VI) improvers (polyisobutylene) show a sharp increase in the pressure-dependent viscosity occurring at 40 and 75 °C. This change in viscosity may have some significant and unanticipated consequences on EHD theory. Four laboratory mixed lubricants consisting of ISO VG 10 polyalphaolefin oil and concentrations of polyethylene (PE) additives with different molecular weights were also examined and show similar behavior to that observed in the commercial lubricant. The PAO/PE mixture undergoes changes from mixture to gel to solution as the PE melts. Preliminary testing shows that as the solution gels there is increased wear of contacting surfaces. Possible mechanisms of viscosity increase under high pressure will be presented.

Tuesday 1:55 Washington B

BC12

Effect of thermal history on the behavior of thixotropic elasto-visco-plastic materials

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During the last decade a lot of interest has been built around what are now known in the literature as Elasto-Visco-Plastic (EVP) materials. These are soft materials that show a complex behavior characterized by both a plastic component, due to the presence of a yield stress below which there is no detectable flow, and a viscoelastic component. Many metals and alloys formed at medium or high temperatures fall into this category as well as waxy crude oils at extreme thermodynamic conditions, such as those experienced during deep-water drilling and transport. Recently, attention has also been focused on EVP materials for bio-inspired applications related to high-performance structural materials. From a modeling perspective, the simplest constitutive responses that capture the canonical behavior are of Bingham-Maxwell or Bingham-Voigt type. However, several different constitutive equations have been proposed in recent years that attempt to capture key features of EVP materials such as waxy crude oils, even in cases where the thixotropy interplays with the strongly non-linear mechanical response of the system. Notwithstanding the substantial progress that has been made, all of the models available in the literature have been developed for the situation of isothermal flows or quasi-equilibrium conditions. Such constraints must be relaxed for many applications such as flow assurance of crude oils in which rapidly quenched non-equilibrium wax microstructures can be developed near the walls of pipes. We show how thermal history influences the rheological response of EVP materials by a series of experiments performed in both steady and oscillatory shear. In particular, we show how spatial temperature gradients can, under some conditions, induce large stress overshoots even in the absence of a shear-induced strong gel network. We also describe modeling efforts to incorporate such behavior in the existing constitutive models for the limit of both small and large temperature gradients.

Tuesday 2:20 Washington B

BC13

The effect of pH and salinity on the rheology of concentrated aqueous suspensions of sphalerite/silica mixtures

Dingzheng Yang¹, Qingxia Liu², Hongbo Zeng², and Lei Xie²

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Understanding the surface properties and interactions of mixed particles is of both fundamental and practical importance in rheology of complex fluids in various engineering applications. In this work, sphalerite (a zinc-bearing mineral) and silica, was chosen as a model mixture. The interactions of sphalerite and silica were characterized using rheology and atomic force microscopy (AFM). The force-distance profiles demonstrated a pH-dependent surface force interaction between sphalerite and silica. Rheology measurements of 30 vol% sphalerite and silica mixtures in 0.001-5 M NaCl solution showed a pH-dependent yield stress with a local maximum around pH 7-10, which shifted towards higher pH values with the increase of NaCl concentration. At ionic strength lower than 0.1 M, sphalerite-sphalerite attractive network induced by the adsorbed zinc hydroxide at the peak pH dominated the yield stress. When ionic strength was greater than 0.1 M, silica-silica acid-base interaction

between associated and dissociated silanol groups was suggested to cause the peak yield stress. Our results indicate that the surface properties of sphalerite-silica mixtures play an important role in the particle-particle interaction and rheological behaviors, which also provides an insight into the basic understanding of the colloidal interactions and rheology of mixed particle systems.

Tuesday 2:45 Washington B

BC14

Melt rheology of polypropylene-clay nanocomposites with silane coupling agents

Weijie Ren and Krishnamurthy Jayaraman

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Silane coupling agents typically have alkoxy groups which react with organoclay in the presence of moisture; the other end of the silane may be chosen polar (such as amine) or non-polar (such as an alkyl group). The choice of the latter group on the silane allows us to tune the interactions among the various components of the polymer nanocomposite: nonpolar linear polypropylene, maleated linear polypropylene and the organoclay. The objective of this research was to investigate the effects of varying interactions on microstructure and rheology of polypropylene-clay nanocomposites with a variety of silane coupling agents. Two different maleated polypropylenes with 0.4 wt% maleic anhydride and 0.8 wt% maleic anhydride were used. Eight different nanocomposites were prepared by melt compounding these components in the same proportions. Transmission electron micrographs were obtained and particle counts and average dimensions were obtained from several micrographs for each case. The nanocomposites were also characterized for the linear viscoelastic storage modulus $G'(w)$ in shear and the transient uniaxial extensional viscosity of the melts at 180C. The results show that while good dispersion can be achieved with both octyl silane and amino silane coupling agents, the increase in low frequency G' -- indicating the strength of the particle-particle network, is significantly less for the cases with amino silane. The octyl silane improves the interaction between the clay and the bulk polymer while the aminosilane produces a bond between the clay and the maleated polypropylene compatibilizer. The particle network is distinctly weakened with the aminosilane coupling agent. The extensional viscosity curves for the cases with dimethoxy amino alkyl silane alone display pronounced strain hardening. The contribution of chain entanglements involving particle attached chains to the rheology is highlighted.

Tuesday 3:10 Washington B

BC15

Rheological characterization of highly filled composite systems for injection molding applications

Kurt A. Koppi

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A series of rheological tools were used for the characterization of highly filled composite systems. The influence of flow on structure property development was evaluated and utilized for designing systems for injection molding applications.

Tuesday 4:00 Washington B

BC16

Cocontinuous blends of immiscible polymers: Modeling stability and cocontinuity range

Aaron T. Hedegaard and Christopher W. Macosko

Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455-0132, United States

Cocontinuous polymer blends are formed by melt compounding two or more immiscible polymers to create multiple continuous interpenetrated networks. These are non-equilibrium structures where the morphology is determined by a combination of processing flow, interfacial properties, and rheology. We have fixed processing conditions but varied rheology and interfacial tension to create cocontinuous morphologies of several immiscible polymer pairs. Viscosity and viscosity ratio influence the range of concentrations where cocontinuity is achievable. Extensional strain hardening using branched polymers significantly broadens the range of cocontinuity. The stability of the blends was evaluated by the rate of coarsening during annealing, which was primarily controlled by ratio of interfacial tension to low shear rate viscosity. Several models from the literature are tested against our experimental continuity data. Models based on droplet packing have some success in predicting the center of the cocontinuous range, but they give no information concerning the range of cocontinuous compositions. Various mechanisms will be discussed to provide insight for predicting the relative size of these ranges.

Tuesday 4:25 Washington B

BC17

Morphological stability of PLA/PBAT and PLA/PBSA blends under shear flow

Mohammadreza Nofar, Amirhossein Maani, Marie-Claude Heuzey, and Pierre J. Carreau

Chemical Engineering, École Polytechnique de Montréal, Montréal, Canada

Blends of 75 wt% amorphous polylactide (PLA) with 25 wt% poly[(butylene succinate)-co-adipate] (PBSA) and poly[(butylene adipate)-co-terphthalate] (PBAT) were separately prepared using an internal batch mixer. The interfacial and viscoelastic properties of these two blends were analyzed and compared with each other. The morphology of the blends was examined after applying annealing and various shear flows. It was shown that annealing up to 20 min did not cause any pronounced morphology changes, nor subsequent modification of the viscoelastic behavior of both blends. However, shearing at 0.05 s⁻¹ for 20 min induced significant droplet coalescence in both blends, while the changes in the viscoelastic response were more prominent in the PLA/PBSA blend. It was also shown that although shearing at 0.2 s⁻¹ for 10 and 20 min caused noticeable droplet coalescence, it did not cause a pronounced change in the viscoelastic behavior of both blends. Moreover, the Palierne model was used to calculate the interfacial tensions between the blend components. It was also utilized to predict the droplet size of the dispersed phase after applying shearing at various rates and times.

Tuesday 4:50 Washington B

BC18

Mechanical responses of a nano-sandwich of thin polymer layer/single layer graphene/thin polymer layerXiguang Li and Gregory B. McKenna*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The interfacial mechanics and reinforcement of a polymer matrix by graphene are important to the understanding of graphene-based nanocomposites, but the methods available for their investigation remain a challenge. Here we report a novel study in which the mechanics of a nano-sandwich model system made of three layers in the form of an ultrathin polymer layer/monolayer graphene/ultrathin polymer layer structure are determined using a nano-bubble inflation method. The stress-strain behavior of the graphene nano-sandwich shows that significant reinforcement is obtained and gives a means of estimating the modulus of the graphene monolayer. Furthermore the method provides a measurement of the interfacial shear strength, as evidenced by an instability in the stress strain response. The bubble inflation method also provides the means to determine the internal stresses that develop between the graphene and the polymer sandwich faces, which are significantly different from the surface tension of a monolithic polymer film.

The authors are thankful to the National Science Foundation under grant DMR-1207070 and to the John R. Bradford Endowment, each for partial support of this project.

Tuesday 5:15 Washington B

BC19

The interplay between hydrodynamic and frictional forces in a shear-thickened suspensionNeil Lin¹, Michiel Hermes², Ben Guy², Wilson Poon², Yu Su³, Roseanna Zia³, and Itai Cohen¹

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At high shear rates, many fluids demonstrate shear thickening behavior, a phenomenon wherein viscosity increases with increasing shear rate. While rheometer measurements provide useful information on the bulk properties of a fluid, a deeper understanding of the shear thickening process requires information about the fluid's microstructure. In particular, although it has been proposed that both frictional forces and hydrodynamic stresses can give rise to shear thickening behavior, the lack of the experimental data on the suspension microstructure makes validating the role of friction and elucidating the interplay between these contributions difficult. Here, using a high-speed confocal rheoscope, we simultaneously measure the microstructure and stress response of a suspension with a highly viscous solvent. This combination allows us to investigate the microstructural dynamics of a shear-thickening suspension. In addition to quantifying the morphology of the shear-induced structures, we also determine the hydrodynamic stress and compare its value to the macroscopic force measurement. By performing comprehensive measurements under oscillatory shear and flow reversal, we address how hydrodynamic and frictional forces compete in the shear thickening regime.

Tuesday 5:40 Washington B

BC20

Interfacial processes at the polymer/polymer interface probed by linear viscoelasticity coupled with FTIR measurementsJaber Nasrollah Gavvani¹, Amir Faramarzi Jolfaei¹, Fatemeh Goharpey¹, Sachin S. Velankar², and Reza Foudazi³

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The chemical reactions occurring at the interface of asymmetric polymer-polymer interfaces was investigated by bulk viscoelastic investigations and IR spectroscopy at the molecular level. Polyisoprene (PI) mixed with maleic anhydride-functionalized PI (PI-MA) and polydimethylsiloxane (PDMS) mixed with amine-functionalized PDMS (PDMS-NH₂) were used as two polymeric phases in this study. The linear viscoelastic properties of the reactive systems were determined and the reaction mechanisms were analyzed by FTIR measurements. The results showed that the complex viscosity (η^*) of the reactive system is sensitive to both diffusion and chemical reaction. There were three distinct stages for the change of η^* with time: (i) η^* increases rapidly at short times and approaches a quasi-steady value times, (ii) η^* does not change by time, and (iii) η^* increases slowly again and reaches a final plateau. The apparent reaction kinetics obtained from the results in stage i can be described by a first-order reaction model. The interphase was quantified at a specific time and oscillation frequency by using rheological modeling. By coupling rheological and spectroscopic methods, the crosslinking reaction between the MA and NH₂ functional groups at the interface was explored.

Symposium CC Confined and Coupled Systems

Organizers: Patrick Anderson and Cari Dutcher

Tuesday 1:30 Washington C CC6

Direct visualization of near-wall structure of sheared monosized suspensions

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High-speed confocal microscopy is used to visualize the structure of flowing suspensions in a microchannel at various shear rates. From these images, real-space particle locations are determined and structure factors are resolved with resolution that allows calculation of the hydrodynamic stresses. Near the wall of the microchannel, the structure of this suspension depends on the topology of the boundary. Smooth walls result in particle chaining in the flow direction and higher order organization of these chains. This order penetrates many particle diameters into the channel. In contrast, rough walls reduce the effect of the boundary on the suspension microstructure. Greater than $12a$, where a is the particle radius, the suspension behaves roughly as seen in the bulk. Away from the boundary, we visualize hydroclusters that result in the shear thickening at higher Péclet number flows. We analyze the internal structure and orientation of these hydroclusters and investigate their distributions over multiple scans.

Tuesday 1:55 Washington C CC7

Flow of particulate suspensions in the 4:1 microcontraction channel: A simulation study

Kyung Hyun Ahn

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

The microchannel flow of complex fluids has drawn wide attention due to possible applications to high end technologies. But its physics has rarely been understood due to the difficulties in getting the microstructural change of the complex fluids during the flow in confined complex geometries. To understand the characteristics of these complex flows, we studied the dynamics of weakly aggregating particle suspensions in three dimensional 4:1 contraction flow using the self-consistent particle simulation method. We observed heterogeneous cluster formation and analyzed it in terms of the competition between flow and interparticle forces. In addition, spatio-temporal fluctuation which originates from the microstructural change and its interaction with the flow was observed. The fluctuation was complex with no characteristic periodicity or pattern. Heterogeneous structure formation and spatio-temporal fluctuation were found to be the main factors that characterize the complex flow of the particulate suspensions in the micro-contraction channel flow.

Tuesday 2:20 Washington C CC8

Flow-induced segregation in confined suspensions: Effect of particle shape and rigidity

Kushal K. Sinha and Michael D. Graham

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Blood and many other multicomponent suspensions display a segregation behavior in which different components of the suspension are differentially distributed in the cross-stream direction during flow in confined geometry such as arteriole or a microfluidic device. In blood, the platelets and leukocytes are strongly segregated to the near wall region and are said to be "marginated". The leukocytes and red blood cells differ from each other in membrane rigidity, shape and size. In our current work, we investigate the effects of particle shape and rigidity on segregation behavior in confined simple shear flow of binary suspensions of fluid-filled elastic capsules. Cell membranes are modeled with a Skalak form of strain energy function and an energy penalty for bending. Three dimensional simulations are performed with an accelerated implementation of the boundary integral method using GGEM solver for solving Stokes flow. The results show that in a mixture of particles with same shape and different membrane rigidity, the stiffer particles marginate i.e. localize in the wall region while the flexible particles anti-marginate i.e. move towards the center of the channel. In a mixture of the particle with same membrane rigidity and different shape, we see that particle with smaller aspect ratio marginate while the particle with higher aspect ratio in the mixture anti-marginate. Segregation effects are studied for wide range of parameters, including confinement ratio and volume fraction. The segregation phenomena is observed in all parameters studied. In both cases, of particle shape and membrane rigidity, segregation can be explained on the basis of heterogeneous pair collision and wall-induced migration of deformable particles away from the wall as shown in previous work of Kumar et al. for neo-Hookean capsules. The mechanistic understanding of component segregation can guide future designs and interpretation of experiments and the development of diagnostic tools for many medical conditions.

Tuesday 2:45 Washington C CC9

Mechanism of wall-induced drift of a single particle in viscoelastic confined flows

Rafael G. Henriquez and Michael D. Graham

Chemical and Biological Engineering, University of Wisconsin, Madison, Madison, WI, United States

The drift mechanism of a single, rigid or deformable particle due to the presence of a wall in Newtonian and viscoelastic fluids under an imposed flow is investigated using direct hydrodynamic simulations of a fluid-filled capsule, with an elastic membrane, and polymers under Couette flow. The fluid-structure interactions are resolved using a Stokes flow formulation of the immersed boundary method, coupled with Brownian dynamics

for the polymers. The capsule membrane is modeled with a neo-Hookean constitutive model. Polymers are modeled as bead-spring chains, with finitely extensible nonlinear elastic springs. To leading order, the particle above a wall is approximated as a point dipole with its image located on the other side of the wall. In this system, the wall-induced drift effect arises from the disturbance fluid velocity caused by the image of the point dipole on the other side of the wall. Wall-induced migration and slip velocities, obtained from theory and simulations, are compared.

Tuesday 3:10 Washington C

CC10

Dynamical role of slip heterogeneities in confined flows

Anne-Laure Vayssade¹, Fabrice Monti¹, Michel Cloitre², and Patrick Tabeling¹

¹*Microfluidique, Mems et Nanostructures, Espci, Paris 75005, France;* ²*Matière Molle et Chimie, ESPCI ParisTech, Paris 75005, France*

Complex fluids are prone to slip at smooth surfaces. The existence of wall slip is of particular importance and interest for many technological processes including die extrusion of complex fluids, ink jet applications, and oil migration in porous media. Today, most of the knowledge on the dynamical role of slip applies to ideal situations where the surfaces are spatially uniform in contrast to what is encountered in real environments where surface roughness and chemistry locally vary so that slip heterogeneities naturally exist. We study a concentrated suspension of submicron gel particles above the jamming transition, which is representative of soft glassy materials. The microgel suspension is driven above its yield stress in a microchannel, we use microparticle image velocimetry to image its motion. The microchannel inner walls impose different slip velocities, creating slip heterogeneities, by tuning independently their affinity for the microgels (using appropriate surface treatments). As the channel height decreases, the velocity profiles cease to have the symmetric shape expected for yield stress fluids. Here, we show that flows in confined systems are controlled by slip heterogeneities below a certain size. We present a theoretical model that accounts for the slip heterogeneities and captures well the velocity profiles. The results can be generalized to all fluids by introducing a length scale l^* below which slip heterogeneities control the flow in confined systems.

Symposium EF Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant and Sascha Hilgenfeldt

Tuesday 4:00 Washington C

EF1

Understanding the physics of nanoemulsion formation

Ankur Gupta, Huseyin B. Eral, T. Alan Hatton, and Patrick S. Doyle

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Nanoemulsions are nano-scale emulsions - i.e. liquid in liquid systems with droplet sizes on the order of 100nm. They can be prepared by high energy methods, such as high pressure homogenization and ultrasonication, as well as low energy methods like composition/temperature phase inversion. These small scale emulsions possess excellent material properties - large surface areas, optical transparency and long shelf life. Because of these properties, they have potential use in the pharmaceutical, food and oil industries. Over the last decade, significant work has been done on making and stabilizing different nanoemulsions. However, there have been very few attempts in understanding the physics of their formation. In this work, we revisit the problem of emulsion formulation via high energy processes. We propose how earlier literature can be modified and applied for understanding current nanoemulsion formation. To verify our proposed theory, we designed careful experiments wherein we prepared several nanoemulsion systems using a high pressure homogenizer. We varied process parameters such as input energy, dispersed phase viscosity and continuous phase viscosity. The size of the nanoemulsions was measured using dynamic light scattering (DLS). Good agreement was observed between the proposed theory and experimental results. Our theoretical understanding of nanoemulsion formation allows for the rational design of future systems.

Tuesday 4:25 Washington C

EF2

Morphology evolution of mesoporous bicontinuous emulsions

Antonio Perazzo, Valentina Preziosi, and Stefano Guido

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Microstructured mesoporous emulsions are often exploited as drug delivery systems, in particular for dermal delivery [1]. Such mesophases are characterized by both viscous and solid-like properties, and can be obtained by addition of water at very low addition rate into an agitated oil/surfactant solution at fixed temperature, whereby surfactants hydration may lead to sponge, lamellar, cubic or hexagonal arrangements. These bi-continuous surfactant solutions show highly viscoelastic behavior and may display also some features typical of lyotropic liquid crystalline phases. These systems show a continuous interplay between viscoelastic phase separation and surfactants self-organization, thus displaying a variety of morphologies. This work has been focused on morphology evolution characterization of the bicontinuous phases of a system composed of mineral oil, two non-ionic surfactants (one hydrophilic and one hydrophobic) and distilled water. During all the experiments, temperature was kept constant at room temperature. The "phase inversion composition" method, i.e., the dropwise addition of water to the oil-surfactant mixture was exploited to obtain the mesoporous bicontinuous structure. To outline bicontinuous emulsion morphology development, confocal microscopy and rheological measurements have been exploited. Rheological measurements probed the increased viscoelasticity induced by water addition up to the point of bicontinuous phase formation. Confocal microscopy revealed the formation of complex mesoporous structures at the microscale,

where a slow phase separation is initially driven by viscoelasticity of the system, thus demonstrating a strong coupling between high viscoelastic behaviour and liquid-crystalline mesophases.

[1] Iwashita, Y., & Tanaka, H. (2006). Self-organization in phase separation of a lyotropic liquid crystal into cellular, network and droplet morphologies. *Nature materials*, 5(2), 147-152.

Tuesday 4:50 Washington C

EF3

Flow induced localized jamming in sheared dense emulsions

Sudeep K. Dutta and Daniel L. Blair

Dept. of Physics and ISMSM, Georgetown University, Washington, DC, United States

The bulk behavior of a dense emulsion under shear flow is well described by the Herschel-Bulkley model, which characterizes a yield followed by continued shear thinning as the strain rate increases. We show through direct imaging with a confocal microscope how dynamics at the local scale change as the applied stress increases above yield. We find that the motion of the emulsion droplets decreases significantly, indicative of a cross-over to affine flow. Furthermore, at short time scales, the drops show super-diffusive behavior at high shear. The onset of these effects occurs at higher shear for higher droplet volume fraction.

Tuesday 5:15 Washington C

EF4

Universal scaling characteristics of stress relaxation in jammed emulsions

Pouyan Boukany, Siddarth Vasudevan, and Brian Tighe

Chemical Engineering Department, Delft University of Technology, Delft 2628 BL, The Netherlands

We study the stress relaxation behaviour of jammed emulsions both by experiments and simulations. The relaxation of scaled shear modulus is found to obey a power law behaviour. We demonstrate that the only parameters determining the relaxation behaviour are the exponent in the power law and average relaxation time for a given volume fraction. We find that exponent is 0.5 and 1 for linear and non-linear response regime respectively. Relaxation time is nearly independent of the applied strain for given volume fraction and it is the average value of the relaxation time obtained for different strains which determines the overall relaxation behaviour of a jammed emulsion. The average relaxation time is found to decrease with increase in the distance from the jamming transition point and obeys a scaling relationship, which is consistent with analytical predictions. We observe strain softening of the shear modulus and found that it scales inversely with strain in the non-linear response regime.

Tuesday 5:40 Washington C

EF5

Modified dissipative particle dynamics: Common Trends in soft suspensions from emulsions to vesicles

Arman Boromand, Safa Jamali, and Joao Maia

Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7038, United States

In this presentation we would like to capture the effect of confinement on the dynamic of multiphase fluids. Due to the multiscale phenomena involved in multiphase flows e.g. droplet dynamics, instabilities and interfacial phenomena, on one hand and difficulty of performing experimental studies under confined situation on the other hand, there are steadily growing interests to tackle this problem through computational studies e.g. boundary integral method has been used to study Newtonian droplets in the Newtonian matrix in bulk and confined geometries; however, it limits to Stokes flow. In this presentation we used Dissipative Particle Dynamics (DPD) as a mesoscale computational technique to study droplet dynamics under confinement. DPD is capable of capturing microscopic phenomena and provide comparison to macroscopic simulations and experiments much faster compare to common microscale computational techniques e.g. Molecular Dynamics (MD). In this presentation, we focus on interplay between droplet size and stress level in shear and extensional flows in bulk and confined geometries. Confined geometries are imposed by Couette geometries and flat walls. Using Couette geometry gives us the advantage of studying mixed flows in which both extensional and shear flow present. Moreover, it will provide a unique way to model extensional flows (mixed) without imposing complex periodic boundary conditions for extensional flows. For this purpose, Newtonian droplet in Newtonian matrix is modeled to ignore any complexity of materials and solely study effect of geometry. Droplet dynamics in this cases will be compared to macroscopic models and experimental results to confirm validity of this mesoscopic simulation method. The last part of the presentation will focus on the dynamic of the soft suspensions which will be modeled by crosslinking of the Newtonian droplets under confinement and bulk.

Wednesday Morning

Symposium PL Plenary Lectures

Wednesday 8:30 Millennium Hall

PL3

Microfluidic tools for the manipulation and analysis of macromolecules, vesicles, capsules, and suspensions

Susan J. Muller

Dept. of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States

The small length scales associated with microfluidics make these devices uniquely suited for a range of studies, including mixing in low Reynolds number-high Peclet number flows, the stability of high Elasticity number flows, the dynamics of individual microscale objects, and migration of particles and vesicles in suspensions. In this talk, I will briefly review recent developments in rapid prototyping methods and describe our recent work using microfluidic stagnation point flows and on migration in suspensions. Microfluidic stagnation point flows, including cross-slot devices and microfluidic four roll mills, have been designed to trap, manipulate, and analyze genomic DNA, particles, drops, capsules, and vesicles. Using these devices, we have demonstrated DNA target sequence detection, site-specific single molecule kinetic analysis of DNA-enzyme interactions, and measurements of the kinetics of polymer-salt induced DNA compaction. More recently, we have extended these studies to single capsules and vesicles, where our interests include measuring membrane properties through controlled deformations, and studies of migration in channel flows of suspensions of particles of controlled size, deformability, and shape.

Symposium SC Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Wednesday 10:00 Commonwealth A

SC31

Correlation of dynamic viscosity, normal stresses and diffusivity of colloidal glasses with excess entropy

Karim Khalil¹, Lavanya Mohan², Michel Cloitre³, and Roger T. Bonnecaze²

¹Department of Chemical Engineering, American University of Beirut, Beirut, Lebanon; ²Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States; ³Matière Molle et Chimie, ESPCI ParisTech, Paris 75005, France

The transport properties of colloidal glasses, such as dynamic viscosity, first and second normal stress differences and shear-induced diffusivity, are determined by the microstructure of the suspension under flow. A thermodynamic measure of the microstructure is the excess entropy, which we show here accurately correlates the transport properties of soft particle glasses across a wide range of volume fractions and particle moduli. Further, we show how the microscale diffusivity of particles in a soft particle glass can be determined directly from macroscopic measurements of its shear viscosity. The excess entropy for soft particle glasses is approximated with the two-body excess entropy computed from the pair distribution function extracted from dynamic simulations [1]. In general the excess entropy increases with increasing shear rate and decreasing particle concentration. Plots of dynamic viscosity, normal stress differences and particle diffusivity versus the excess entropy for varying volume fractions and particle moduli collapse onto universal curves. On these universal curves, the viscosity and normal stress differences appear to diverge at a critical excess entropy while the diffusivity appears to vanish. Diffusivity plotted versus dynamic viscosity reveals a very accurate correlation between the two. This result provides a means to obtain the particle diffusivity from the viscosity through standard rheometric measurements.

[1] J. R. Seth, L. Mohan, C. Locatelli-Champagne, M. Cloitre, and R. T. Bonnecaze, *Nat. Mater.* 10, 838 (2011).

Wednesday 10:25 Commonwealth A

SC32

Stress relaxation and aging in colloidal glasses

Lavanya Mohan¹, Roger T. Bonnecaze¹, and Michel Cloitre²

¹Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States; ²Matière Molle et Chimie, ESPCI ParisTech, Paris 75005, France

Glasses have the capacity to store mechanical stresses when they solidify. Internal stresses are known to have a great impact on the mechanical behavior and the long-term evolution and aging of glasses. Generally they adversely affect their durability but when properly controlled they can be used to design unique materials with exquisite mechanical properties. This question has stimulated intense research for the case of metallic, polymeric, and inorganic glasses.

In this talk we address the origin and the evolution of internal stresses and aging in colloidal glasses when they are suddenly brought to rest from steady shear flow. Our approach uses a combination of rheological and real space microscopy experiments on well-defined microgel suspensions,

and particle scale 3D simulations. Upon flow cessation the stress decays according to two different processes, which are well separated in time and cause a spontaneous motion of the particles [1]. The dynamics of strain relaxation on the application of a zero stress instead of a zero shear rate is dramatically different. Applying a probe stress or strain reveals that aging at zero stress and zero shear rate (flow cessation) are also quite different. We present and analyze the microscopic mechanisms which drive the amplitude and the kinetics of the stress relaxation as well as the local particle dynamics in each regime. We discuss the generality of our results in relation with the behavior of various glassy materials.

[1] L. Mohan, R. T. Bonnecaze, M. Cloitre, Phys. Rev. Lett. 111, 268301 (2013).

Wednesday 10:50 Commonwealth A

SC33

Probing particle-level stress fluctuations in a colloidal suspension

Neil Lin, Matthew Bierbaum, Sethna P. James, and Itai Cohen

Department of Physics, Cornell University, Ithaca, NY, United States

Measurement of stress thermal fluctuations in materials gives direct access to macroscopic mechanical properties including viscosity in fluids, as well as bulk and shear moduli in solids. At the same time, probing single-particle stresses reveals the underlying mechanism of nonlinear responses in various inhomogeneous systems such as glasses and polycrystals. While it has been impossible to experimentally measure these temporal and spatial fluctuations with conventional mechanical setups, we are able to probe those quantities using an alternative method that relies only on the particle configuration. Here, we directly image the microstructure of a colloidal suspension using a high-speed confocal microscope. From all particle positions we calculate the structure anisotropy of the suspension from which we infer particle-level stresses. With this technique, we measure the bulk viscosity of a colloidal liquid in excellent agreement with macroscopic rheological measurements and simulations. Furthermore, these local measurements allow us to experimentally visualize the stress distribution around various defects such as grain boundaries, stacking faults, and vacancies in a colloidal polycrystal. This experimental approach can be applied to study a broad range of nonlinear processes including sheared glasses, crystal indentation and cracking.

Wednesday 11:15 Commonwealth A

SC34

Trapped dynamics and pair interactions of concentrated nanoparticle suspensions

Yu Ho Wen and Lynden A. Archer

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

Small-amplitude oscillatory shear (SAOS) flows on polymerically stabilized silica nanoparticles were employed to access the trapped particle dynamics in jammed suspensions. We demonstrate that a master curve spanning nearly 20 decades can be created using time-concentration superposition (TCS) principle, by horizontally shifting $G'(\omega)$ and $G''(\omega)$ of each concentration with respect to a reference. Fourier-transformed frequency response of the jammed suspension with an extended frequency range compares favorably with the master curve, confirming self-similar core dynamics even in jammed systems. Scrutiny of high-frequency shear modulus and small-angle X-ray scattering (SAXS) structure factor suggests repulsive pair interactions over a wide range of particle concentrations investigated. Additionally, we exploited dynamic light scattering (DLS) to correlate core dynamics with rheology, and show that interdigitated ligands have a profound influence on the microviscosity and cage dimensions.

Wednesday 11:40 Commonwealth A

SC35

Jamming and yielding of binary colloidal glasses

Akanksha Agrawal and Lynden A. Archer

Chemical and biomolecular engineering, Cornell university, Ithaca, NY 14850, United States

We report on jamming, yielding, and flow of binary mixtures of self-suspended silica nanoparticles densely grafted with Polyethylene glycol (PEG)(MW~5000g/mol). The ratio of volume fraction of the smaller particles to the total volume fraction of the silica cores, x_s , is shown to sensitively affect both the yielding and jamming transitions of these systems. For $x_s > 0.25$ a two-step yielding is observed in oscillatory shear measurements, which we discuss in terms of the breaking of small and big particle cages. Similar two-step yielding has been observed previously in attractive glassy systems containing polymeric depletants. Here we find that a variety of factors, including depletion-like interactions produced by small particles on their larger counterparts controls the strength of the cages and the critical stress at which the suspensions yield. As the x_s is increased, the particles jam more presumably because the small particles exert a larger osmotic force on the bigger particles in suspension. Transmission electron microscopy (TEM), small angle x-ray scattering (SAXS) and x-ray photon correlation spectroscopy (XPCS) measurements are used to interrogate the quiescent structure and dynamics of the materials and to shed light on particle-particle correlations and cage structure of the materials.

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Wednesday 10:00 Commonwealth B

BB31

Shape transitions of vesicles in extensional flows: Dumbbells, pearling, and buckling

Vivek Narsimhan¹, Andrew P. Spann², and Eric Shaqfeh¹

¹*Chemical Engineering, Stanford University, Stanford, CA 94305, United States;* ²*Institute of Computational and Mathematical Engineering, Stanford University, Stanford, CA 94305, United States*

When flexible vesicles are placed in an extensional flow (planar or uniaxial), they undergo a wide range of shape transitions. At intermediate aspect-ratios and high extension rates, a vesicle stretches into an asymmetric dumbbell separated by a long, cylindrical thread. At high aspect-ratios, the vesicle extends symmetrically without bound, in a manner similar to the breakup of liquid droplets. During this "burst" phase, the vesicle will further undergo "pearling" if the extension rate is above a critical value - i.e., the vesicle forms necklace-like structures in its central neck reminiscent of the Rayleigh-Plateau instability. In this talk, we describe the mechanisms behind these shape transitions by solving the Stokes equations around a single, fluid-filled particle whose interfacial dynamics are governed by a Helfrich energy (i.e., the membrane is inextensible with bending resistance). We find that the shape transitions described above have their origins in a modified Rayleigh-Plateau analysis, even though the shapes look qualitatively different from each other. The stability criteria determined by our simulations and scaling analysis agree well with in-vitro experiments. In the last part of this talk, we discuss the early time response of vesicles in uniaxial compressional flow. We find that vesicles undergo a variety of buckling/wrinkling instabilities, the physics of which we characterize using analytical theories. We hope that this work will lend insight into the stretching/compressing dynamics of other types of biological particles with nearly incompressible membranes, such as cells.

Wednesday 10:25 Commonwealth B

BB32

Manipulating and separating polymers and particles at the microscale using conformation-dependent electrophoretic mobility

Harsh Pandey and Patrick T. Underhill

Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

Many separation techniques rely on different physical or chemical characteristics of the objects being separated. This includes separations based on size, total charge, or strength of interaction with a substrate. Recently there are many contexts in which it is important to manipulate or separate objects with different deformabilities, such as red blood cells or proteins. The deformability of an object is also important because it is related to the rheological response, especially in terms of elastic effects.

We have developed a coarse-grained Brownian dynamics simulation model that incorporates the change in electrophoretic mobility of rigid as well as flexible objects with conformation. The model incorporates the effect in a computationally efficient way, and has been validated by comparing with experiments with double-stranded DNA. In this talk, we will describe the results of computer simulations using the new model in which we quantify the stretch and residence time of polymers in a combination of electric field gradients and pressure-driven flow. The coupling of the stretch and mobility leads to a new way trap and manipulate biomaterials. A comparison of the simulations with single molecule experiments will also be shown.

Wednesday 10:50 Commonwealth B

BB33

The rheology of nanoparticles in blood for improved cancer therapy

Erik Carboni¹, Yang Guo², Grant Bouchillon³, Andrea Kadilak¹, Leslie Shor¹, and Anson W. K. Ma²

¹*Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT, United States;* ²*Institute of Materials Science, University of Connecticut, Storrs, CT, United States;* ³*Department of Civil and Environmental Engineering, University of Connecticut, Storrs, CT, United States*

There has been a growing interest in using nanoparticles as drug carriers, especially for cancer treatment [1]. However, little is known about the rheology of nanoparticles in blood flow, which must be understood if the nanoparticles are to be administered intravenously. Modeling studies [2, 3] showed that nanoparticles can undergo a "margination" phenomenon wherein the nanoparticles trend toward the periphery of blood vessels. The implication is a higher chance for the nanoparticles to diffuse into the tumor through the leaky vasculature typically found near tumor sites. Experimentally, most existing studies use particle adhesion to channel walls during flow as a mechanism for quantifying the margination propensity of particles but adhesion is also affected by other factors, further complicating the interpretations of experimental results [4]. In this presentation, we will disclose our latest findings on directly tracking the motion and distribution of nanoparticles within microfluidic devices that mimic blood vessel bifurcations. To unravel the fundamentals of margination, particles of different sizes and shapes have been studied in both water and bovine blood. This work is supported by NSF EAGER award #1250661.

[1] Davis, ME. Fighting cancer with nanoparticle medicines - The nanoscale matters. *MRS Bulletin*. 2012;37:828-835. [2] Decuzzi P, Lee S, Bushan B, Ferrari M. A theoretical model for the margination of particles within blood vessels. *Annals Biomed. Eng.* 2005;33(2):179-190. [3] Kumar A, Graham MD. Margination and segregation in confined flows of blood and other multicomponent suspensions. *Soft Matter*.

2012;8(41):10536-48. [4] Carboni E, Tschudi K, Nam J, Liu X, Ma AWK. Particle margination and its implications on intravenous anticancer drug delivery. *AAPS PharmSciTech*. 2014;Online First.

Wednesday 11:15 Commonwealth B

BB34

A multiscale Adhesive Dynamics model to study the interaction of nonspherical neutrophils with the endothelium

Anne D. Rocheleau¹, Ronen Sumagin², and Michael R. King¹

¹*Biomedical Engineering, Cornell University, Ithaca, NY 14853, United States;* ²*Pathology and Laboratory Medicine, Emory University, Atlanta, GA 30322, United States*

During inflammation, circulating neutrophils roll on the endothelium lining blood vessels. This process, mediated by PSGL-1 on neutrophils and P-selectin on endothelial cells, allows neutrophils to exit the bloodstream into the surrounding tissue to target pathogens. Neutrophils extrude pseudopods during this cascade, but the behavior of this unique nonspherical geometry has not yet been examined. A three-dimensional computational model called Multiparticle Adhesive Dynamics (MAD) was used to simulate the hydrodynamics and P-selectin/PSGL-1 binding kinetics involved in nonspherical neutrophil rolling. MAD is based on the Completed Double Layer Boundary Integral Equation Method (CDL-BIEM) used to solve the integral representation of the Stokes equation in shear flow. MAD produces realistic cell rolling and collision behavior as well as bond formation and breakage kinetics and has been adapted for neutrophils, tumor cells, and platelets. For this study, a Gaussian-shaped pseudopod was added to a spherical cell, and the surface was meshed with QUAD9 elements. A range of physiological shear rates, bond formation rates, receptor densities, and initial positions were examined. Time-dependent model outputs included: translational and rotational position; cell contact area and time; and individual bond formation and breakage events. In contrast to the transient endothelial contact exhibited in the hydrodynamic model, the neutrophil's translation in the flow direction is slowed due to P-selectin/PSGL-1 binding in the MAD model, leading to neutrophil tethering. This behavior was consistent with in vivo data of murine neutrophils with pseudopods in the bloodstream. Tethering was conserved across a range of shear rates and was resistant to receptor count changes. A range of initial orientations were tested, and simulations in which tethering events occurred had the greatest contact on the side of the neutrophil pseudopod. This insight may lead to strategies to downregulate the adhesion cascade in the context of disease.

Wednesday 11:40 Commonwealth B

BB35

Impact of blood rheology and hemodynamics on the adhesive landscape of functionalized nanocarriers to the blood vessel wall

Hsiu-Yu Yu, Helena Vitoshkin, David M. Eckmann, Portonovo S. Ayyaswamy, and Ravi Radhakrishnan

University of Pennsylvania, Philadelphia, PA 19104, United States

In intravascular functionalized-nanoparticle-based targeted drug delivery, the interplay between the hemodynamics and the receptor-ligand interactions plays an important role in affecting the binding of such nanocarriers (NCs) to the endothelial cells. Owing to the wide spectrum of time and length scales involved in this dynamical process, a unified theoretical framework bridging the microscale many-body hydrodynamic interactions among the red blood cells (RBCs) and NCs, and the nanoscale adhesive dynamics for NC binding, would provide useful insight into the tailored design of functionalized NC for specific targeted biophysical environments. To this end, we present a coarse-grained theoretical model for studying NC-cell adhesive dynamics in the presence of RBCs using a combined framework of generalized Langevin equations (GLEs) and dynamical density-functional theory (DDFT). The polystyrene-based functionalized nanoparticle is modeled as a hard sphere with surface-tethered ligands that interact with the receptors on the endothelial cells. At the microscale within the vessel tube, through DDFT with rigorous formulation and minimization of the RBC free energy functional under flow, we obtain the spatial RBC distribution and RBC-driven marginating potential for a given flow rate and vessel diameter. At the nanoscale close to the cell surface on the vessel wall, to investigate the process of NC-cell adhesion, we simultaneously solve a set of non-Markovian GLEs for NC motion and ligand-receptor pair relaxation in the presence of marginating potential, glycocalyx resistance, particle-wall hydrodynamic interactions, and thermal fluctuations. We analyze the velocity and position autocorrelation functions along suitable coordinates, and the predicted correlation functions for NC motion are verified by finite-element direct numerical simulations of Navier-Stokes fluid around a moving nanoparticle at different separations from the vessel wall. We acknowledge support from NIH through grant NIH 1R01EB006818-05.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Wednesday 10:00 Commonwealth C

SM31

Simple desktop calculations for slip-link predictions of entangled polymers

Maria Katzarova¹, Ling Yang¹, Marat Andreev², and Jay D. Schieber¹

¹*Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL, United States;* ²*Physics, Illinois Institute of Technology, Chicago, IL 60616, United States*

The discrete slip-link model (DSM) is a robust mesoscopic theory that has great success predicting the rheology of flexible entangled polymer liquids and gels. With just three parameters--the molecular weight of a Kuhn step M_K ; entanglement activity; and Kuhn step friction--the DSM is

able to predict simultaneously both nonlinear rheology and the linear viscoelasticity of monodisperse linear, polydisperse linear, branched, and cross-linked systems. Recently, we have proposed a hierarchy of slip-link models connected through successive coarse graining. Since the hierarchy is integrated, knowledge gleaned from a more-detailed level of description can inform a less-detailed one, or vice versa. In the most coarse-grained version of the DSM we exploit heavily the universality observed in the shape of the relaxation modulus of linear, monodisperse, entangled polymers. Furthermore, we present analytic expressions for the relaxation modulus of linear monodisperse melts. The glassy mode dynamics which are coarse-grained out from the DSM are added back into these expressions by using a Rouse chain with fixed ends to represent the fast motion of Kuhn steps between entanglements. We test these expressions against experimental data for a number of chemistries and molecular weights with good agreement. Using these analytic expressions, the polymer density, M_K , and the low-frequency cross-over between G' and G'' , it is now very easy to estimate parameter values and obtain predictions over the experimentally accessible frequency range without performing numerical calculations. Additionally, the more coarse-grained version of the DSM has allowed a significant speed-up of the numerical calculations. For instance, a typical shear-flow experiment of say, polyisoprene with 30 entanglements, can now be calculated in seconds using a single graphics card on a desktop. Simultaneously, we have developed a graphical user interface to facilitate running simulations.

Wednesday 10:25 Commonwealth C

SM32

Molecular scale simulations of rheological behavior – Importance of polydispersity

Nichoals A. Rorrer and John R. Dorgan

Colorado School of Mines, Golden, CO 80401, United States

Polydispersity plays an important role in polymer physics influencing both processing approaches and final properties. Despite the obvious physical importance of polydispersity, studies usually simulate monodisperse chains or occasionally, a few different chain lengths. This work explores the consequences of polydispersity on dynamics and rheology. Polymer melts are simulated under static conditions, in confined geometries, under shear flow, and undergoing parabolic flow. Monodisperse and polydisperse melts demonstrate a transition from Rouse to Reptation dynamics based on chain length; however, the polydisperse melts possess lower characteristic times and a broader transition between the dynamic scaling regimes. Polymer melts possessing the same length average chain length (analogous to weight average molecular weight) exhibit the same zero shear viscosity regardless of their polydispersity index (PDI). As the PDI is increased the transition from the zero shear viscosity regime to the shear thinning region becomes broader. Depending on the distribution that is mapped into the simulation, there can be an emergence of an infinite shear viscosity, that is an upper Newtonian plateau. Under confinement it is again found that all melts demonstrate the same zero shear viscosity. However, the critical shear rate for shear thinning is decreased. For quiescent conditions at plate spacings above six radii of gyration, there is a slight preference of shorter chains at the wall. However, when the melts are subject to extreme degrees of confinement, migration behavior is present with the shortest chains being preferentially present at the walls. For shear flow, no enhanced migration is evident whereas for parabolic flow this excess of shorter chains becomes exacerbated. Results are in post facto agreement with many experiments and help explain important processing effects including die drool. The present study illuminates the need for including polydispersity in realistic simulations of polymer flows.

Wednesday 10:50 Commonwealth C

SM33

Dynamics of individual molecules in entangled polymeric melts under homogenous shear flow: An atomistic simulation study

Mohammad Hadi Nafar Sefiddashti, Brian J. Edwards, and Bamin Khomami

Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, United States

Nonequilibrium molecular dynamics (NEMD) simulations of an entangled $C_{700}H_{1402}$ linear polyethylene system containing 276 chains (corresponding to 193200 particles) were performed to investigate the chain dynamics over a wide range of Weissenberg numbers (Wi) under steady shearing flow. The simulations allow for a detailed examination of the effects of individual chain dynamics on many fluid properties, such as the rheological characteristic functions, chain configuration and orientation, topology, and multiple timescales, all as functions of Wi . A key finding is that the probability distribution function of the end-to-end vector, $|\mathbf{R}_{ete}|$, at high Wi is bimodal, as was the case for the unentangled ($C_{78}H_{158}$) and moderately entangled ($C_{400}H_{802}$) melts examined in prior simulation studies. The low $|\mathbf{R}_{ete}|$ peak is associated once again with the dynamical rotation/retraction cycles experienced by individual chains, and the high $|\mathbf{R}_{ete}|$ peak corresponds to the highly stretched and oriented macromolecules. To understand the underlying physics of the aforementioned phenomena, the relevant system timescales were determined. Specifically, the autocorrelation function of the unit end-to-end vector showed a periodic behavior at high Wi which was associated with the onset of "vorticity excursion" of individual chains within a background of highly stretched chains. The disengagement (τ_d) and rotational (τ_{rot}) relaxation times of the system were extracted by fitting a functional form of $A \exp(-t/\tau_d) \cos(2\pi t/\tau_{rot})$ to the autocorrelation function data. The number of entanglements and other topological features of the liquids were also computed as functions of Wi , and examined with regard to reptation and anisotropic diffusion theory. The key implications of these simulations with regard to the current state of rheological theory will also be discussed.

Wednesday 11:15 Commonwealth C

SM34

Simulation of dilute solutions of flexible polyelectrolyte chains: Equilibrium properties and force-extension behaviour

Mahdy Malekzadeh Moghani and Bamin Khomami

Chemical and Biomolecular Engineering Department, The University of Tennessee, Knoxville, TN, United States

Macromolecules with ionizable groups are ubiquitous in biological systems. Due to the complex interaction between the chain decorrelation length and the electrostatic decorrelation length, both equilibrium properties and micro-mechanical response of polyelectrolyte (PE) dilute solutions are

vastly different than neutral chains. In this research, extensive hi-fidelity Brownian Dynamics (BD) simulations utilizing the bead-rod description of polyelectrolytes is conducted in order to explore their universal equilibrium behavior, as well as the scaling of the Kuhn step length (l_{ES}) with salt concentration c_s and their force-extension behavior. Results obtained based on this model, indicate that $l_{ES} \sim c_s^{-0.5}$. This is in agreement with the previous theoretical predictions and accurately predicts the initial non-linear region of the force-extension of PEs recently examined via single chain experiments. Moreover, a series of force laws for various charge densities were developed via a new numerical scheme.

Wednesday 11:40 Commonwealth C

SM35

Hi-fidelity Brownian dynamics simulation of non-equilibrium properties of macromolecules in good solvents: A bottom-up approach

Mahdy Malekzadeh Moghani and Bamin Khomami

Chemical and Biomolecular Engineering Department, The University of Tennessee, Knoxville, TN, United States

Recently through hi-fidelity Brownian Dynamics (BD) simulations of the bead-rod model of the polymeric chain, a new force law in form of a real function was developed which accurately represents force-extension behavior of a single macromolecule in good solvents. Here, both analytical and BD methods are employed in order to explore the effect of solvent quality on both equilibrium properties and dynamical behavior through this bottom-up approach. Results indicate that the new force law captures features such as higher shear-thinning at mid-range of Peclet number ($1 < Pe < 10$) in comparison with the FENE force law and decreasing the slope of the coil to stretch transition, which is absent in predictions of micromechanical bead-spring models constructed by inclusion of excluded volume interactions while retaining standard (ILC, FENE) entropic force laws for flexible macromolecules.

Symposium NF Non-Newtonian Fluid Mechanics and Stability

Organizers: Bamin Khomani and Sarah Hormozi

Wednesday 10:00 Washington A

NF16

Laminar-turbulent boundary and its implication for friction drag reduction in Newtonian and viscoelastic turbulent flows

Li Xi¹ and Michael D. Graham²

¹*Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S4L7, Canada;* ²*Chemical and Biological Engineering, University of Wisconsin, Madison, Madison, WI, United States*

Maximum drag reduction (MDR), the universal upper bound for polymer-induced turbulent drag reduction, has remained an unsolved problem despite decades of research. Recent advances revealed that dynamics at MDR are likely dominated by a class of weak turbulent states. These states exist in both Newtonian and viscoelastic turbulence and polymer additives do not seem to alter their behaviors. The nature of these states however remains unknown. The current study takes an a priori approach and explores the domain of weak turbulence near the boundary separating laminar and turbulent states. Dynamical trajectories along this boundary can be numerically computed through a pair of direct numerical simulation (DNS) solutions that tightly pinch the boundary. Trajectories on this boundary converge to an asymptotic "edge state". Edge states are found for Newtonian and viscoelastic systems at a range of parameters. It is observed that viscoelasticity has a negligible effect on the statistics of these solutions. This confirms the existence of weak turbulent states that cannot be suppressed by polymer additives, explaining why polymer-induced drag reduction must be bounded by an upper limit. Dependence of these states on the Reynolds number (Re) is more complex: although at one low Re the mean velocity profiles correspond closely to experimental observations for polymer solutions in the MDR regime, at higher Re, these profiles are higher than that of MDR. The quantitative origin of MDR may lie in a domain between the edge state and the turbulent basin.

Wednesday 10:25 Washington A

NF17

The dynamics of burst and hibernation in Newtonian and viscoelastic turbulence

Sung-Ning Wang and Michael D. Graham

Chemical and Biological Engineering, University of Wisconsin, Madison, Madison, WI, United States

Introducing a small amount of long-chain polymers into flowing liquids leads to substantial reduction of friction drag. This phenomenon has been widely used in fluid transports such as the Alaska pipelines. However, the whole theoretical picture of the phenomenon is not fully-understood. One of the most promising approaches towards understanding this is the dynamical approach. Xi and Graham have shown that in both Newtonian and viscoelastic turbulence, there exists intervals exhibiting characteristics resembling the polymer solutions at the maximum drag reduction (MDR) regime, such as low friction drag and weak vortex motions. These low-drag intervals are called hibernating turbulence, while the rest are called active turbulence. In addition, it has been shown that at moderate Weissenberg numbers (Wi), viscoelasticity suppresses the active turbulent dynamics, while at high Wi, it stabilizes the dynamics of hibernating turbulence, allowing it to dominate in the MDR regime. Another well-known intermittent phenomenon in turbulent flows is the turbulent burst, which is associated with large enhancement of the energy dissipation rate (D). We determine the relation between the two intermittent events, turbulent burst and hibernation. In Newtonian and viscoelastic turbulence with small Wi, it is found that for most of events with increasing D, the duration (the length of time during $dD/dt > 0$) is short and the magnitude (the increase of D during $dD/dt < 0$) is small. The duration and magnitude are strongly correlated. There are occasional occurrences of a long and large increase of D, corresponding to the turbulent burst. It is shown that although a hibernating period does not necessarily lead to a turbulent burst,

these bursts occur *only* after hibernation. We propose that the turbulent burst is associated with the instability that drives the flow from hibernation back to the active states. High viscoelasticity suppresses this instability, allowing the hibernating turbulence to predominate the turbulent dynamics.

Wednesday 10:50 Washington A

NF18

Role of geometry on large mach number instabilities around confined cylinders

Xueda Shi and Gordon F. Christopher

Mechanical Engineering, Texas Tech University, Lubbock, TX 79409-1021, United States

Flow of viscoelastic fluids around a confined cylinder is a hallmark fluids problem because it resembles industrial processes and is easily simulated. This flow displays multiple regimes with elastic and inertio elastic instabilities that occur at critical Deborah or Reynolds numbers. Practical limitations have restricted the experimentally explored range of Deborah number; using microfluidic channels, these limitations have been overcome. We have recently shown the existence of 2 new instabilities that occur at high Deborah number; a downstream instability of temporally and spatially varying streamlines, which is a precursor to an upstream instability in which the upstream stagnation point separates from the cylinder, creating an upstream vortex that oscillates in a growth and collapse cycle.

We have expanded the known phase space of these instabilities by systematically characterizing the role of the cylinder aspect ratio (cylinder diameter vs. channel depth) and the blockage ratio (cylinder diameter vs. channel width) for symmetrically placed cylinders in microfluidic channels. Furthermore, we have extended the phase space to non-inertial regimes by altering the viscosity and elasticity of the low viscosity Boger solutions tested. We find these new instabilities can be understood by examining a phase space consisting of the Elasticity number and the viscoelastic Mach number, which indicate the onset of the downstream instability to occur at Mach number of ~ 1 and the onset of the upstream instability at a Mach number of ~ 10 , regardless of geometry or Elasticity number. These results indicate that the onset of the instabilities occurs due to a change of type phenomenon in the flow. Finally, we characterize flow patterns of both instabilities as functions of the Elasticity number and the viscoelastic Mach number.

Wednesday 11:15 Washington A

NF19

Models for viscoelastic fluids and their effects on flow instabilities

Yinglong Guo¹ and John L. Bassani²

¹*Applied Mathematics and Computational Science, University of Pennsylvania, Philadelphia, PA 19104, United States;*

²*Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States*

A new class of constitutive models for viscoelastic fluids are developed that extend classical models such as Oldroyd-B and FENE fluids, i.e. fluids containing elastic dumbbells that represent polymer molecules. In the current work, we consider included phases that themselves are viscoelastic. Constitutive equations are constructed utilizing results from representation theory for tensor-valued functions, while those equations can be motivated from simple mechanistic models of the inclusions. One key result, for example, leads to a polymer stress that not only depends explicitly on the configuration tensor but also on the rate of stretching through a bilinear function of those two tensors. Several basic problems are studied including simple shear and Poiseuille flows. We demonstrate that certain instabilities depend on the Weissenberg number but also significantly on the contributions to the polymer stress from the viscoelastic inclusions. Certain features of the predictions are consistent with both numerical simulations and experiments.

Wednesday 11:40 Washington A

NF20

Transient response of a soft glassy fluid in porous medium

Arijit Sarkar¹ and Donald L. Koch²

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Theoretical investigation is carried out to understand flow of Nano Organic Hybrid Materials whose response to time shearing flow is similar to soft glassy fluid elements. We chose porous medium, consisting of a random array of cylindrical posts in a channel, as a candid complex flow. Flow through porous medium can be described by combination of simple flows in different directions. We use 4-roll mill to demonstrate the effect of shear flow in different direction. We derive a simplified analytical model for flow of soft glassy fluid elements in fixed bed by including spatial strain derivatives by assuming a closure in configurational space. We show different regimes of relaxation in fixed bed and demonstrate a methodology to test closure. Simulations are carried out using Brownian dynamics with microstructure of polymers to describe a dilute dispersion of fluid elements. We present stresses in terms of 2nd moment of stretch of the soft-glassy fluid elements (made of dumbbells). We first test the model for shear and elongation and show the different regimes of rheological responses in a complex flow. We test the closure and show the limit to which the closure is applicable.

Symposium SF Self-assembly and Flow-induced Systems/Gels

Organizers: Eric Furst and Anne Grillet

Wednesday 10:00 Washington B

SF16

Rheological characterization of fracture-healing behavior displayed by a physically associating polymer gel subjected to shear deformation

Kendra A. Erk and Travis Thornell

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Alcohol-swollen polymer gels are used as model physically associating systems for rheometer-based gel fracture and healing experiments. The model gel is thermoreversible, composed of acrylic triblock copolymer dissolved in a midblock-selective solvent. At elevated temperatures, the copolymer is fully dissolved and the system behaves as a viscoelastic liquid with near Maxwellian relaxation. As the system is cooled, the copolymer self-assembles into a three-dimensional transient network composed of spherical endblock aggregates interconnected by flexible midblock bridges. The relaxation time increases dramatically as temperature is reduced, such that at room temperature the system behaves as a viscoelastic gel. During shear inception experiments at relatively high shear rates, the physical crosslinks within the gel's network structure are disrupted, and the gel displays a corresponding overshoot in the measured stress response due to cohesive fracture, which is confirmed by particle tracking flow visualization techniques. When the fractured gel is heated above a critical temperature (33-36C) and then cooled to room temperature, the physically crosslinked network is re-formed and the gel recovers its original elasticity. Interestingly, partial to full recovery of the fractured gel can also be achieved by room temperature aging at zero shear rate. This healing behavior at different aging times and temperatures can be quantified using rheometry by re-fracturing an aged gel after the desired aging time and comparing the original value of the stress overshoot peak with the post-aging overshoot value. By studying the fracture-healing response of this model gel system at different aging times and temperatures, the observed healing kinetics can be related with simple mathematical models to the gel's characteristic relaxation behavior and temperature sensitivity.

Wednesday 10:25 Washington B

SF17

Thin films of homopolymers and cylinder-forming diblock copolymers under shear

Arash Nikoubashman¹, Raleigh L. Davis¹, Brian T. Michal², Paul M. Chaikin³, Richard A. Register¹, and Athanassios Z.

Panagiotopoulos¹

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We studied ultrathin films of homopolymers (PS) and cylinder-forming diblock copolymers (PS-PHMA) under shear. We performed pad shearing experiments as well as particle-based computer simulations that correctly take into account hydrodynamic interactions and chain entanglements. Excellent quantitative agreement for static as well as dynamic properties in both the homopolymer and diblock copolymer cases was achieved. In particular, we found that the homopolymer thin films exhibit a distinct shear thinning behavior, which is strongly correlated with the disentanglement and shear alignment of the constituent polymer chains. For the PS-PHMA films, we show that shear can be used to induce long-range ordering to the spontaneously self-assembled microdomains, which is a necessary prerequisite for most templating applications, such as the fabrication of nanowire grids used in deep UV polarizers. Furthermore, we developed a model for predicting the onset of shear alignment based on equilibrium dynamics data, and found good agreement with our shear simulations. This work demonstrates how particle-based simulations can be used to faithfully simulate specific polymer melts, and that they allow for microscopic insight into these systems, which is essential for better understanding and tuning of the macroscopic film properties. Therefore, the method we developed holds promise for a faster and more cost-effective route for designing custom tailored materials.

Wednesday 10:50 Washington B

SF18

Interaction of nonionic block copolymer with poly(acrylic acid) and poly(ethylene oxide) in aqueous medium

Abhinav M. Pragasheeswaran and Shing B. Chen

Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore

Self-assembly of poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide) (PEO-PPOy-PEOx; commercially known as Pluronic®) triblock copolymers in aqueous solution has been of considerable interest in academics and in industries. In this work, the effects of non-ionic homopolymer PEO and weak polyelectrolyte poly(acrylic acid) (PAA) on the micellization and gelation behavior of Pluronic® F127 in aqueous solution are investigated. Focus is placed on how the medium pH, the concentration and molecular weight of homopolymers affect the critical micellization temperature (CMT), heat of micellization (ΔH), critical gelation temperature (CGT), gel strength (G') and thermoreversibility of F127. Both PAA and PEO were found to lower the CMT of F127 with the decrease proportional to the concentration and molecular weight of the homopolymers. ΔH was drastically reduced with addition of PAA, manifesting its hindering effect on the micelle formation. This effect, however, was not observed with PEO, indicating that PAA has stronger interaction with F127 than PEO. Both the homopolymers act against the gelation process of F127 as evidenced by increased CGT and decreased gel strength with increasing concentration of PEO or PAA. Disruption of structural

order along with the aforementioned hindering effect on micelles is thought to be the reason for the observed changes in the gelation behavior. Both the micellization and gelation processes are thermoreversible in F127/PEO/H₂O and F127/PAA/H₂O systems.

Wednesday 11:15 Washington B

SF19

Structural dynamics of surfactant solutions in planar extensional flow

Binbin Luo and Wesley Burghardt

Chemical & Biological Engineering, Northwestern University, Evanston, IL 60208, United States

We report in situ x-ray scattering investigation of the structure of aqueous surfactant solutions in planar extensional flow. Samples were studied in a cross-slot stagnation flow cell fed by a syringe pump using a highly collimated synchrotron x-ray beam that provides for spatially resolved measurements of fluid structure in the stagnation region of the flow. Prior attempts to use planar stagnation flows for either x-ray or neutron scattering employed low-aspect ratio flow geometries in which the kinematics are dominated by parasitic velocity gradients along the incident beam direction. In contrast, our cross-slot flow cell employs an aspect ratio of 5:1, providing a much more ideal two-dimensional extensional flow field in the stagnation region. This device has been used to study two different surfactant systems, one a wormlike micelle solution at high salt concentration which exhibits rheology similar to that of entangled polymers. Here the focus is on the degree of micelle orientation produced as a function of extension rate. We have also studied a system that forms lamellar ordering. In addition to induced alignment of the mesophase structure, it is also possible to interrogate flow-induced changes in lamellar d-spacing in this material.

Wednesday 11:40 Washington B

SF20

Study of diffusion effects in shear banding micellar solutions

Natalie Germann¹, Antony N. Beris², and L. Pamela Cook³

¹*Center of Life and Food Sciences, Technical University of Munich Weihenstephan, Freising 85354, Germany;* ²*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States;* ³*Department of Mathematical Sciences, University of Delaware, Newark, DE 19716, United States*

This theoretical modeling work follows in continuation to our modeling efforts on the shear banding behavior of wormlike micellar solutions. By employing an extension to the nonequilibrium treatment of chemical reaction kinetics for media with an internal structure, we described the dynamic breakage and recombination processes of the micelles (1). Standard Fickian and stress-induced diffusion was added in a thermodynamically consistent fashion (2). In this talk, we will address the influence of the various diffusion effects to the solution of the problem with typical results presented and limiting cases analyzed. Of particular emphasis will be the stress-induced diffusion as it does appear to affect the smoothness of the solution indicating it as a key parameter to spectral approximations. The connection to the physics will be made and typical applications where the diffusion effects are important will be discussed.

(1) N. Germann, L. P. Cook, and A. N. Beris. Nonequilibrium thermodynamic modeling of the structure and rheology of concentrated micellar solutions, *J. Non-Newt. Fluid Mech.*, (196):51-57, 2013. (2) N. Germann, L. P. Cook, and A. N. Beris. Investigation of the inhomogeneous shear flow of a wormlike micellar solution using a thermodynamically consistent model, *J. Non-Newt. Fluid Mech.*, (207):21-31, 2014.

Symposium EF Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant and Sascha Hilgenfeldt

Wednesday 10:00 Washington C

EF6

Drainage and stratification kinetics of foam films

Yiran Zhang, Subinuer Yilixiati, and Vivek Sharma

Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States

Baking bread, brewing cappuccino, pouring beer, washing dishes, shaving, shampooing, whipping eggs and blowing bubbles all involve creation of aqueous foam films. Typical foam films consist of two surfactant-laden surfaces that are ~ 5 nm - 10 micron apart. Sandwiched between these interfacial layers is a fluid that drains primarily under the influence of viscous and interfacial forces, including disjoining pressure. We experimentally elucidate the influence of these different driving forces and interactions on drainage kinetics of horizontal foam films using Scheludko-type cell with interferometry, imaging and color science. Interestingly, for certain low molecular weight surfactants, as well as colloids and polyelectrolyte-surfactant mixtures, a layered ordering of macromolecules, micelles or particles inside the foam films leads to a stepwise thinning phenomena called stratification. Thinner, darker domains spontaneously grow within foam films. Quantitative characterization of domain growth, and of step size in stepwise thinning, yield critical insights into the rheology and microstructure of the foam films and the strength and nature of interaction forces, including oscillatory structural forces. A better understanding of drainage and stratification kinetics of individual foams films, as influenced by the choice of compositions, will provide control over parameters that determine foams stability, lifetime and rheology (flow behavior). Ultimately, understanding hydrodynamics and thermodynamics of single foam films will enable design and creation of foams that drain more rapidly (are fragile and unstable) or more slowly (are stable and long lasting) as desired for applications like food and beverages, oil recovery, pharmaceuticals and cosmetics.

Wednesday 10:25 Washington C

EF7

The mechanics of low-density open-cell foams: Linear elasticity and quasi-static crushingAndrew M. Kraynik¹, Stavros Gaitanaros², and Stelios Kyriakides²¹*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91105, United States;*²*Aerospace Engineering and Engineering Mechanics, The University of Texas at Austin, Austin, TX 78712, United States*

Ordered structures, such as the Kelvin cell and Weaire-Phelan, are natural starting points for modeling low-density open-cell foams but they lack two key features of real materials: random cellular morphology and polydispersity. Finite element analysis is used to calculate Young's moduli of random polydisperse foams (with up to 1728 cells) based on three classes of structure: 1) Voronoi polyhedra from random packings of monodisperse spheres of varying density, 2) Laguerre polyhedra from dense packings of polydisperse spheres, and 3) soap froths produced by minimizing surface area with the Surface Evolver. The cell vertices are connected with straight beams of uniform Plateau-border cross section to model the network of struts in open-cell foams. The Young's moduli of the Voronoi foams are the highest and increase with polydispersity, while the Young's moduli of the more realistic structures based on soap froth geometry are the softest and relatively insensitive to polydispersity. All of the Young's moduli differ by less than a factor of two. The bulk moduli of all of the structures decrease with polydispersity. Essentially monodisperse soap-froth-based structures are used to investigate the crushing behavior of Al-alloy open-cell foams. The struts are modeled as shear-deformable beams with variable cross sections to match the shapes found in real foams; they are discretized with beam elements in LS-DYNA, and the Al-alloy is modeled as a finitely deforming elastic-plastic material. The quasi-static crushing response exhibits a relatively stiff linearly elastic regime that terminates into a load maximum, which is followed by an extended plateau during which localized cell crushing initiates and gradually spreads throughout the specimen. When most of the cells are crushed, the densified material, in which struts contact, stiffens again. Beam contact is an essential feature of the crushing simulation. The models reproduce all aspects of quasi-static crushing.

Wednesday 10:50 Washington C

EF8

Multiscale phenomena in liquid foam fractureSascha Hilgenfeldt¹, Peter S. Stewart², and Stephen H. Davis³¹*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* ²*School of Mathematics and Statistics, University of Glasgow, Glasgow G12 8QW, United Kingdom;* ³*Engineering Sciences and Applied Mathematics, Northwestern University, Evanston, IL 60208, United States*

The dynamics of a fracturing liquid foam is studied for the case of a single layer of foam bubbles between parallel plates (a quasi-two-dimensional foam). Developing a node-based model for the dynamical process of fracturing upon application of a pressure gradient (injection of air into the foam), we highlight the presence of important physical processes on a variety of length and time scales, serving as connections to many aspects of foam research in general. This includes the instability of thin films, the deformation of Plateau borders, and the translation of Plateau borders along the plates bounding the foam. We show that a multiscale model naturally emerges from the separation of time and length scales, and compare the results to experimental data. We investigate the rate dependence of the failure and the role of viscosity and surface rheology.

Wednesday 11:15 Washington C

EF9

Probing foam stability in porous media with micromodelsSibani Lisa Biswal*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Foam mobility control and novel oil displacement mechanisms were observed in a microfluidic device representing a porous media system with layered permeability. Foam was pre-generated via a flow-focusing microfluidic device and injected into an oil-wet, oil saturated 2-D PDMS microfluidic device. The device is designed with a central fracture flanked by high-permeability and low-permeability zones stratified in the direction of injection. A blended surfactant system was used to produce stable foam in the presence of oil. Oil saturation and pressure-drop across the microfluidic device were measured as a function of time and injected pore volume, indicating an increase in apparent viscosity for foam with an accompanying decrease in oil saturation. In contrast to control experiments, foam was shown to more effectively mobilize trapped oil by increasing the flow resistance in the fracture and high-permeability zones and by diverting surfactant solution into adjacent low-permeability zones. Foam was seen to separate into gas-rich and aqueous-rich phases depending on matrix permeability, suggesting that it is not appropriate to treat foam as a homogeneous dispersion of gas and liquid.

Wednesday 11:40 Washington C

EF10

Impact of rheological properties on the foaming behavior of linear and branched polylactideNaqi Najafi¹, Marie-Claude Heuzey¹, Pierre J. Carreau¹, Daniel Therriault², and Chul B. Park³¹*Chemical Engineering, École Polytechnique de Montréal, Montréal, Canada;* ²*Mechanical Engineering, Ecole Polytechnique de Montréal, Montréal, Canada;* ³*Mechanical and Industrial Engineering, University of Toronto, Toronto, Canada*

In this work, a chain extender (CE), Joncryl © ADR, was added to a polylactide (PLA) at two concentrations, 0.4 and 0.7 wt%, using two different strategies. The rheological properties and foamability of the neat PLA and PLA containing the CE were studied. The steady and transient rheological properties of the neat PLA and CE-treated PLAs revealed that the introduction of the CE profoundly affected the melt viscosity and elasticity. The linear viscoelastic properties of CE-enriched PLAs suggested that a long chain branching (LCB) structure was formed from the reaction with the CE. LCB-PLAs exhibited an increased viscosity, more shear sensitivity, upturning at high viscosity in Cole-Cole plots, and longer relaxation time in comparison with the linear PLA. The LCB structure was also found to affect the transient shear stress growth and

elongational flow behavior. A prominent overshoot was found in the transient shear response of the LCB-PLAs due to an increase of the entanglement density. The LCB-PLAs also exhibited a pronounced strain hardening, whereas no strain hardening was observed for the linear PLA. Batch foaming of the linear and LCB-PLAs was also examined at foaming temperatures of 130, 140, and 155 °C. In addition to the improvement of the cell integrity, the increased melt strength and elasticity, resulting from LCB, increased the void fraction by more than two times and the cell density by more than two orders of magnitude.

Wednesday Afternoon

Symposium SC Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Wednesday 1:30 Commonwealth A

SC36

Metastability and arrested phase separation in asymmetric mixtures of soft and hard colloids

Domenico Truzzolillo, John Marakis, and Dimitris Vlassopoulos

FORTH and University of Crete, Heraklion, Greece

Inspired by the hard colloid - linear polymer paradigm, where the depletion mechanism is responsible for the formation of gels and attractive glasses, we consider asymmetric mixtures of soft and hard spheres. We achieve an entropic mixture by taking advantage of the well-known tunable pair interaction potential of star polymers. The effective hard spheres are much smaller in size and their addition to soft-sphere glasses induces melting via depletion, and eventually leads to a re-entrant state. Aging is inherent in these metastable states and we investigate it over long periods of time. We provide rheological and complementary experimental information for supporting the assignment of the re-entrant regime to arrested phase separation. Finally, we compare against predictions from mode coupling theory discuss the role of softness. Work in collaboration with the groups of C. N. Likos (Vienna) and M. Gauthier (Waterloo).

Wednesday 1:55 Commonwealth A

SC37

Rheology of a bimodal suspension containing rigid and soft particles

Nina C. Shapley, Olanike Isijola, and Anik Chaturbedi

Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08854, United States

The steady shear rheology of a bimodal suspension of neutrally buoyant, noncolloidal spheres in a viscous, Newtonian liquid is investigated. The smaller particles are alginate gel microbeads, which are deformable and porous, and the larger particles are rigid PMMA spheres. Potential applications of such a system include composites processing and separation column packing. This work extends a previous study of the steady shear rheology of a concentrated bimodal suspension to cover a broader concentration range, including values of the total particle volume fraction below 0.5, and to examine various particle diameter ratios. Measurements are acquired in a parallel plate rheometer under shear rates ranging from 5 to 200 s⁻¹. We seek to identify the total and relative concentration ranges and size ratios over which enhanced shear thinning or non-monotonic viscosity curves are observed. Mapping the regions of contrasting rheology over a broader concentration and size range will provide further insight into the flow of bimodal suspensions containing both rigid and soft particles.

Wednesday 2:20 Commonwealth A

SC38

Effect of particle size dispersity on the rheology of depletion mixtures of polymers and bidispersed colloids

Rahul Pandey and Jacinta C. Conrad

Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States

We used confocal microscopy, particle-tracking, and bulk rheology to study the effects of varying particle size dispersity on the viscoelastic and structural properties of bidispersed colloid-polymer mixtures, which serve as simple models of attractive bidispersed suspensions. We synthesized slightly charged bidispersed poly(methylmethacrylate) spheres with particle size ratio $a_s/a_L \approx 0.43$ that were labeled with distinct fluorescent dyes and suspended them in an organic solvent mixture that nearly matched their index of refraction and density. To induce a controlled short-range interparticle depletion attraction, we added non-absorbing linear polystyrene (molecular weight $M_w = 281,700$ kDa) at a concentration of $c_p = 25$ mg/ml. We measured the bulk rheology, dynamics and structural properties of suspensions as a function of the ratio of volume fraction of large particles to total volume fraction (r) while holding constant the total volume fraction of particles ($\Phi_T \approx 0.15$). A suspension of only the small particles ($r = 0$) exhibited strong shear thinning; appreciable changes in the viscosity as a function of shear rate appeared only when r was increased above 0.87. This rheological change coincided with a structural change in the suspensions: samples with $r < 0.87$ contained a connected network whereas those with $r = 0.87$ contained disconnected clusters of large and small particles. Our results suggest that the viscoelastic properties of attractive bidispersed suspensions can be controllably tuned by varying the particle size dispersity. This result will enable the development of polydispersed suspensions with controlled rheology for a wide range of technological applications, including paints and coatings, lubricants, and drilling fluids.

Wednesday 2:45 Commonwealth A

SC39

Doping colloidal spheres with dimers: An additional handle on suspension rheology.Brian D. Leahy and Itai Cohen*Department of Physics, Cornell University, Ithaca, NY 14853, United States*

Colloidal suspensions of spherical particles have a rich rheology, exhibiting both significant shear thinning and shear thickening. Their multifaceted rheology has found implementations in areas ranging from designing better paints to creating flexible body armor. However, for hard spheres only the volume fraction and Peclet number can be tuned, limiting the range of designer rheologies. The advent of nonspherical colloidal particle synthesis promises to change this, but currently nonspherical particles are expensive and time-consuming to synthesize in large batches. In this presentation, we explore the effects of a small amount of nonspherical colloidal dimers on the rheology of a dense spherical colloidal suspension in the shear-thinning and shear-thickening Peclet regimes. Using a custom built confocal rheometer, we explore the possibility of cost-effectively tuning the rheology of a spherical colloid suspension by doping with a small amount of dimers. The doped suspension is imaged with simultaneous stress measurements under oscillatory shear at both small and large amplitudes and over a range of frequencies. In addition to the macroscopic sample rheology, we also examine how the dimer particles rotate in the suspension and align due to the applied shear.

Wednesday 3:10 Commonwealth A

SC40

Dynamics of cubic colloidsJohn R. Royer¹, George L. Burton¹, Daniel L. Blair², and Steven D. Hudson¹¹*Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States;* ²*Dept. of Physics and ISMSM, Georgetown University, Washington, DC, United States*

There have been significant advances in the synthesis of anisotropic particles, however little is known about how shape and directional interactions influence particle dynamics in a suspension. We address this issue by studying the bulk rheology and micro-scale particle dynamics in suspensions of hollow, silica cubic superballs. These colloidal superballs resemble cubes, but with rounded corners. They are particularly well-suited for studying the role of anisotropy since they are mono-disperse, readily dyed and index-matched for confocal imaging, and can be synthesized in bulk quantities. Using confocal microscopy to image dilute, quiescent suspensions, we find the long-time diffusion coefficient decreases with packing density as $D/D_0 \sim 1-3.1\phi$, differing from the standard hard-sphere slope of -2.1. Investigating the rheology of these superballs, we find that the intrinsic viscosity is close to the hard sphere value of 2.5, and consistent with recent numerical predictions by D. Audus and J. Douglas. This suggests that while these cubic superballs behave very similar to spheres at the single particle level, shape effects manifest themselves in the particle interactions. We further investigate these shape-effects using confocal-rheometry to characterize shear-induced diffusion in these cubic superballs. Using depletion, we also investigate the role of attractive, directional interactions, tuning the interaction strength by varying the depletant size and concentration.

Wednesday 4:00 Commonwealth A

SC41

Modelling capillary break-up of particulate suspensionsClaire McIlroy and Oliver G. Harlen*School of Mathematics, University of Leeds, Leeds, United Kingdom*

A diverse range of materials can be manipulated using inkjet technology, the most common being particulate suspensions. Most graphical inks contain solid pigment particles rather than dyes and in many non-graphical applications, such as printed electronics, the functional components of the ink are solid particles. However, there is relatively little known about particulate effects on the stability of jets. The presence of particles increases the bulk viscosity of a fluid. Thus, particles are expected to retard thinning and delay the time to breakup. However, experimental measurements suggest that once the filament thins to approximately five particle diameters, the thinning no longer follows the behaviour predicted by the bulk viscosity; thinning is 'accelerated' due to the effects of finite particle size. Our hypothesis is that accelerated thinning arises from variations in local particle density. As the filament thins, variations are amplified, leading ultimately to sections of the filament containing no particles at all. Sections of the filament that have a low particle density have a lower viscosity and can therefore thin more easily. To test this hypothesis, we have constructed a simple one-dimensional model in which the viscosity is determined from the local particle density, found by tracking individual particles within the suspension. Particles only contribute to the dynamics through the local viscosity, so the direct effects of hydrodynamic interactions between particles and the effect of the individual particles on the free surface are not included. Nevertheless, our model is able to reproduce the accelerated thinning found in experiments.

Wednesday 4:25 Commonwealth A

SC42

Colloidal aggregates formation and breakup under oscillatory flowMaxime Liard¹, Didier Lootens², Nicos Martys³, and Pascal Hebraud¹¹*DON, IPCMS, Strasbourg 67034, France;* ²*SIKA, Zurich CH-8048, Switzerland;* ³*NIST, Gaithersburg, MD 20899-8615, United States*

The kinetic build-up of aggregates in attractive colloidal suspensions under flow is studied. A concentrated colloidal suspension of silica particles in water, in the presence of divalent salt, is submitted to an oscillatory flow. The evolution of the response moduli is measured as a function of time. It is observed that the elastic modulus does not monotonously increase with time, but exhibits a maximum. When the amplitude of the oscillations is decreased, this maximum of elasticity is more pronounced and appears at longer times. A dynamical phase diagram, describing this maximum elasticity as a function of the shear amplitude and the suspension volume fraction, is reported. This phenomenon is attributed to the

competition between colloidal aggregates formation and breakup under flow. Experimental results are then compared to numerical simulations, allowing us to interpret the evolution of the system elasticity as a function of the suspension microstructure.

Wednesday 4:50 Commonwealth A

SC43

Structural origins and nonlinear mechanics during yielding of a heterogeneous colloidal gel

Juntae Kim¹, Dimitri Merger², Manfred Wilhelm², and Matthew Helgeson¹

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We investigate the yielding of a colloidal gel comprised of nanoscale oil droplets in water driven by thermo-reversible interdroplet attractions. The system forms a heterogeneous structure that is best described as a two phase system at the micron scale containing droplet-rich domains of fractal clusters and droplet-poor domains. By combining large amplitude oscillatory shear (LAOS) measurements with simultaneous ultra-small angle neutron scattering (rheo-USANS), we characterize both the nonlinear mechanical processes and strain-dependent microstructural changes through the yielding transition. We find that the material undergoes a broad yielding process in which the nonlinearity evolves over an order of magnitude in strain amplitude between the initial yield point and flow. By analyzing the intracycle response as a sequence of physical processes, we monitor several parameters throughout the nonlinear yielding process, including the residual elasticity, yield stress and recoverable strain of the network. Frequency-dependent measurements show significant rate-dependence of the yielding process, which is driven by poroelastic effects. Correlating these results with structural parameters extracted from rheo-USANS data reveals that the material passes through a "top-down" cascade of structural breakdown. First, the droplet-lean domains consolidate into large voids, which saturate near the initial yield point. Second, at higher amplitudes, cluster-cluster correlations become increasingly homogenous, suggesting a de-percolation of cluster-cluster bonds as the ultimate process determining the transition to flow. We note that all significant structural changes occur on the μm -scale, suggesting that large-scale rearrangements of thousands of particles, rather than the immediate rearrangement of particle-particle bonds, are responsible for the yielding behavior of heterogeneous colloidal gels.

Wednesday 5:15 Commonwealth A

SC44

Bond strength in colloidal depletion gels from direct measurement of thermal rupture force distributions

Kathryn A. Whitaker¹, Lilian C. Hsiao², Michael J. Solomon², and Eric M. Furst¹

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Stability and shelf life of colloidal depletion gels is industrially relevant for manufacturing materials such as paints, foods, pharmaceuticals, and personal care products. The rheology of gels, including their elastic modulus and yield stress, is a multi-scale function of colloidal interactions and microstructure. We recently formulated a new model depletion gel to directly measure and relate the particle interactions, gel structure, and macroscopic rheology in a single system. Predicting the macroscopic rheology of depletion gels has often relied on theoretical calculations to estimate the interactions. This new model system provides sufficient index of refraction contrast between the particles and the solvent to utilize optical trapping in order to directly measure the interparticle forces between pairs of particles in a dilute suspension. Fluorescent polyhydroxystearic acid (PHSA) stabilized polymethyl methacrylate (PMMA) particles were suspended in a solution of 37% by mass cyclohexane and 63% by mass cyclohexyl bromide (CHB). Non-adsorbing polystyrene depletant ($M_w = 900,000 \text{ g/mol}$, $c = 0-10 \text{ mg/mL}$, $c/c^* = 0.0-0.93$) was added to the solvent to induce an interparticle attraction. This talk focuses on the direct measurement of colloidal rupture forces that constitute the "bonds" between particles in a gel. Optical tweezers are used to bring a pair of particles into contact and subsequently pull them apart. Thermal rupture force distributions are calculated by averaging many approach and retraction bond rupturing cycles between pairs of particles [1]. The largest forces from each distribution agree well with the forces predicted by a combined DLVO and Asakura-Oosawa potential. Verification of the interparticle potential is a first step toward connecting the microscopic properties with some of the measurable bulk properties of the gels such as the modulus, stability, coarsening, and yield stress.

[1] Swan, J., Shindel, M. and Furst, E. M., Phys. Rev. Lett., 109, 198302 (2012).

Wednesday 5:40 Commonwealth A

SC45

Micromechanics and non-linear rheology of reversible colloidal gels

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We study via dynamic simulation the nonlinear rheological response of a weak colloidal gel during transient and steady shear flow and under gravitational forcing. The gel is formed from a dispersion of 750,000 Brownian spheres initially at 20% volume fraction that interact via a hard-sphere repulsion and short-range attraction (as generated by a polymer depletant, for example). The $O(kT)$ strength of attractions leads to formation of a bi-continuous, space-spanning network that exhibits elastic and viscous behaviors: the gel may sustain its weight under gravity, or may yield and flow when forced, but with a higher viscosity than its dispersed-particle counterpart. When flow is stopped, the gel network reforms and elastic behavior returns. Because the colloid-colloid bonds are reversible, the gel coarsens with age, both structurally and rheologically. A stress overshoot during startup of imposed shear is followed by oscillations in the stress whose amplitude and frequency depend on the strength of the flow, particle attractions, and gel age. These behaviors, along with delayed yield under shear stress and gravitational forcing are explored from a micro-mechanical perspective.

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Wednesday 1:30 Commonwealth B

BB36

Microrheology of therapeutic protein solutions

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A key challenge encountered in the current development of therapeutic protein solutions is the need to measure the rheology of the drug solutions and identify a stable, syringeable formulations in a large composition space. Commercially available techniques such as capillary viscometry and rotational rheometers are frequently used, but require large sample volumes, on the order of milliliters of fluids. This restricts the number of rheological measurements in the early development stage, as there are only small amounts of proteins typically available.

This talk will focus on characterizing the viscosity of protein therapeutics over a wide range of compositions with a minimal amount of material. Microrheology techniques are powerful methods to study scarce biomaterials¹, and we use multiple particle tracking (MPT) in combination with microfluidic stickers² to provide a high throughput sample processing platform for protein therapeutics. This work examines the microviscosity of three proprietary monoclonal antibody solutions at 10 sample compositions with temperatures ranging from 5 to 45°C. The protein solutions behave like Newtonian fluids over a frequency range of 0.05 to 50 s⁻¹, and no microstructures have developed. Viscosity-temperature dependence is discussed on the basis of modified Arrhenius formula.

¹K.M. Schultz & E.M. Furst., *Soft Matter* **8**, 2012. ²D. Bartolo et al., *Lab Chip* **8**, 2008

Wednesday 1:55 Commonwealth B

BB37

A microfluidic imaging method to study red blood cell membrane viscoelasticity

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Red blood cells (RBCs) possess the unique capacity of undergoing cellular deformation during their flow in human microcirculation. RBCs deformability, mainly due to the viscoelastic properties of the cell membrane, enables the flow through capillaries smaller than cell size and to carry out the gas transport[1, 2]. Since an impaired RBC deformability is associated with various diseases, it could be used as an indicator of specific pathological conditions, providing a label-free biomarker for determining cell status and properties of clinical relevance. Here, we report on an imaging-based systematic microfluidic investigation of RBC suspensions flowing either in microcapillaries[3-6] or in a microcirculation-mimicking device containing a network of microchannels of diameter comparable to cell size[7]. RBC membrane rheological behavior is investigated by analyzing the transient behavior of single RBC shape[4] and by measuring the membrane viscoelastic properties in converging/diverging microchannels[7]. The comprehension of the single cell behavior led to the analysis of the RBC flow-induced clustering[6]. The main result is the development of a novel technique to estimate cell membrane viscoelastic properties, that can be used for the analysis of pathological RBCs.

[1] S. Guido and G. Tomaiuolo, *C. R. Physique*, 2009, 10, 751-763. [2] S. Shattil, B. Furie, H. Cohen, L. Silverstein, P. Glave and M. Strauss, *Hematology: Basic Principles and Practice*, Churchill Livingstone, Philadelphia, 2000. [3] G. Tomaiuolo, M. Simeone, V. Martinelli, B. Rotoli and S. Guido, *Soft Matter*, 2009, 5, 3736-3740. [4] G. Tomaiuolo and S. Guido, *Microvasc Res*, 2011, 82, 35-41. [5] G. Tomaiuolo, D. Rossi, S. Caserta, M. Cesarelli and S. Guido, *Cytom Part A*, 2012, 81. [6] G. Tomaiuolo, L. Lanotte, G. Ghigliotti, C. Misbah and S. Guido, *Phys Fluids*, 2012, 24, 051903-051908. [7] G. Tomaiuolo, M. Barra, V. Preziosi, A. Cassinese, B. Rotoli and S. Guido, *Lab Chip*, 2011, 11, 449-454.

Wednesday 2:20 Commonwealth B

BB38

Novel stochastic method using constraints for modeling of blood rheology

Kyung Hyo Kim and Lewis E. Wedgewood

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

Blood is often treated as continuum fluid or an empirical constitutive equation is used to study a blood flow. However, it would be impossible to observe neither the deformation nor the elasticity of the cell. We introduce a novel Brownian Dynamic simulation technique with constraint method to predict the movement of biological cells. This method is based on kinetic theory where the stress tensor and the stochastic differential equation (SDE) of motion depend on the configuration of the microstructure of the fluid. The constraints using Lagrange multiplier method describes the effect of the biological cell conserving its overall size throughout the motion of flow while allowing the shape to deform. Blood is considered as suspension of deformable red blood cells (RBCs) in a dilute solution of Newtonian fluid. A discrete model of bead-spring RBC is constructed with linear Hookean spring to give flexibility to deform. To demonstrate the capability of the method, the minimalist bead-spring model to represent the RBC was simulated. In this study, geometrical holonomic constraints were set to be total surface area and volume. The model is tested under shear and shear free flow. An assumption was made that the friction tensor is isotropic. The rheological material properties

are obtained through simulation. Due to the elimination of degree of freedom, the model does not have flexibility to change its shape compared with previous study. We conclude that the proposed framework is foundation to simulate further extended model of the blood flow or study rheology of biological cells.

Wednesday 2:45 Commonwealth B

BB39

Modeling of human blood rheology in transient shear flows

Alex J. Apostolidis, Matthew J. Armstrong, and Antony N. Beris

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This investigation is a continuation of our efforts to model blood flow rheology from steady-state [1] to time-dependent. The basis is a structural parameter thixotropic model. A modified version of the "Delaware model" [2] is used so that, at steady state, it reduces to the Casson constitutive model for low and moderate shear rates, consistent to [1]. Interestingly, at higher shear rates the model asymptotes to a Newtonian behavior, consistent to some earlier, previously unexplained, data by Merrill and Pelletier [3]. Exploiting the parameterization developed for the steady state Casson model [1], the transient thixotropic model introduces only four additional parameters, all with a specific physical meaning: two maximum strain values, representing the behavior at zero and at infinite shear rates, respectively, and two kinematic parameters, governing the relaxation of the structural parameter and the elastic modulus. The model is validated against a number of time-dependent shear flow data due to: a) a rectangular step increase [4], b) a triangular step change (hysteresis curves) [5], and c) LAOS [6]. This extensive comparison shows the capability of our model to capture well at least the low and modest shear rates behavior.

[1] Apostolidis, A. J., and A. N. Beris, *J. Rheol.* 58, 607-633 (2014). [2] Mujumdar, A., A. N. Beris, and A. B. Metzner, *J. Non-Newtonian Fluid Mech.* 102, 157-178 (2002). [3] Merrill, E. W., and G. A. Pelletier, *J. of Applied Physiology* 23, 178-& (1967). [4] Bureau, M., J. C. Healy, D. Bourgoïn, and M. Joly, *Biorheology* 17, 191-203 (1980). [5] Bureau, M., J. C. Healy, D. Bourgoïn, and M. Joly, *Rheol. Acta* 18, 756-768 (1979). [6] Sousa, P. C., J. Carneiro, R. Vaz, A. Cerejo, F. T. Pinho, M. A. Alves, and M. S. N. Oliveira, *Biorheology* 50, 269-282 (2013).

Wednesday 3:10 Commonwealth B

BB40

Large amplitude oscillatory shear of model synovial fluids

Zhenhuan Zhang and Gordon F. Christopher

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Synovial fluid is a viscoelastic solution which is the main lubricant in diarthrodial joints. It is primarily composed of the polysaccharide hyaluronic acid and proteins including albumin, globulin, and lubricin. The rheology of synovial fluid has been widely studied due to its relevance to the health and wear of human joints. Most studies have focused on its viscosity, friction coefficient, or linear viscoelastic moduli. However, human joint motion is typically large oscillatory deflections; therefore, synovial fluid's lubricating abilities would be better evaluated based on its non-linear viscoelastic properties. In order to better understand the material properties relevant to human motion, we have characterized a model synovial fluid's non-linear response using large amplitude oscillatory shear (LAOS).

Compared to small amplitude oscillatory shear, there is not a unified methodology to analyze LAOS results. Commonly used analysis techniques include Fourier transform rheology or stress decomposition, which may not accurately reflect a materials instantaneous non-linear response. We have analyzed LAOS results of model synovial fluids using the sequences of physical process method, which provides instantaneous non-linear storage and loss moduli as a function of time during oscillation. Experiments are designed to simulate ideal human knee movements, resulting in non-linear moduli representative of synovial fluid's actual response during motion. We find that during oscillation, non-linear moduli exhibit time dependent stiffening/thickening, which may impact its biological function. Results between model synovial fluids and pure hyaluronic acid solutions are compared in order to observe any dependence of non-linear rheology on the interaction of components in synovial fluid. Results explore the non-linear rheological properties of synovial fluid and may provide guidance for medical treatments of arthritis and design on human prostheses in the future.

Wednesday 4:00 Commonwealth B

BB41

Swimming dynamics of Escherichia coli in dilute polymer suspensions

Alison E. Koser and Paulo E. Arratia

Mechanical Engineering of Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States

The run-and-tumble dynamics of *E. coli* in Newtonian fluids has been extensively studied. However, outside the laboratory, *E. coli* is known to live in many complex media including biological fluids in the digestive system and soils. Here, we experimentally investigate the role of polymer concentration on the swimming dynamics of *E. coli* using particle tracking methods. We find that the addition of small amounts of polymer to water drastically changes the run-and-tumble behavior of *E. coli* cells, enhancing translation while hindering rotational diffusion. Here, the cells are suspended in dilute solutions of carboxy-methyl cellulose (CMC) and are imaged far from any surfaces. We find that the average velocity of the cells increases as the polymer concentration (and viscosity) increases; a similar result was found by Schneider and Doetsch [1]. But unlike previous results, we find that the addition of polymer molecules to the fluid leads to cell trajectories that are highly correlated in time; cells move in nearly straight lines and rotational diffusion is greatly reduced. Our experiments show that this combination of increased speed and suppressed reorientation dramatically changes overall cell dynamics in the presence of polymers.

[1] W.N. Schneider and R.N. Doetsch, *J. Bacteriol.* 117(2), 696-702 (1974).

Wednesday 4:25 Commonwealth B

BB42

Chemical surfing of active particles and connection to chemotaxis of slime mold coloniesHassan Masoud¹, Howard A. Stone², and Michael J. Shelley³¹*Courant Institute and Princeton University, New York, NY, United States*; ²*Princeton University, Princeton, NJ, United States*;³*Courant Institute, New York, NY, United States*

We study theoretically the motion of particles located at a liquid-gas interface. These particles release a chemical species that locally changes the surface tension. The consequent gradients in surface tension and the associated Marangoni flow then move the particles along the interface. We call this surfing. First, we consider the surfing of a single spheroidal particle at a semi-infinite interface and derive closed-form expressions for the self-induced surfing speed. Our derivations are based on the Lorentz reciprocal theorem which eliminates the need for developing the detailed flow field. Next, we probe the collective surfing of particles located at the interface of a finite-depth liquid layer. We calculate the linear stability condition of this system and examine the consequences of instability on the flow in the bulk. We also show that for sufficiently deep and shallow fluid layers this system yields the two-dimensional Keller-Segel model for the collective chemotaxis of slime mold colonies.

Wednesday 4:50 Commonwealth B

BB43

Swimming dynamics of microorganisms in viscoelastic fluids near a wallGaojin Li¹, Alireza Karimi¹, and Arezo Ardekani²¹*University of Notre Dame, Notre Dame, IN, United States*; ²*Mechanical Engineering, Purdue University, West Lafayette, IN, United States*

Microorganisms swimming in viscoelastic fluids are ubiquitous in nature; this includes biofilms grown on surfaces, *Helicobacter pylori* colonizing in the mucus layer covering the stomach and spermatozoa swimming through cervical mucus inside the mammalian female reproductive tract. Previous studies have focused on the locomotion of microorganisms in an unbounded viscoelastic fluid environment. However in many situations, microorganisms are interacting with a solid surface and their relevant hydrodynamic interaction is poorly understood. In this work, we numerically study the near-wall motion of a microorganism in a viscoelastic fluid. An archetypal low-Reynolds number swimmer, called "squirmers" is used to model the motile cell. The background viscoelastic fluid is modeled using a Giesekus constitutive equation to capture both viscoelasticity and shear-thinning effects observed in biological samples. We found that the fluid viscoelasticity and shear-thinning effects strongly affect the near-wall motion of a neutral squirmer and a pusher. However, a puller squirmer is less affected.

Wednesday 5:15 Commonwealth B

BB44

Swimming and transport in a hexatic liquid crystalThomas R. Powers¹, Madison S. Krieger¹, and Saverio E. Spagnolie²¹*School of Engineering, Brown University, Providence, RI 02912, United States*; ²*Department of Mathematics, University of Wisconsin-Madison, Madison, WI 53707, United States*

Recent experiments with bacteria in liquid crystalline solutions have revealed that nematic order affects the swimming behavior of bacteria. Motivated by these observations, we study a simple model of low-Reynolds-number swimming in an anisotropic fluid, that of an infinitely long two-dimensional sheet deforming via propagating transverse or longitudinal waves and immersed in a hexatic liquid crystal. The liquid crystal is categorized by the dimensionless Ericksen number Er , which compares viscous and elastic effects. Paying special attention to the anchoring strength at the interface of the liquid crystal and the swimmer, we calculate how swimming speed depends on Er for small amplitude waves. We also calculate the fluid transported by the swimming motion.

Wednesday 5:40 Commonwealth B

BB45

Undulatory swimming in shear-thinning fluidsDavid A. Gagnon, Nathan C. Keim, and Paulo E. Arratia*Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States*

The swimming behavior of micro-organisms can be strongly affected by the rheology of their fluidic environment. In this talk, we use tracking and velocimetry methods to investigate the swimming behavior of the nematode *Caenorhabditis elegans* (~1 mm length, 80 μ m diameter) in shear-thinning fluids. While no significant differences were found between the swimming kinematics (e.g. swimming speed) in shear-thinning fluids and in Newtonian fluids, we find substantial differences in the resulting flow fields. Velocimetry data show that shear-thinning viscosity enhances vorticity and increases circulation near the strongest body vortex, located near the head of the nematode. Furthermore, shear-thinning behavior increases the magnitude of fluid velocity near the nematode's tail. These findings are in good agreement with recent theoretical and numerical results.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Wednesday 1:30 Commonwealth C

SM36

The general low-frequency prediction for asymptotically-nonlinear material functions in oscillatory shear

N Ashwin Bharadwaj and Randy H. Ewoldt

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We use a fourth-order fluid expansion to make general predictions for asymptotically-nonlinear material functions in oscillatory shear, a characterization protocol sometimes known as MAOS (medium-amplitude oscillatory shear). The calculation applies to any viscoelastic fluid in the terminal regime, defined by the limit of Deborah number much less than one. Two viscous nonlinearities appear at third order, with shear stress scaling ω^3 , and are inter-related by a constant multiplicative factor. Two elastic nonlinearities appear at fourth order, with shear stress scaling ω^4 , and are also inter-related by a constant multiplicative factor. These nonlinear measures are decoupled from the linear material functions G' and G'' because they depend on different expansion coefficients. Experimental measurements are presented for all four asymptotic shear material functions using a linear and well-entangled homopolymer of polyisoprene. The experimental observations are consistent with both the predicted frequency scaling and the predicted interrelations in the terminal regime. Signs and magnitudes cannot be universally predicted, leaving these as free parameters that depend on the specifics of the material microstructure or constitutive model. These general results explain previous observations involving different materials and constitutive models, and provide an important reference for future experiments, analytical results, and numerical computations of these rheological fingerprints.

Wednesday 1:55 Commonwealth C

SM37

The QL-LAOS methodology applied to viscoelastic liquids

Alexandra A. Alicke, Maria Eduarda Pfeiffer, and Paulo R. de Souza Mendes

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Recently we proposed a novel approach for using large amplitude oscillatory shear flow experiments (LAOS) to determine---in a simple, direct and robust manner---the mechanical behavior of soft solids (de Souza Mendes et al., 2014). While at present all LAOS analyses focus on the structure-changing motions, our methodology---quasi-linear LAOS or QL-LAOS---relies for the most part on data obtained from constant-structure motions, which simplifies dramatically the experiments and the analysis, and provides material functions the physical meanings of which are quite evident. Here we present the results and conclusions of an investigation the goal of which was to verify the applicability of the QL-LAOS methodology to viscoelastic liquids also. To this end, we selected two viscoelastic systems, namely an aqueous solution of polyacrylamide and an aqueous solution of xanthan gum, and performed measurements at several different combinations of stress amplitude and frequency. The results demonstrate that the methodology is also suitable to viscoelastic liquids.

P. R. de Souza Mendes, R. L. Thompson, A. A. Alicke, and R. T. Leite, The quasilinear large-amplitude viscoelastic regime and its significance in the rheological characterization of soft matter, *J. Rheol.* 58(2) 537-561 (2014).

Wednesday 2:20 Commonwealth C

SM38

Normal stress differences in large-amplitude oscillatory shear flow for dilute rigid dumbbell suspensions

Andrew M. Schmalzer¹, R. Byron Bird², and A. Jeffrey Giacomin³

¹*Mechanical Engineering Dept. and Rheology Research Center, University of Wisconsin-Madison, Madison, WI 53706, United States;* ²*Chemical Engineering Dept. and Rheology Research Center, University of Wisconsin-Madison, madison, WI 53706, United States;* ³*Chemical Engineering, Queen's University, Kingston, Canada*

We examine the simplest relevant molecular model for large-amplitude oscillatory shear (LAOS) flow of a polymeric liquid: the suspension of rigid dumbbells in a Newtonian solvent. We find explicit analytical expressions for the shear rate amplitude and frequency dependences of the zeroth, second and fourth harmonics of the first and second normal stress difference responses. We include a detailed comparison of these predictions with the corresponding results for the simplest relevant continuum model: the corotational Maxwell model. We find that the responses of both models are qualitatively alike. The rigid dumbbell model relies entirely on the dumbbell orientation to explain the viscoelastic response of the polymeric liquid, including the higher harmonics in large-amplitude oscillatory shear flow. Our analysis employs the general method of Bird and Armstrong (1972) for analyzing the behavior of the rigid dumbbell model in any unsteady shear flow.

We derive the first three terms of the deviation of the orientational distribution function from the equilibrium state. Then, after getting the "paren functions," we use these for evaluating the normal stress differences for large amplitude oscillatory shear flow. We find the shapes of the first normal stress difference versus shear rate loops predicted to be reasonable. We find that the second normal stress difference is not proportional to the first, and that its shape differs markedly from that of the first. we discover the same remarkable qualitative similarity between the predictions of the rigid dumbbell model and the corotational Maxwell model for the first normal stress difference. We find no qualitative similarities between the dumbbell and the continuum models for any of the predictions coefficients of the second normal stress differences in large-amplitude oscillatory shear flow.

Wednesday 2:45 Commonwealth C

SM39

Quantifying the linear and non-linear rheology of sprayable complex liquidsBavand Keshavarz¹, Gareth H. McKinley¹, Eric C. Houze², John R. Moore², and Michael R. Koerner²¹*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, United States;*²*Axalta Coating Systems, Wilmington, DE 19803, United States*

Air-assisted atomization and spraying of complex liquids is a key process in many industrial applications as well as in physiological situations such as coughing and sneezing, but the effects of different rheological properties on these processes are poorly understood. Rheological properties measured in linear deformations or steady simple shear flow correlate poorly with the observed results of atomization. In order to better understand these issues a selection of canonical latex-based fluids that are widely used in commercial paint spraying operations were characterized in both the linear and non-linear regions. These complex fluids tend to exhibit power-law like characteristics in both small amplitude oscillatory shear (SAOS) and stress relaxation tests. A Fractional Maxwell Model (FMM) augmented with an appropriate nonlinear damping function can quantitatively predict this response in both linear and nonlinear deformation regions. However despite this accurate description of these model sprayable materials, the steady shear measurements and small amplitude oscillatory data do not provide much insight into understanding the observed differences in the atomization results. We show that the nonlinear intra-cycle coefficients obtained from large amplitude oscillatory shear (LAOS) tests can help us to understand these nonlinear phenomena in a better and more meaningful way. This new framework can connect the rheological fingerprints of a material that are obtained from a relatively straightforward test such as LAOS to widely-used industrial terminologies such as "stringiness" and "sprayability" that heuristically describe a given fluid's spraying performance.

Wednesday 3:10 Commonwealth C

SM40

The nonlinear rheology of multiscale complex fluids: Deriving empirical rules in rheology from fractional constitutive equationsAditya Jaishankar and Gareth H. McKinley*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, United States*

The relaxation processes of a wide variety of soft materials frequently contain one or more broad regions of power law-like relaxation in time and frequency. Fractional constitutive equations have been shown to be excellent models for capturing the linear viscoelastic behavior of such materials. However, these fractional constitutive models cannot describe the non-linear behavior of such power-law materials. We show how predictions of non-linear viscometric properties such as shear thinning in the viscosity and in the first normal stress coefficient can be quantitatively described in terms of a nonlinear fractional constitutive model. We adopt an integral K-BKZ framework and modify it for power law materials exhibiting Mittag-Leffler type relaxation dynamics at small strains. Only one additional parameter is needed to predict nonlinear rheology, which is introduced through an experimentally measured damping function. Empirical rules such as the Cox-Merz rule are frequently used to estimate the nonlinear response of complex fluids from linear response. We use the fractional model framework to assess the performance of such heuristic rules and quantify the systematic offsets that can be observed between experimental data and the predicted nonlinear response. We also demonstrate how an appropriate choice of fractional constitutive model and damping function results in a nonlinear viscoelastic constitutive model that predicts a flow curve identical to the elastic Herschel-Bulkley model. This new constitutive equation satisfies the Rutgers-Delaware rule that is appropriate for yielding materials. This K-BKZ framework can be used to generate canonical three-element mechanical models that provide nonlinear viscoelastic generalizations of other empirical inelastic models such as the Cross model. In addition to describing nonlinear viscometric responses, we are also able to provide accurate expressions for the linear viscoelastic behavior of materials that exhibit shear-thinning Cross-type or Carreau-type flow curve.

Wednesday 4:00 Commonwealth C

SM41

Model-based framework rheologyRoney L. Thompson¹, Alexandra A. Alicke², and Paulo R. de Souza Mendes²¹*Mechanical Engineering, Unversidade Federal Fluminense, Niterói, Rio de Janeiro 22776-070, Brazil;* ²*Mechanical**Engineering, PUC-Rio, Rio de Janeiro, RJ 22453-900, Brazil*

In the present work we show that most of the material functions available in the literature originate from some constitutive model, and demonstrate the importance of determining the model involved in the material function of interest and of evaluating its appropriateness with respect to the material under rheological characterization. We call this approach Model-Based Framework Rheology, (MBFR). This methodology provides a different interpretation of the material behavior by considering the material parameters of a chosen model as rheological functions of the material. In this sense, the detachment from a constant behavior of a parameter gives a measure of how far the material is from the chosen model from the perspective of this parameter. In particular, we demonstrate that the usual material functions that arise in the analyses of SAOStrain and LAOStrain experiments are directly related to the Kelvin-Voigt model, while the ones that appear in the analyses of SAOStress and LAOStress experiments are directly related to the Maxwell model. Finally, we show the advantages of moving a step further and use a Jeffreys-based framework for SAOS and LAOS data analyses of materials that exhibit transition from solid-like to liquid-like behavior, like gels. This is the simplest model that covers the full range of regimes experienced by this kind of materials, namely: elastic solid - viscoelastic solid - viscoelastic fluid - viscous fluid.

Wednesday 4:25 Commonwealth C SM42
Chain relaxation of polystyrene-block-ethylene-co-butene-1-block-polystyrene copolymer after applying LAOS in the presence of modified graphene

Amir Faramarzi Jolfaei, Jaber Nasrullah Gavvani, Fatemeh Goharpey, and Hosein Nazockdast

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The effect of amine modified graphene on the alignment and its recovery to the initial state of hexagonally packed cylindrical (HEX) microdomains of polystyrene-block-ethylene-co-butene-1-block-polystyrene (SEBS) copolymers was studied. By applying the large amplitude oscillatory shear (LAOS) in different frequencies, cylindrical microdomains aligns toward or perpendicular to the flow direction. Due to HEX cylinders near graphene platelet, which are not aligned parallel or perpendicular to the flow direction, the orientational factor of HEX cylinders in SEBS/graphene nanocomposites is smaller than that of neat SEBS. Chain relaxation that was probed by measuring linear viscoelastic measurements for different resting times after alignment, indicated that the recovery of the cylinders orientation in the nanocomposite sample was lower than that of the neat SEBS sample. Moreover for both samples, $G'_{\text{perpendicular}} > G'_{\text{random}} > G'_{\text{parallel}}$. This is because of the ability of the unentangled PS blocks to move along the direction of the cylinder axis, and thus relaxed the stress in the PEB matrix in the parallel alignment.

Wednesday 4:50 Commonwealth C SM43
Slip heating in die drool

Peter H. Gilbert and A. Jeffrey Giacomin

Chemical Engineering, Queen's University, Kingston, Canada

When molten plastic is extruded from a die, it can collect on the open die face. Called die drool, this phenomenon costs plastics manufacturers by requiring shutdown for die cleaning. This has been attributed to cohesive failure within the fluid at an internal surface, where the fluid slips on itself; the corresponding isothermal analysis led to an analytical solution for the drool rate [Schmalzer and Giacomin, *J. Polym. Eng.*, 33, 1 (2013)]. We account for the frictional heating at the cohesive slip interface, which we call slip heating. We focus on slit flow, which is used in film casting, sheet extrusion, curtain coating, and in many other unit operations. In slit flow, the magnitude of the heat flux from the slipping interface is the product of the shear stress and the slip speed. We present the solution for the temperature rise in pressure-driven slit flow subject to constant heat generation at the cohesive slip interface. We solve the energy equation in Cartesian coordinates for the temperature rise, for both the transient and steady temperature profiles, in both the drool layer and the bulk polymer. We then evaluate the effect of this temperature rise on the rate of die drool. For this simplest relevant non-isothermal problem, we neglect viscous dissipation and convective heat transfer in the melt and model viscosity as an Arrhenius function of temperature. We find that slip heating diminishes die drool and arrive at two sufficient dimensionless conditions for the accurate use of our results: $Br \ll 1$ or $Gi \ll 1$.

Wednesday 5:15 Commonwealth C SM44
Development of an algorithm determining continuous relaxation time spectrum

Jung-Eun Bae and Kwang Soo Cho

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It is important to determine relaxation time spectrum because it can be converted into various viscoelastic functions. However, it is known that extracting relaxation spectrum is an inverse problem which suffers from ill-posedness. Consequently, various methods have been suggested to find the most effective algorithm determining relaxation spectrum. In this study, new algorithm is developed based on the approximation of logarithmic relaxation spectrum on the double-logarithmic scale. The Chebyshev polynomial of the first kind and the Levenberg-Marquardt method are used to solve the inverse problem. New algorithm is applied to model spectrums and experimental data. It is found that the Chebyshev-Logarithmic algorithm (referred as C-L algorithm) gives non-negative and plausible relaxation spectrum. It provides the identical relaxation spectrum without regards to initial conditions. In order to improve the ability of algorithm, additional approaches are also considered.

Wednesday 5:40 Commonwealth C SM45
In-situ structural and thermo-rheological characterization of model thermoplastic polyurethane systems in shear and extensional flows

Joao Maia, Ricardo Andrade, Creusa Ferreira, and Jesse Gadley

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This study focuses on the in situ study of the polymerization kinetics and structural development at high temperatures of model thermoplastic polyurethanes (TPUs) of varying hard-to-soft segment ratios. TPUs are multi-block copolymers usually consisting of hard and soft segments. The hard segments, which are composed of diisocyanate and short-chain diols as chain extenders, are most often thermodynamically incompatible with soft segments that are made of polyethers or polyesters. Therefore, phase separation occurs with hard segments forming domains that consist in either glassy or semi-crystalline regions, which act as physical cross-links and provide stiffness and reinforcement. The reversibility of these regions enables melt processing of these materials at temperatures above the highest melting temperature of the domains. In order to gain some insight into this complex relationship between thermo-mechanical history and TPU structure, we study the thermo-rheological behavior of different model multi-block copolymer TPUs in shear and uniaxial extension, the former via simultaneous rheo-FTIR and the latter via uniaxial extensional rheometry. We then establish how this impacts polymerization kinetics and structural development at high temperatures. In what regards the latter, this study sheds new light on a previously unexplained structural transition observed when TPUs are annealed at temperatures in the vicinity of the hard block network dissociation temperature.

Symposium NF Non-Newtonian Fluid Mechanics and Stability

Organizers: Bamin Khomani and Sarah Hormozi

Wednesday 1:30 Washington A

NF21

Flow of thixotropic elasto-viscoplastic materials through a planar 1:4 sudden expansion

Fernanda Link¹, [Sergio L. Frey](#)¹, Monica F. Naccache², and Paulo R. de Souza Mendes²

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Finite element solutions are obtained for the steady inertialess flow of incompressible thixotropic elasto-viscoplastic materials through a planar sudden expansion. The goal of the study is to understand the role of thixotropy, elasticity and plasticity. A recently proposed constitutive model for this kind of materials is employed. It consists of a modified version of the Oldroyd-B model in which the viscosity, relaxation and retardation times are all functions of the structure parameter, a scalar field that gives the structuring level of the microstructure. It is governed by an evolution equation and varies within the range [0,1]. The constitutive and conservation equations are approximated by a Galerkin least-squares-type formulation in terms of the fields of structure parameter, extra-stress, pressure and velocity. In this method the proper amount of artificial diffusivity is added in the streamline direction to allow the use of equal-order combinations of Lagrangian finite element interpolations and also to approximate in a stable manner flows in which elasticity is important (high values of the Deborah number). Results are presented in terms of the effect of elasticity, plasticity and thixotropy on the fields of structure parameter and elastic deformation, and on the shape and size of the yielded and unyielded regions. The energy loss due to the expansion is also given as a function of these parameters.

Wednesday 1:55 Washington A

NF22

"Breakage" of non-Newtonian character in flows through porous medium: Evidence from NMR data and numerical simulations

Thibaud Chevalier¹, Stéphane Rodts², Jérémy Bleyer², Xavier Chateau², and [Philippe Coussot](#)²

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The flow of yield stress fluids through porous media is of interest for injection of muds, slurries or cement grouts to reinforce soils or structures, or in oil recovery processes. It was suggested that such flows exhibit two original trends: as the pressure drop increases a wider region of fluid starts to flow, an effect occurring at a local scale; at a macroscopic scale the flow starts only along a specific path throughout the porous medium [1-2] and as the pressure drop is increased more flowing paths progressively form within the porous medium. From measurements using a NMR technique (pulsed-gradient spin echo (PGSE)) not affected by spatial resolution problems, we show [3] that the velocity field of a yield stress fluid flowing through a disordered well-connected porous medium is very close to that for a Newtonian fluid. In particular it is shown that surprisingly no arrested regions exist at a local or a macroscopic scale even at very low velocities for which the solid regime is expected to be dominant. From numerical simulations of yield stress fluid flows through a model porous medium using a new numerical computation based on a variational approach we confirm this result, which by extrapolation suggests a general explanation: a fluid, whatever its complexity, flowing in a rapidly varying geometry tends to essentially undergo controlled deformations. With the help of energy dissipation considerations these results finally make it possible to deduce a generalized form of the Darcy's law for complex fluids, which provides an insight in the physical origin of the coefficients involved in the so far observed Darcy's law for non-Newtonian fluids.

[1] M.T. Balhoff, and K.E. Thompson, *AICHE J.* 50 (2004) 3034-3048. [2] M. Sahimi, *AICHE J.* 39 (1993) 369-386. [3] T. Chevalier et al., *Phys. Rev. E*, 89, 023002 (2014).

Wednesday 2:20 Washington A

NF23

Flow of a yield stress fluid in a self-affine fracture

[Thibaud Chevalier](#) and Laurent Talon

Laboratoire FAST, Université Paris-Sud, CNRS, Orsay, France

The flow of yield stress fluids through porous media is of interest in various applications such as oil recovery. Some original trends were recently pointed out: in glass bead packing, NMR experiments [1] shown that even at low velocities there is no arrested region in yield stress fluid. On the contrary, different flow regimes with dead zones at low velocities where point out from Lattice Boltzman simulations in stochastically reconstructed porous media.[2]. The heterogeneity of the medium seems to have an important role on the flow behavior. Some authors [3] focus on these aspects by looking at a wavy-walled channel: they link the geometrical gradient to the discrepancy between the lubrication approximation and the real flow with plug and fouling region. We present some numerical simulations based on Lattice Boltzman of yield stress fluid flowing through a self-affine aperture. It is a disorder porous medium often found in rock fractures. We show that despite the breakage of plug due to heterogeneities, the macroscopical flow curve, i.e. the pressure loss as a function of the flow rate, is not far from the lubrication theory relation [4]. Furthermore, inside the fracture, after each plug breakage, the flow recovers the lubrication regime. It suggests that even if the heterogeneities locally disturb the flow, thanks to that breakage it can adapt itself to the geometry. Indeed, by looking at the evolution of the plug distribution with

the flow rate, we show that it is directly related to the heterogeneities of the medium. They control the plug breakage inside the flow but despite that, it has a low impact on the macroscopical response of the flow.

[1] T. Chevalier et al., Phys. Rev. E, 89, 023002 (2014). [2] L. Talon et al., Eur. Phys. J. E. (2013) 36:139. [3] A. Putz et al. JNNFM 163 (2009) 62-77 - A. Roustaei and I.A. Frigaard JNNFM 198 (2013) 109-124. [4] L. Talon et al. (2014) Effective rheology of Bingham fluids in a rough channel. Front. Physics 2:24.

Wednesday 2:45 Washington A

NF24

Displacement of yield stress fluid in horizontal pipe

Gustavo L. Moises¹, Ian Frigaard², and Monica F. Naccache³

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Displacement of a yield stress fluid by another along a duct is a common flow in petroleum engineering applications (e.g. restart of gelled pipelines, cementing process). Two key features of these flows are: (i) difficulty to start the flow; (ii) only part of the fluid may be displaced. Whereas computational simulations of the displacement process generally show relatively structured displacement fronts, experimental studies are significantly more complex. Here we present an overview of our ongoing experimental work on displacing yield stress fluids in horizontal pipes. The experiments are conducted using Carbopol as the displaced fluid and Newtonian solutions as displacing fluids, focusing on iso-dense displacements. For higher Reynolds numbers (Re) of the displacing fluid, the front advances steadily along the center of the pipe, leaving behind a thin residual layer, with an uneven longitudinal variation. This regime is defined by the value of the ratio between the yield stress and a typical inertial stress of the advancing front: $Re/Bi < 1$, where Bi is the Bingham number. As inertial effects diminish we observe a transition to a regime in which the wall layers become progressively wavy. In this regime, the front velocity and the residual layer thickness are correlated, indicating a dynamic coupling of the frontal region in the formation process. To quantify this complex process in a manner that it can be used for industrial design, both computational simulation and simplified analytical modeling are also performed. Numerical simulations are being developed using the Fluent software (Ansys Inc). The conservation equations are solved via the finite volume technique, and the multiphase Volume of Fluid method. The numerical results show good agreement with the experimental ones. In addition, velocity, stress and strain-rate fields are obtained for several combinations of the governing parameters, in order to identify the mechanisms that lead to different flow patterns during the displacement.

Wednesday 3:10 Washington A

NF25

Pair-particle trajectories in Bingham shear flow

Hassan Fahs¹, Guillaume Ovarlez², and Xavier Chateau²

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Using numerical simulations we discuss the hydrodynamic interactions of two particles suspended in a Bingham fluid subjected to linear shear flow. The computations are based on the fictitious domain method with distributed Lagrange multipliers. Most of our simulations are for two equal radii cylinders in two dimensions but some examples are given for two spheres in three dimensions. Fluid and particle inertia are not taken into account ($Re=0$). Three different contact models (smooth particles, Glowinsky model and Cunha-Hinch model) have been implemented. We calculate the change between the initial and final streamlines caused by roughness as a function of the initial separation of the particles, the Bingham number and the roughness size. We put into evidence that Bingham number has a strong impact on the asymmetry of the trajectories: larger the Bingham number larger the net displacement across streamlines caused by a collision. We also show that Glowinsky and Cunha-Hinch roughness models have similar effect on the collision for well chosen Glowinski model's parameters. To conclude shear-induced microstructure in non-Brownian dilute suspensions of rough particles is computed which allows to determine the pair distribution function.

Wednesday 4:00 Washington A

NF26

Large amplitude oscillatory shear for a model of thixotropic yield stress fluids

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The PEC model of Larson exhibits thixotropic yield stress behavior in the limit of a large ratio of relaxation time to retardation time. We consider large amplitude oscillatory shear for this model. We analyze the dynamic behavior in the limit of large relaxation time. We identify regimes of fast, slow and yielded dynamics and use matched asymptotics to construct the overall dynamics as a combination of these regimes. The ratio of the period of the oscillation to time scales over which yielding and unyielding occur has a crucial influence on the qualitative dynamics.

Wednesday 4:25 Washington A

NF27

Non-Newtonian effects in a continuous squeeze flow film of a structured liquidEdtson E. Herrera-Valencia¹, Mayra L. Sanchez Villavicencio², Roberto Mendoza Serna¹, Eduardo Vazquez Zamora¹, and Raul R. Mora Hernandez³

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In this work, the viscoelastic behavior of a complex structural liquid in a continuous squeeze flow is analyzed. This flow is generated by allowing a continuous flow of liquid into the narrow gap between two circular plates through the lower plate. In order to characterize our complex liquid, the Boek-Pearson constitutive equation is used (BM). The BM model separates the stress contributions of the structured fluid and the solvent. The solvent is modeled as a purely Newtonian liquid, and the complex fluid is characterized with the upper convective Maxwell equation coupled with a kinetic equation that describes the changes of the structures due to the relaxation and kinetic mechanisms respectively. In order to solve the set of non-linear partial differential equation, a non-dimensional perturbation scheme is suggested in terms of a small parameter, which is the ratio between two characteristic length scales. To zero order in the perturbation parameter (neglecting the inertial mechanisms of the momentum equation), it is found that the normal force on the upper disc is directly related to structure of the fluid, which is a function of the Weissenberg number. The thixotropy, shear-thinning, shear thinning, yield stress and concentrations effects are analyzed through a group of characteristic dimensionless numbers associated to structural, kinetics and viscoelastic mechanisms respectively. To first order, the effects of the rupture and structural mechanism play an important role in the elasticity. The present theory, model and computations contribute to the evolving fundamental understanding of lubrication systems through rheology and flow systems.

Wednesday 4:50 Washington A

NF28

Finite element modeling of blood flow in the branched brachial bifurcation using non-Newtonian parameters obtained from rheological measurements of normal blood samples of variable hematocrit levelsRoy D. Wilcox*Chemistry and Physics, Lincoln Memorial University, Harrogate, TN 37752, United States*

Rheological parameters were obtained on approximately 30 normal blood samples with hematocrit levels varying from 32-50% using an Ares G-2 rheometer with a cone and plate configuration. The parameters were obtained using controlled shear stress measured shear rate and controlled shear rate measured shear stress experiments. Data was obtained over a broad range of shear rates and viscosity with the controlled stress measurements since once the yield stress was exceeded, shear rates rapidly increased to large values. The results show that blood viscosity can be modeled using the Bingham, Carreau, and Power Law Nonnewtonian constitutive equations to varying goodness of fit levels based on least square regression and chi square minimization. Specific Nonnewtonian model parameters were used in conjunction with appropriate boundary conditions for the branched brachial artery to conduct finite element modeling (FEM) of blood flow using commercial CFD software. The FEM study used a parametric sweep from maximum to minimum inlet blood velocities encountered over a pulse cycle and solving for pressures using the Navier Stokes governing equation and appropriate boundary conditions for inlet and outlet pressures. Studies were extended to include higher than normal inlet velocities that might be encountered in stress tests. Convergence of solutions was highly dependent on goodness of fit obtained from chi squared minimization of model data. Once solutions for pressure as a function of velocity were obtained, post processing of data provided values for dynamic viscosity, Reynolds number, and shear rate on the domain and pressures at the bifurcation. Additional data used in support of this investigation include Doppler velocimetry measurements of maximum velocity versus pulse time on numerous patients and velocity variation in the brachial artery from the upper to lower branch which is indicative of the velocity profile.

Wednesday 5:15 Washington A

NF29

Red blood cell aggregation investigation and characterization in a microfluidic deviceRym Mehri, Catherine Mavriplis, and Marianne Fenech*Mechanical Engineering, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada*

Red blood cells (RBC) are the most abundant cells in human blood, representing 40 to 45% of the blood volume. These cells have the particularity to deform and bridge together to form aggregates under very low shear rates. Due to their unique mechanical properties, RBC represent the focus of numerous experimental and numerical studies, especially, at the microscopic level. In fact, the theory and mechanics behind aggregation are not yet completely understood. Understanding the conditions of aggregate formation could provide a better understanding of the mechanics behind this phenomenon and could help to determine aggregate behaviour related to clinical application such as diabetes and heart disease. The purpose of this work is to develop a method to analyze quantitatively RBC aggregates in microcirculation under constant shear rates based on image processing. For this purpose, RBC suspensions are analyzed in 150x33 μm and 120x60 μm Polydimethylsiloxane (PDMS) microchannels. The RBC suspensions are entrained using a second fluid to obtain a linear velocity profile within the blood layer and thus achieve a wide range of constant shear rates. The shear rate is determined using a micro Particle Image Velocimetry (μPIV) system, while RBC aggregates are visualized using a high speed camera. The videos captured of the RBC aggregates are analyzed using a MATLAB program to determine the aggregate sizes based on the images intensities. Average aggregate sizes were found for a wide range of constant shear rates (between 1 and 10 s^{-1}). Using these results, the RBC are characterized in a simple geometry (straight rectangular microchannels) and in more complex geometries such as bifurcations, merging channels and more anatomically accurate vessels. These last microchannels are designed from arteries of the human retina and capillaries

of a cat mesentery pictures to be fabricated in PDMS. The results of the investigation can be used to help develop new numerical models for non-Newtonian blood flow.

Wednesday 5:40 Washington A

NF30

Design of an experimental setup for the study of the effect of swimming microbot's morphology on the complex fluid flows in microchannels

Sergio Martinez-Aranda, Francisco J. Galindo-Rosales, and Laura Campo-Deaño

Centro de Estudos de Fenómenos de Transporte, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal

Microbots have been developed for several purposes as in the case of industrial applications, planetary exploration or biomedicine [1]. The manufacturing of microbots for their use in biomedicine entails several aspects, such as the morphology, that can varies according to the function they have to perform; the biocompatibility with human fluids and conducts, and the power supplied for their movement. However, experimental studies related to the influence of the size and shape of these microbots in the flow dynamics of complex fluids are still an open and challenging issue demanding further investigations.

In this work, we design an experimental setup to study the optimization of the morphology of microbots in order to achieve a most effective motion when they swim through different conduits of the human body, taking into account the viscoelastic properties of the biofluids. For that end, four different geometries will be studied: a square, a sphere and two ellipsoids with different aspect ratio which will be placed in the middle of a straight microchannel by means of permanent magnets outside of the microchannel and subject to different flow rates conditions. This technique will ensure that the geometry is fixed at the desired position of the channel without any supporting material that could interfere in the flow dynamics. Numerical analyses based on magnetic fluid and fluid structure interaction were firstly performed in order to check the feasibility of the setup, therefore preliminary flow visualizations were carried out together with micro-PIV experiments using blood analogue solutions, as viscoelastic biofluids, previously developed by the group [2].

Authors would like to acknowledge financial support from FCT, COMPETE and FEDER through project EXPL/EMS-TRA/2306/2013 and grants IF/00148/2013 and IF/00190/2013.

[1] Ghanbari, A. et al Journal of Intelligent and Robotic Systems, 63 (2011), 399-416. [2] Campo-Deaño, L., et al. Biomicrofluidics, 7 (2013), 034102.

Symposium SG Solids and Glasses

Organizers: Tom Engels and Jim Caruthers

Wednesday 1:30 Washington B

SG1

Experiments needed for critical evaluation of constitutive models for glassy polymers

James Caruthers and Grigori Medvedev

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The mechanical response of glassy polymers exhibits a rich set of characteristic features in both linear and non-linear regimes, which is made even more complicated by a strong dependence on the thermal and deformational history. Capturing this diversity of nonlinear relaxation behavior is a significant challenge for constitutive modeling. Traditionally most experiments and associated modeling efforts are limited to a particular experiment - primarily the uniaxial constant strain rate deformations, where the goal is to describe yield and occasionally post-yield softening and subsequent strain hardening. The isotropic phenomena such as enthalpy and volume relaxation are typically omitted as well as anisotropic load controlled experiments such as creep and creep-recovery. Moreover, even in strain history controlled deformations multi-step experiments such as loading-unloading, stress relaxation, reloading, etc. are only rarely considered. As a result, many a sophisticated model in the literature tailored to describe a constant strain rate loading miss qualitative features of the nonlinear mechanical response under different conditions. The goal of this communication is to develop a set of critical experiments that any constitutive model for a glassy polymers should capture in order to be considered a viable candidate. The criterion for including a particular experiment into the data set is the ability to significantly challenge existing constitutive models. Experimental results will be presented for an epoxy system, and the data will be used to critically analyze the predictions of both traditional viscoelastic and viscoplastic constitutive models as well as a recently developed Stochastic Constitutive Model.

Wednesday 1:55 Washington B

SG2

Yielding, failure and strain hardening in uniaxial compression of polymer glasses

Panpan Lin¹, Jianning Liu², and Shi-Qing Wang²

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We investigate the mechanical behavior of such common polymer glasses as bisphenol A polycarbonate and polystyrene as well as their mixtures. The in situ thermal measurements have allowed us to delineate the nature of the stress in the strain hardening in the post-yield regime. At low temperatures, compression produces fracture at high compression ratios although the uniaxial compression is completely homogeneous at high temperatures. We will analyze our observations in the context of our recent molecular model [1] for yielding and failure of polymer glasses in large deformation.

[1] "A phenomenological molecular model for brittle-ductile transition and yielding of polymer glasses", S. Q. Wang, S. W. Cheng, P. P. Lin and X. X. Li, *J. Chem. Phys.*, to be published (2014).

Wednesday 2:20 Washington B

SG3

The age of polymer glasses: What is the effect of stress?

Tom Engels¹ and Leon Govaert²

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Although studied abundantly over the past half century, the aging of polymer glasses is far from understood, nor is the glass transition to which it is intimately connected for that matter. Aging is the struggle of a non-equilibrium glass to reach its equilibrium configuration, being hampered in this struggle by long relaxation times. It can be measured in various ways, eg. volumetric, enthalpic, but also by mechanical means where the increase in the yield stress with aging time and temperature is a well-known phenomenon. Next to temperature annealing, as a means to enhance the rate of aging, also stress annealing has been studied. Recent insights based on (coarse grained) molecular dynamics, however, question the existence of such a stress enhanced aging rate, and rather connect it to the orientation of the covalent polymer chain. In this presentation we show experimental results on mechanically rejuvenated polycarbonate, in both tension and compression, that clearly show that the increase in yield stress due to aging under load cannot be explained by an orientational effect and that under load the system shows an increased rate of aging. We'll also discuss some implications of this stress induced aging for practical applications of polymer glasses.

Wednesday 2:45 Washington B

SG4

Identifying structural flow defects in amorphous solids

Samuel S. Schoenholz¹, Ekin D. Cubuk², Jennifer Rieser¹, Brad D. Malone², Douglas J. Durian¹, Efthimios Kaxiras², and Andrea J. Liu¹

¹*Physics, University of Pennsylvania, Philadelphia, PA, United States;* ²*Physics, Harvard University, Cambridge, MA, United States*

Solids relax via localized rearrangements. In crystals these events are initiated at identifiable topological defects in the material. Consequently, the study of these defects has become the bedrock of modern theories of ordered solids. By analogy, successful phenomenological theories of amorphous solids are predicated on the existence of similar structurally meaningful regions known as shear transformation zones (STZ). While recent work has shown that echoes of structural defects in amorphous solids can be seen in low-frequency sound waves, they have never been directly observed. We show that "soft spot" can be identified in amorphous solids from local structure alone. To accomplish this we perform inference on many measures of a particle's neighborhood simultaneously using the method of support vector machines. We demonstrate the success of this technique on two disparate systems: a sheared, thermal, Lennard-Jones glass (in silica) and a two dimensional pillar composed of macroscopic disks under mechanical compression. We show that in the thermal glassy system, soft spots can be identified as regions of the system whose correlations are those of a higher temperature liquid.

Wednesday 3:10 Washington B

SG5

Various aspects of brittle and ductile behavior of different polymer glasses

Xiaoxiao Li and Shi-Qing Wang

University of Akron, Akron, OH 44325, United States

Although brittle-ductile transition (BDT) in polymer glasses has been studied extensively in the past, our understanding of the BDT is rather limited at a molecular level. Our recently proposed molecular model [1] for yielding and failure of polymer glasses in large deformation is the first of its kind, capable of rationalizing various aspects of the BDT. This work studies additional features associated with the BDT. Our experiments reveal remarkable differences between PMMA and other brittle glasses such as PS and SAN. For example, at the same temperature the more ductile PMMA shows brittle failure whereas PS and SAN are ductile at comparable rates of extension.

[1] "A phenomenological molecular model for brittle-ductile transition and yielding of polymer glasses", S. Q. Wang, S. W. Cheng, P. P. Lin and X. X. Li, *J. Chem. Phys.*, to be published (2014).

Wednesday 4:00 Washington B

SG6

Rheology of glass-forming polymers at the nanometer size-scale: Films and surfaces

Gregory B. McKenna, Heedong Yoon, Astrid K. Torres Arellano, and Meiyu Zhai

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

There is considerable discussion in the literature concerning the dynamics of glass-forming materials, especially polymers, at the nanometer size scale. Of particular interest is the wide-spread view that increases in the mobility, especially as seen in reduced glass transition temperatures T_g , occur due to enhanced surface dynamics. One way of addressing such a perspective is to perform rheological measurements both on ultrathin films and on the film surface itself. Here we describe work in which ultrathin films are examined using both a novel nanobubble inflation test and a liquid dewetting experiment. We further look at surface dynamics using a spontaneous particle embedment method. Examination of the results shows that while the thin films may show highly accelerated dynamics, their behaviors are surprisingly non-universal and, in some instances contrary to what is observed for the surface dynamics. Furthermore, the surface dynamics themselves do not exhibit typical glass-forming material

temperature dependence, suggesting that the surface either does not exhibit cooperative dynamics or it does not exhibit a glass transition at all. In either case, the surface then cannot readily be identified as the cause of observed reductions in T_g . We further remark that a great stiffening of the rubbery plateau in ultrathin films is observed and this may be consistent with observations that surface dynamics of polymers above the macroscopic glass transition seem to be slower than the macroscopic dynamics.

The authors thank the National Science Foundation under grants DMR-1207070 and CHE-1112416, the Office of Naval Research under project N00014-11-1-0424, and the John R. Bradford endowment at Texas Tech, each for partial support of this work.

Wednesday 4:25 Washington B

SG7

Effect of micro and nano particles on yielding, strain softening and strain hardening of PMMA

Josef Jancar¹ and Robert S. Hoy²

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Micro (MP) and nano (NP) particles were used as "probes" that alter local chain packing, the degree of correlated molecular motion and structural relaxation times in PMMA. We show that the extent of these alterations is proportional to the specific particle-PMMA interface area and the spatial distribution of interparticle distances. We focus on the effect of the test and structural variables as well as thermal history on two measures of the extent of strain softening, i.e., difference between the upper and lower yield stress and between the upper and rejuvenated yield stress. All 3 yield stresses increase with filler volume fraction, with the extent of the elevation increasing with T and always greater for NP compared to MP filled systems at identical filler content. The yield stresses exhibit different T and strain rate dependences resulting in qualitative differences between the strain softening response of systems deformed in temperature and strain rate domains. While the T and strain rate response of the difference between the upper and lower yield stress corresponded to regions I and II identified by van Breemen et. al.(1), the other stress difference response exhibited behavior corresponding to the regions I, II and III. We also illustrate key features of the relationship between the mechanically rejuvenated yield stress and strain hardening modulus (2). The observed trends are supported by kinetic analyses and exploited to test recently proposed models of plastic flow and strain hardening. Our results should lead to an improved understanding of the factors controlling the plastic deformation of polymer composites.

(1) van Breemen LCA, Engels TAP, Klompen ETJ, Senden DJA, Govaert LE, *J Polym Sci Polym Phys* (2012), 50, 1757. (2) Jancar J, Hoy RS, Lesser AJ, Jancarova E, Zidek J, *Macromolecules* (2013), 46, 9409.

Wednesday 4:50 Washington B

SG8

Stochastic constitutive model prediction of tertiary creep and recovery in glassy polymers

Grigori Medvedev and James Caruthers

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Traditionally the focus of the studies of the mechanical response of glassy polymers has been on the yielding behavior under constant strain rate loading, where numerous constitutive models have been proposed. However, these traditional viscoelastic and viscoplastic constitutive models often become grossly inadequate when applied to load controlled experimental conditions, namely non-linear creep and recovery from creep. Two features present a particular challenge: the tertiary stage of the creep and the recovery after a large deformation creep. The traditional models miss the acceleration of creep during the tertiary stage entirely. With respect to the nonlinear creep-recovery response, the traditional nonlinear viscoelastic/viscoplastic constitutive models where the relaxation time depends on the deformation history predict a very abrupt recovery response upon unloading as compared to a much smoother recovery observed experimentally. Representative examples of these two nonlinear responses will be shown for lightly cross-linked PMMA and an epoxy material, where the creep and recovery behavior has been studied as a function of temperature and aging time. A recently developed Stochastic Constitutive Model that acknowledges dynamic heterogeneity in the glass state naturally predicts both the tertiary creep and the smooth recovery from creep. The features of the Stochastic Model enabling the prediction will be highlighted.

Wednesday 5:15 Washington B

SG9

A molecular model for mechanics of polymer glasses

Shi-Qing Wang¹, Shiwang Cheng², Panpan Lin², and Xiaoxiao Li¹

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Polymer glasses differ from most other types of glassy materials because they can be ductile under tensile extension. Remarkably, a ductile polymer can turn brittle and vice versa. For example, upon cooling, the glass changes from ductile to brittle at a temperature known as the brittle-ductile transition temperature (BDT). Physical aging causes the ductile glass to be brittle. Mechanical "rejuvenation" or pressurization brings a brittle polymer into a ductile state. Finally, one glass can be ductile more than 200 degrees below T_g while another polymer is already brittle even just 10 degree below T_g . Polystyrene and bisphenol A polycarbonate are at the two extremes in the family of polymer glasses. How to rationally such a wide range of behavior in terms of a molecular picture has been a challenging task. This talk describes a newly developed molecular model that can provide a coherent framework to understand deformation, yielding and failure of polymer glasses under large deformation.

Wednesday 5:40 Washington B

SG10

Resolution of the local segmental mode in amorphous polymers: Do the chain relaxation modes affect the structural relaxation?Luigi Grassia*Dep. Industrial and Information Engineering, Second University of Naples, Aversa 81030, Italy*

The mechanisms responsible of the softening "glass to rubber" dispersion in amorphous polymers are the segmental, sub-Rouse, Rouse and terminal relaxation modes. These four mechanisms are additive and their contributions to the overall creep compliance can be described with a stretched exponential function. For polystyrene and polycarbonate the softening dispersion is too narrow and generally it is not possible to resolve the four different mechanisms simply looking at the retardation spectra. Dissolution of these polymers into a solvent diminishes the intermolecular coupling, makes the retardation spectra wider and helps for the identification of the contribution of each single mode to the overall retardation spectra. Here the retardation spectra experimentally obtained for different polystyrene solutions and for bulk star-polystyrene have been fitted using stretched exponentials. It is assumed that the segmental relaxation follows the Andrade creep ($1-n_a=1/3$) and that the Rouse mode is described by a simple exponential function ($n_R=0$), in addition to the relaxation mechanisms additivity. It was found that, differently to what is generally assumed in the literature, the segmental relaxation terminates slight before the shoulder of the overall retardation spectra. This happens because also the sub-Rouse and the terminal modes contributions to the short time tail of the retardation spectrum are not negligible with respect to the segmental one. We, indeed, observe that in the time window, where the segmental retardation spectrum begins to decrease, even the small fraction of the Sub Rouse and terminal relaxation mode cannot be neglected when compared to the segmental retardation strength. Finally, the comparison of the shear retardation spectra with the bulk compliance retardation spectra suggests that the structural relaxation could be affected by either the segmental and chain modes.

Symposium EF

Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant and Sascha Hilgenfeldt

Wednesday 1:30 Washington C

EF11

Scaling analysis and mathematical theory of the interfacial stress rheometerSean Fitzgibbon and Eric Shaqfeh*Chemical Engineering, Stanford University, Stanford, CA 94305, United States*

The interfacial stress rheometer uses the oscillations of a magnetic needle suspended on an interface to characterize the dynamic moduli of thin films. We present several Green's function for the ISR flow field and use them to build numerical solutions based on the boundary element method and multipole expansions. Using dimensional analysis, the crucial momentum dissipation length scales are identified, and analytic singular perturbation solutions are introduced. These exact and approximate solutions are useful in calibrating and interpreting current ISR and double-wall ring experiments, and they have a strong bearing on future ISR design.

Wednesday 1:55 Washington C

EF12

Influence of interfacial rheology on the dynamics of the tear filmM. Saad Bhamla and Gerald G. Fuller*Chemical Engineering, Stanford University, Stanford, CA, United States*

The tear film covers the surface of the eye, protecting and lubricating the cornea. Of particular interest in this presentation is meibum, a viscoelastic insoluble lipid layer that is spread from the glands lining our eyelids. Past work has focussed on the role of this oily layer in reducing evaporation, although conflicting evidence on its ability to reduce evaporative loss has been published. We present here the beneficial effects that are derived through the interfacial viscoelasticity of this meibum layer. Using interfacial rheology measurements, meibum is shown to be remarkably viscoelastic. By measuring the drainage and dewetting dynamics of thin aqueous films capped with viscoelastic insoluble layers, we offer evidence that these layers strongly stabilize the films because of their ability to support surface shearing stresses. Our findings suggest an alternative view for the role played by meibum in the tear film. This view can help explain the origin of meibomian gland dysfunction, or dry eye disease, where abnormal compositions of the lipid mixture fail to offer the proper mechanical resistance against rupture and dewetting of the tear film.

Wednesday 2:20 Washington C

EF13

Elasticity of microscale volumes of viscoelastic soft matter by cavitation rheometryLeonid Pavlovsky¹, Mahesh Ganesan¹, John G. Younger², and Michael J. Solomon¹*¹Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States; ²Emergency Medicine, University of Michigan, Ann Arbor, MI 48109, United States*

We evaluate the application of cavitation rheometry to characterize the elasticity of soft, viscoelastic liquids that may be confined to volumes as small as 1 μ L. Cavitation rheometry, a technique developed by Zimberlin et. al (Soft Matter, 3(6), 765-767, 2007), is a simple, rapid method to extract the elastic modulus of a material, E, by measuring the pressure necessary to create a bubble, or cavity, within it. This pressure has been shown to be an estimate of the elastic modulus in a limit where the bubble size is small relative to size of the specimen and the material is purely

elastic. We extend this method in three ways for possible applications in high throughput materials characterization and in vivo tissue diagnostics. First, we show that viscoelastic samples can be approximated with the purely elastic neo-Hookean model provided that the time scale of the cavity formation is measured. Second, we extend the cavitation rheometry method to accommodate cases in which the sample size is no longer large relative to the cavity dimension. Finally, we implement cavitation rheometry to show that the new theory accurately measures the elastic modulus of viscoelastic samples with volumes ranging from 4 mL to as low as 1 μ L.

Wednesday 2:45 Washington C

EF14

Targeted synthesis of core/shell microcapsules using interfacial rheology, shell micromechanics and morphology analysis

Philipp Erni

Research Division, Materials Science, Firmenich SA, Meyrin, Geneva 1217, Switzerland

Core/shell microcapsules are important in many industrial applications where protection, delivery and controlled release are desired. In particular, dense polymer capsules allowing the release of a core liquid by mechanical rupture are relevant for the delivery of volatile molecules such as fragrances and flavors and similar bioactive compounds. Here, we present methods and results to demonstrate how interfacial rheology and shell mechanics influence the synthesis, storage and delivery of core/shell capsules formed from oil-in-water emulsions via interfacial polymerization. We track the formation of the capsule shell using different monomer chemistries via the evolution of the interfacial shear moduli during shell formation. Of specific interest is the feedback of the membranes' rheological properties for the mass transfer processes that control the interfacial polymerization: monomer transport from the bulk affects the time-dependent interfacial rheology, and vice-versa. In particular, we show how different interfacial rheological profiles lead to variations in the resulting shell morphology. In addition, we study the shells after synthesis using large-deformation micromechanical testing on single microcapsules; these experiments provide additional insight as compared to traditional small-deformation testing performed by colloidal probe AFM. Based on these approaches, we discuss the interplay between shell mechanics and performance for the release of volatile compounds upon mechanical rupture.

Wednesday 3:10 Washington C

EF15

The surface tension of yield stress fluids

Philippe Coussot¹ and Jalila Boujlel²

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In coating, spreading, adhesion, of yield stress fluids the area of the air-fluid interface is significantly increased. It thus becomes critical to appreciate the role of capillary effects in these processes. However, due to the presence in the liquid of various components and in particular a high volume fraction of non-liquid elements such as bubbles, droplets, colloids, etc, the surface tension of these fluids may not be easily predictable. Following Israelachvili's approach [1] we find that for yield stress fluids the creation of interface requires in addition to the surface energy of the interstitial liquid, a term related to the potential energy of interaction of the elements in the jammed structure. If the element size is sufficiently small this term is negligible in the absence of flow. The point is that in practice a flow is necessary to create some air-fluid interface. In order to measure the surface tension of yield stress fluids we developed [2] a technique inspired from the Wilhelmy and du Nouy ring techniques for simple liquids. It consists to withdraw a blade from a bath of such a material. We show that just before a progressive breakage of the film, the force amplitude goes through a maximum which is independent of the initial depth of penetration and the timing for blade lifting, but increases with the material yield stress and the blade thickness. This critical force is shown to reflect both capillary and viscous effects, even at vanishing blade velocity. We demonstrate that the ratio of this force to the blade perimeter provides the surface tension of the yield stress fluid in the limit of low ($\ll 1$) yielding Capillary number. Moreover all our data for the force to perimeter ratio fall along a master curve which may be used to deduce the surface tension from measurements obtained at Capillary number up to 1, even if viscous effects are significant.

[1] J.N. Israelachvili, Intermolecular and surface forces (Academic Press, Boston, 1992). [2] J. Boujlel, P. Coussot, *Soft Matter*, 9, 5898 (2013).

Wednesday 4:00 Washington C

EF16

Stability of monoclonal antibody solutions subject to expansion/compression cycles at the air/water interface

Gigi L. Lin¹, Jai A. Pathak², and Gerald G. Fuller¹

¹*Chemical Engineering, Stanford University, Stanford, CA, United States;* ²*Formulation Sciences Dept., MedImmune, Gaithersburg, MD, United States*

The specificity of monoclonal antibodies (mAb) for their target antigens underpins their efficacy in targeting debilitating conditions in human health. In addition to the thermal, ionic, and pH environment of the antibody solution, the interfacial hydrodynamic stresses encountered by monoclonal antibodies under typical manufacturing, filling and shipping conditions may also induce and/or accelerate partial unfolding and sub-visible particle formation that can compromise their efficacy and safety during administration to the patient. We demonstrate that dilatational surface deformations are more detrimental to antibody stability when compared to constant-area shear of the air-water interface. Dilatation of air bubbles in antibody solution can result from pressure fluctuations in the solutions during product formulation and during shipment of containers. We have constructed a dilatational interfacial rheometer that utilizes orthogonal methods of pressure and curvature measurements to study the interfacial viscoelasticity vis a vis protein stability under interfacial aging. Extraordinary shape transitions such as 'buckling' are observed as the air bubbles in antibody solution are deflated beyond critical surface concentrations. Small and large amplitude oscillatory dilatation measurements of the stress response to frequency sweeps are used to understand the relaxation timescales that describe the adsorbed interfacial film, likely involving the processes of partial unfolding, aggregation, and particle shedding from the interface. Additionally, the surface stress response to

step-strain pulses and the wash out of the protein solution with cell volumes of buffer, inform the dominance of either diffusive relaxation or of surface-relaxation processes. We find data that may describe the (ir)reversibility of protein adsorption, suggesting that adsorbed proteins may be ejected from the air/water interface only when the bubble is deflated faster than the timescale of surface structural rearrangement. These rheological studies frame a molecular understanding of the nature and magnitude of protein-protein interactions at the complex-fluid interface and between the interface and bulk solution.

Wednesday 4:25 Washington C

EF17

Adsorption/desorption kinetics versus interfacial rheology of lung surfactants replacements

Eline Hermans and Jan Vermant

Chemical Engineering, KU Leuven, Leuven, Belgium

Lung surfactant plays an important role in the functioning of the human lung. Under certain conditions, these complex fluids may malfunction, either in premature born infants or in adults having acute respiratory distress syndrome. To alleviate this malfunctioning, both natural and synthetic lung surfactant replacements are used which are inserted into the lung. Interfacial rheological properties play a role during the spreading of these lung surfactant replacements into the lung, and possibly also during breathing. In the present work, we try to identify the role of either the kinetics of adsorption/desorption and the rheological response in shear and dilation. Adsorption/desorption kinetics have a time scale which depends on surface concentration, which competes with the viscoelastic time scales of the true deviatoric rheological response of the interface. We try to separate these effects experimentally. Experiments using rectangular and radial throughs as well as shear rheology are used. The results suggest that for good functioning of these replacements, the deviatoric rheological properties of the interface should be such that viscosities and moduli are small during spreading. Metastable structures are observed which could be playing a crucial role during functioning of the lung surfactant.

Wednesday 4:50 Washington C

EF18

Polymer structure and rheology at fluid-fluid interfaces

Joseph Samaniuk and Jan Vermant

ETH Zurich, Zurich, Switzerland

Polymer structure and rheology at interfaces have great consequences in biology and chemistry, and there are many examples where our current knowledge of these systems has commercial applications in products like paints, cosmetics, foods, and advanced materials. At fluid-fluid interfaces polymers have found commercial applications as stabilizers in cosmetic and food products, and there are areas of biology where polymers at fluid-fluid interfaces play an important role. An ongoing debate amongst those investigating polymer structures at fluid-fluid interfaces is whether or not the polymer adopts an entangled structure similar to that in bulk solutions of concentrated polymer above a critical molecular weight, or whether the polymer adopts a non-entangled structure analogous to bulk solutions of polymer chains below a critical molecular weight. We have investigated this by measuring the interfacial rheological properties of two similar polymers: poly(tert-butyl methacrylate) (PtBMA), and poly(tert-butyl acrylate) (PtBA), each at an air-water interface. The results we will present do not support the entanglement theory, and additionally indicate that the discussion of polymer structure at an air-water interface need not be restricted to a debate over polymer microstructure. For example, we will show that PtBA forms large heterogeneities at all levels of surface coverage, and that its interfacial rheological behavior is surprisingly different than that of the PtBMA that forms relatively uniform layers at all surface coverages.

* Authors affiliated with both the Department of Chemical Engineering at KU Leuven, and the Department of Materials at ETH Zurich.

Wednesday 5:15 Washington C

EF19

Microrheology studies of the mechanical evolution of interfacial protein layers and biofilms

Daniel B. Allan¹, Liana Vaccari², Daniel M. Firester¹, Aayush Singh³, Jian Sheng⁴, Daniel H. Reich¹, Kathleen J. Stebe², and Robert L. Leheny¹

¹*Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD, United States;* ²*Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA, United States;* ³*University of California, Berkeley, Berkeley, CA, United States;* ⁴*Department of Mechanical Engineering, Texas Tech University, Lubbock, TX, United States*

We report microrheology studies of two interfacial biomaterials: monolayers of the protein lysozyme adsorbing at the air-water interface and biofilms forming at an oil-water interface. The experiments employ passive and active microrheology techniques to investigate the linear and nonlinear rheological response, respectively. Following formation of a new interface, the linear shear rheology of both systems, which we interrogate through the Brownian motion of spherical colloids at the interface, undergoes a characteristic evolution in which the interfacial layers become viscoelastic with a complex shear modulus that has approximately power-law frequency dependence. The power-law exponent characterizing this frequency dependence decreases steadily with increasing layer age. Meanwhile, the nonlinear microrheology, probed via the rotational motion of magnetic nanowires at the interface, reveals a layer response characteristic of a shear-thinning power-law fluid with a flow index that increases with age. We will discuss this mechanical evolution in the context of the soft glassy rheology model. Specifically, the linear and nonlinear responses qualitatively fit well together as those of a soft glassy material that approaches a glass phase with increasing layer age.

Wednesday 5:40 Washington C

EF20

Interfacial rheology and dynamic mesostructure measurements of densely aggregated particle laden interfacesSourav Barman and Gordon F. Christopher*Mechanical Engineering, Texas Tech University, Lubbock, TX 79409-1021, United States*

The study of particle laden interfaces has increased significantly due to the prevalent use of particle stabilized Pickering Emulsions in many industrial sectors. Pickering emulsion's bulk properties are highly dependent on interfacial rheology, which is a function of particle laden interfaces' mesostructure determined by particle properties, bulk conditions and flow. However, there have been very few attempts to correlate dynamic interfacial mesostructure to rheology, making it difficult to understand the mechanisms that dictate particle laden interfaces' deformation response. To overcome this problem, a double wall ring interfacial rheometer has been modified to allow real time, simultaneous interfacial visualization and shear rheology measurements of densely aggregated particle laden interfaces.

Using this tool, we have studied a particle laden interface system composed of 3 micron polystyrene particles on an air/water interface at high surface concentrations. To control mesostructure, salt was added to the water subphase, creating aggregated clusters of particles on the interface. We provide simultaneous measurements of mesostructure and rheology for both small amplitude oscillatory shear and steady deformations and correlate dynamic mesostructure to rheology to understand the physical mechanisms behind observed rheological behaviors. During interfacial steady shear, we delineate the regime between shear thinning and yielding of the interface through rheology and analysis of associated deforming mesostructure. Furthermore, we observe that yielding can occur for these systems well before the interface becomes jammed due to strong inter-particle attraction allowing less dense interfaces to maintain a rigidly confined state, which can be seen by analyzing mesostructure. These unique measurements should have significant impact on the design and understanding of particle laden interfaces.

Thursday Morning

Symposium AP Award Presentations

Metzner Award Presentation

Thursday 8:00 Millennium Hall

AP1

Low-dimensional material functions for describing asymptotically-nonlinear viscoelasticity

Randy H. Ewoldt

Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Material functions underlie our understanding of rheology and form the descriptive language of rheologists. Rheological properties generally require high-dimensional descriptions of the nonlinear material behavior. Here we use asymptotic expansions to outline low-dimensional measures for describing leading-order nonlinear responses in large-amplitude oscillatory shear (LAOS). This amplitude-intrinsic regime is sometimes called medium amplitude oscillatory shear (MAOS). These intrinsic nonlinear material functions are only a function of oscillatory frequency, and not amplitude. We clarify the theory of what measures exist and give physically meaningful interpretations to magnitudes and signs. Experimental measurements for a transient polymer gel network (PVA-Borax in water) and a thixotropic jammed soft particle suspension (Carbopol 940 in water) both present novel rheological signatures that have not been predicted by existing constitutive models. Constitutive models are developed and analytically solved for the asymptotically-nonlinear signatures in each case. For the polymer gel, the model fit infers a characteristic persistence length of network polymers. For the thixotropic suspension, we develop a simple thixotropic-viscoelastic constitutive model that can fit the experimental data that no other model is known to fit. The work has implications for (i) conceptual understanding of nonlinear mechanical responses, (ii) constitutive model selection, and (iii) inverse problems to probe microstructural and molecular features of structurally-complex soft materials.

Symposium SC Suspensions and Colloids

Organizers: Jacinta Conrad and Saeid Savarmand

Thursday 8:40 Millennium Hall

SC46

Manipulation of the mechanical properties of colloidal gels by steady and oscillatory shear

George Petekidis, Esmaeel Moghimi, and Nick Koumakis

IESL and Department of Material Science and Technology, FORTH and University of Crete, Heraklion, Crete 70013, Greece

The structural and rheological properties of intermediate volume fraction colloid polymer gels are examined during and after steady and oscillatory shear flow using rheometry, confocal microscopy, light scattering and Brownian Dynamics simulations. Our main objective is to rationalize the microscopic mechanisms through which one can tune the mechanical properties of such metastable colloidal gels by imposing different types of external shear and flow. Experimentally, the gels consist of model hard sphere particle dispersions of $\phi = 0.44$ with the addition of non-adsorbing linear chains, while BD simulations are conducted for hard spheres with the superposition of an AO potential for depletion attractions. Structural analysis shows that variation of the applied shear rate produces strong changes in the structure of the gels both when under shear and during gel reformation at cessation. Larger rates are characterized by disperse particles and the total breakage of structures at rest, which after cessation evolve with time into strong solids with relatively homogeneous structures. However, smaller rates show large inhomogeneous structures under flow, which do not evolve after cessation and additionally exhibit reduced elasticity and as such are weaker solids. Furthermore oscillatory shear is far more efficient than steady shear creating gels with stronger differences in their elastic modulus. Thus by tuning the way a gel is sheared, one may vary the final strength and structure of the resulting gel. Work in collaboration with R. Besseling, W. C. K. Poon and J. F. Brady

Thursday 9:05 Millennium Hall

SC47

Study of the rheology and wall slip of carbon black suspensions for semi-solid flow batteries

Ahmed Helal¹, Kyle Smith², Frank Fan², Xin wei Chen², João Miguel Nóbrega³, Yet-Ming Chiang², and Gareth H. McKinley¹

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Electrolyte suspensions containing carbon black nanoconductor particles (KetjenBlack) show promise for novel semi-solid flow cell designs. Characterizing the rheology and wall-slip behavior of these suspensions is crucial to estimate mechanical efficiency losses, optimize cell performance, and guide cell design. In these suspensions, the carbon black particles form a fractal network that percolates at low volume fractions

(< 0.5 vol%) and exhibits a gel-like behavior resulting in complex rheology (yield stress, shear thinning, finite size effects) coupled with wall slip. In this work, we will present experimental methods to characterize both the shear rheology (under steady and small amplitude oscillatory shear) and the slip behavior of these suspensions, using a torsional rheometer with a plate-plate geometry. The results obtained show that these suspensions exhibit a linear dependence of the slip velocity on shear stress and a critical shear stress for the onset of slip. A systematic study of the effect of the carbon black loading on the suspension yield stress, slip velocity, elastic modulus and conductivity will be performed and used to aid the design of future flow cells.

Thursday 9:30 Millennium Hall

SC48

Shear-enhanced aggregation of uniform and Janus spheres in the dilute-sphere limit: A Brownian dynamics simulation approach

Maziar Mohammadi, Jun Liu, Eric D. Larson, and Ronald G. Larson

University of Michigan, Ann Arbor, MI, United States

Brownian dynamics (BD) simulations are performed to study the binding kinetics in the dilute-sphere limit by considering interactions of two spheres under shear flow across the entire range of Peclet numbers, spanning both perikinetic (diffusion-controlled) and orthokinetic (flow-controlled) coagulation regimes. The dilute regime is attained by carrying out two-sphere simulations in periodic boxes of different sizes and extrapolating toward the infinite box limit. Effects of particle type (Janus and isotropic particles), shear rate, hydrodynamic interactions (HI), box size (cubic and rectangular), and inter-particle potential are explored. We find that rectangular boxes, with increasing box length in the direction of flow, overcome a particle "shadow effect" that cannot be overcome with cubic boxes unless huge boxes are used. With rectangular boxes, we obtain converged binding kinetics at moderate and high Peclet numbers, while cubic boxes of increasing size allow converged results in the absence of flow. We consider the effect of binding in a secondary minimum controlled by a combination of electrostatic repulsion and depletion attraction. Results are computed using both realistic interaction potentials and replacing the potential with a simple cut off gap distance at which binding is deemed to occur. The accuracy of this simple cut-off method and its sensitivity with respect to different cut off distances are studied. Numerical results illustrate that for zero and high shear rates, the constant of extrapolation of average binding times per unit volume for infinite box length approach predictions of Smoluchowski theory. Finally, we compute binding times for Janus particles which have both repulsive and attractive faces, as a function of Peclet number.

Thursday 10:25 Millennium Hall

SC49

Nanodiamond gels: Colloidal and rheological properties

Nancy A. Burns¹, Srinivasa R. Raghavan², Akbar Shojaei³, and Saad A. Khan¹

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Nanodiamonds, i.e., sp³-hybridized nanoscale carbon particles, are being widely explored for biomedical applications such as drug delivery and medical imaging because the particles are relatively nontoxic and their surfaces can be easily functionalized. However, little is known about the colloidal and rheological properties of nanodiamond dispersions. Here, we initially report a study on nanodiamonds dispersed in a nonpolar liquid, mineral oil. We find that the nanodiamonds form colloidal gels at low particle concentrations (~ 5 wt%). Gelation is likely to be due to attractive interparticle forces (van der Waals and hydrogen-bonding), resulting in a fractal network of the particles. Much like other particulate gels, nanodiamond gels show thixotropic behavior, i.e., the gel network is disrupted by large deformations (steady or oscillatory shear) and is re-formed upon cessation of shear. However, after oscillatory shear at a large strain-amplitude (1000%), the recovery is incomplete and the modulus of the recovered gel is only half its original value. In contrast, near-complete recovery of the modulus is observed after steady shear. Functionalization of nanodiamond surfaces with methacrylate groups eliminates gelation and gives a stable, low-viscosity dispersion. In contrast, nanodiamonds in glycerol are found to form a colloidal gel that strengthens with time, and is independent of surface functionalization. We discuss the possible mechanisms leading to the difference in behavior in the two solvent systems studied.

Thursday 10:50 Millennium Hall

SC50

Numerical computation of permeability in unstable colloidal gels

Alexander M. Mertz¹, Marc S. Ingber¹, Alan Graham², Antonio Redondo², and Lev Gelb³

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In unstable colloidal gels, the viscous flow through the non-neutrally buoyant colloidal network determines the initial rate of collapse [1]. The resistance to this flow through the network is characterized by the permeability. The permeability is generally accepted to be a power-law function of volume fraction, where the power is dependent on the fractal dimension of the network. To test this with direct numerical simulations, randomly generated diffusion-limited-cluster-aggregated networks of spheres are generated periodically. These networks will be characterized using the fractal dimension by measuring the length of the network strands with different sized measurement scales [2]. The permeability is then determined using finite element solutions of Darcy's Law of pressure-driven flow of Newtonian fluids through the networks. An effective permeability of small sections of the network is calculated with analytic expressions that have been shown to be in good agreement with FEM solutions to Stokes equations. The results are in reasonable agreement with the available experimental data.

[1] S. Manley, J. M. Skotheim, L. Mahadevan, and D. A. Weitz, "Gravitational Collapse of Colloidal Gel," PRL 94, 218302 (2005). [2] B. Mandelbrot (1967). "How Long Is the Coast of Britain? Statistical Self-Similarity and Fractional Dimension", Science 156 3775, 636 (May 5, 1967).

Symposium BB Biomaterials and Biological Systems

Organizers: Randy Ewoldt and Kelly Schultz

Thursday 8:40 Commonwealth B BB46

Swimming in circles: Using bacterial circulation as a non-contact microrheological probe

Arthur A. Evans

Physics, University of Massachusetts, Amherst, Amherst, MA 01003, United States

Hydrodynamic interactions between bacteria and nearby boundaries effect the overall swimming trajectories of micro-organisms. Due to the chirality of bacterial swimming gaits, fluid-fluid interfaces and no-slip boundaries effect the circulation in a qualitatively different fashion. Using continuum theories of membrane rheology and micro-organism hydrodynamics, I examine here the effect of a boundary defined by a rheologically complex membrane on the trajectories of a model bacterium. In particular, I find that there is an interaction length scale over which circular swimming behavior changes handedness, indicating that bacterial swimming near soft boundaries may be used to determine the flow properties of the interface.

Thursday 9:05 Commonwealth B BB47

Dynamics of active suspensions in confinement: Kinetic theory and numerical simulations

Barath Ezhilan and David Saintillan

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The dynamics of biologically active suspensions in confined geometries is investigated by incorporating accurate boundary conditions within the kinetic theory framework [Saintillan and Shelley, Phys. Fluids. (2008)]. Even in the absence of wall hydrodynamic interactions or imposed flow, swimming microorganisms have a tendency to accumulate at confining boundaries due to self-propulsion. Satisfying a zero wall-normal translational flux condition on the active particle probability distribution function captures this effect. Using a moment-closure approximation, analytical expressions for the concentration/polarization profiles are derived. When an external flow is imposed on active suspensions in confined geometries, peculiar dynamics like near-wall upstream swimming and trapping of swimmers in high shear regions have been reported in recent experiments. Motivated by these observations, the effects of a Poiseuille flow are also considered and an analytical expression for the net upstream velocity is derived in the weak flow limit. A finite-volume numerical simulation of the 1D kinetic equation is used to investigate the dynamics in strong flows. A depletion of active particles from the center of the channel because of an effective trapping in high shear regions is reported, in agreement with microfluidic experiments [Rusconi et al. Nat. Phys. (2014)]. Asymptotics in the strong flow limit are performed to derive a scaling for the depletion layer thickness and understand the dependence of the extent of depletion on flow strength. Previous phenomenological models have predicted the existence of a spontaneous flow transition in confined active suspensions that lead to unidirectional flow with net fluid pumping. Using a linear stability analysis and 3D finite volume simulation of the equations for the orientational moments, we discuss in detail the effect of confinement on the stability properties of the equilibrium states and characteristic correlation length scale of the coherent patterns.

Thursday 9:30 Commonwealth B BB48

Theory of locomotion in complex fluids

Gwynn Elfring¹ and Eric Lauga²

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Microorganisms often swim in environments that cannot be classified as Newtonian. Biological fluids can contain polymers or other heterogeneities which may yield complex rheology. For a given set of boundary conditions flows can be substantially different in complex fluids, while non-Newtonian stresses can alter the gait of the microorganisms themselves. Heterogeneities in the fluid may also occur on length scales on the order of the swimmer leading to additional complexity. In this talk we will discuss a theoretical description of the effects on locomotion of a non-Newtonian constitutive relation and discuss our current understanding of the interplay between swimming kinematics and the nonlinear response of the fluid.

Thursday 10:25 Commonwealth B

BB49

Emulsion-templated nanocomposite gel microparticles for lung imaging and drug deliveryBryan R. Benson¹, Nathalie M. Pinkerton¹, Brian K. Wilson¹, Derek Adler², Dayuan Gao², Srinivas Mettu³, Raymond Dagastine³, Patrick J. Sinko², Howard A. Stone⁴, and Robert K. Prud'homme¹¹*Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States;* ²*Rutgers University, Piscataway, NJ, United States;* ³*The University of Melbourne, Melbourne, Australia;* ⁴*Princeton University, Princeton, NJ, United States*

Using a shear emulsification technique, uniform droplets in the range of 10 to 50 microns can be generated and formed into nanocomposite gel microparticles. The microparticles enable targeting to the lung by filtration from the venous circulation. The size and modulus of the particles affect residence time in the lungs. UV radical polymerization and Michael addition polymerization reactions are compared as approaches to gel the PEG emulsion droplets. A fluorescent dye in the solid core of the NP was used to investigate the effect of reaction chemistry on the integrity of encapsulated species. When formed via UV radical polymerization, the fluorescence signal from the NPs indicated degradation of the encapsulated species by radical attack. The degradation decreased fluorescence by 90% over 15 min of UV exposure. When formed via Michael addition polymerization, the fluorescence was maintained. The modulus of the gels was tuned over the range of 5 to 50 kPa by changing the polymer concentration between 20 and 70 vol %. We investigated the modulus in bulk gel samples as well as in individual microparticles using AFM nanoindentation. NP aggregation during polymerization, driven by depletion forces, was controlled by the reaction kinetics. The ester bonds in the gel network enabled CGMP degradation. The gel modulus decreased by 50% over 27 days, followed by complete gel degradation after 55 days. This permits ultimate clearance of the CGMPs from the lungs. We investigated the biodistribution and clearance of the gel microparticles by using near-IR fluorescence to image the location of the particles in vivo at multiple time points over a month.

Symposium SM Polymer Solutions and Melts

Organizers: Hiroshi Watanabe and Deepak Doraiswamy

Thursday 8:40 Commonwealth C

SM46

Mechanical characterization of thin polymer membranes at fuel cell operating conditionsBenjamin R. Caire, Melissa A. Vandiver, Andrew M. Herring, and Matthew W. Liberatore*Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States*

While chemical degradation typically dominates membrane failure pathways in a fuel cell, mechanical breakdown due to humidity cycling is a common occurrence. The sorption and desorption of water can cause pin hole cracks which lead to fuel crossover and stack failure. As part of a broader effort to develop novel, thin, highly conductive, and robust anion exchange membranes, creating a test fixture for mechanical characterization at relevant fuel cell operating conditions is being explored. New polymers are synthesized in small quantities and films are typically on the order of 10-100 microns thick to increase ion transport. A modified Sentmanat Extensional Rheometer (SER) is used to perform tensile-like testing on thin membranes at relevant fuel cell conditions using a humidity delivery system developed for the TA Instruments ARES-G2 rheometer to allow for testing at a range of temperatures (30-100°C) and relative humidity conditions (0-95% RH). Along with a typical tensile test, we explore a "water stress" test (similar to dynamic mechanical analysis) in which the rheometer is used to measure the tension as the humidity is cycled from dry to wet. This test gives insight into the force of water entering and exiting the membrane as well as the hysteresis of humidity cycling on the stress. The moduli from the water stress cycling will be compared with the moduli obtained from the stress-strain curve at fixed temperature and relative humidity conditions. The new instrumentation and test procedures will be benchmarked with Nafion(R) N115, and novel ionomers synthesized by the team will be featured as well.

Thursday 9:05 Commonwealth C

SM47

Effect of hydration on mechanical properties of anion exchange membranesMelissa A. Vandiver¹, Benjamin R. Caire¹, Yifan Li², Daniel M. Knauss², Andrew M. Herring¹, and Matthew W. Liberatore¹¹*Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States;*²*Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States*

Anion exchange membranes facilitate ion transport in polymer electrolyte membrane fuel cells. An AEM must have a high ionic conductivity, low gas/fuel crossover, and be chemically and mechanically stable over the lifetime of the fuel cell. Development of thin polymer films is critical to reduce membrane resistance. As membrane thickness is decreased, maintaining membrane integrity becomes increasingly difficult. Additionally, humidity changes during fuel cell operation cause sorption and desorption of water in the polymer. Repeated swelling and contraction puts significant stresses on the membrane and can lead to cracks, pinholes, and eventual membrane failure. Water taken up by the polymers at high humidity acts as a plasticizer increasing elasticity of the films. However, previously tested AEMs displayed low elasticity and elongation under dry conditions, which could lead to pinholes and cracks during humidity cycles. A new polyethylene-b-poly(vinylbenzyl trimethylammonium) diblock AEM has been synthesized with improved elongation and elasticity. This polymer can be solution processed into thin (10 micron) films. Extensional tests of the polyethylene diblock were performed under dry and saturated gas conditions. At dry conditions the polyethylene diblock has a moderate Young's modulus (120 ± 20 MPa), a good elongation to break (170 ± 30 %), and reasonable strength (21 ± 5 MPa). When hydrated, water in the membrane has a plasticizing effect reducing the modulus by 73% and increasing elongation by 53%, but

only reducing strength by 10%. The minor reduction in strength between dry and hydrated conditions demonstrates the improved robustness of the polyethylene diblock over previous chemistries. Continued studies of the polyethylene diblock will cycle humidity while measuring modulus to determine how mechanical properties change over time in a working fuel cell. Advanced knowledge of AEM mechanical properties will aid in design of robust membranes to improve fuel cell lifetime.

Thursday 9:30 Commonwealth C

SM48

Polymer degradation in drag-reducing flows in pipes at fixed inlet pressure

Edson J. Soares, Lucas Silveira, Gustavo A. Barrientos, Fabrício Thomaz, Renata T. Silva, and Anselmo S. Pereira

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We analyze here the loss of efficiency of drag reducing flows in a pipe-line when small amounts of Polyethylene Oxide (PEO) are diluted in water. In our experimental apparatus, the total pressure loss is fixed, sustained by a pressurized vessel. The solution's friction factor is measured and compared to the value previously obtained for pure water at the same Reynolds numbers. Our tests are conducted for a wide range of concentration and molecular weight. We show that the drag reduction (DR) falls and reaches a steady state after a certain number of passes through the pipe flow apparatus. The loss of efficiency is supposedly related to the mechanical molecular scission, which stops when the molecule's mean-length reaches its final value, after a long enough time over an intense turbulent flow. It is worth noting that, during the molecular scissions, the drag in test section increases and the flow rate decreases, at the same time.

Thursday 10:25 Commonwealth C

SM49

Rheology of enhanced oil recovery polymers for high-temperature and high-salinity reservoirs

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In Polymer flooding, an aqueous polymer solution is injected into the oil reservoir for improved mobility control which results in better sweep efficiency and incremental oil. Although, polymer flooding is an established enhance oil recovery (EOR) technique applied to both sandstone and carbonate reservoirs. However, its application to high-temperature and high-salinity reservoirs is still a challenge, as most synthetic polymers such as hydrophobically modified polyacrylamide (HPAM) degrade at high-temperature and do not tolerate high-salinity due to the screening of ionic interactions. In this study, we investigate the rheological behavior of a series of potential EOR polymers, HPAM and Schizophyllan biopolymer. The effect of temperature and salinity on the rheological behavior of the polymer solutions is analyzed and it is found that bio polymer shows excellent temperature and salinity tolerance up to 120 °C and 220,000 ppm respectively. The Schizophyllan solution shows no viscosity reduction when kept at 120° C under inert atmosphere for over 120 days. This remarkable thermal stability and salt tolerance are attributed to the nonionic nature and the triple helical structure of Schizophyllan. Whereas the acrylamide based polymer solutions show reasonable temperature stability but very poor salinity tolerance. In addition to mechanical and thermal stability, the dynamic oscillatory behavior of the polymer solutions is also studied as a function of polymer concentration and testing temperature. Linear viscoelastic regions are identified and the storage and loss modulus are also investigated. Moreover, Maxwell model is used to fit the dynamic rheological results and relaxation time is determined. The rheological properties are measured with rotational shear rheometer equipped with a high pressure cell. Identifying thermally stable, salt-tolerant polymer with high thickening efficiency is a major contribution towards field applications of polymer flooding for high-temperature and high-salinity reservoirs.

Thursday 10:50 Commonwealth C

SM50

Effect of viscoelastic properties of polymer solutions on Stribeck scaling

Eugene Pashkovski and Reid Patterson

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Analytical solution of Reynolds equation for self-aligned parallel plates (SAPP) introduced by Christian Clasen [*J.Rheol.* **57**(1), 197 (2013), *Rheol. Acta* **52** (3), 201, (2013)] helps to bridge tribology and classical bulk rheology that have been traditionally apart from each other. The SAPP fixture can be used in commercial rheometers for investigating hydrodynamic lubrication regime for Newtonian and non-Newtonian fluids. Tribo-rheological data can be presented in the form of Stribeck curve, i.e. as dimensionless shear stress (friction coefficient) as a function of dimensionless angular velocity. While Stribeck scaling is straightforward for Newtonian fluids, no such simple scaling exists for polymer solutions. To investigate possible type of scaling for weakly viscoelastic non-Newtonian fluids, we use Stribeck curves generated within wide range of applied axial forces and use power-law approximation to create a master curve with the slope of hydrodynamic branch defined by the power law exponent. Shear stress and viscosity calculated from Stribeck curves are compared with these obtained from conventional and Ultra-High Shear rheometers. Possible role of the first normal stress difference in Stribeck scaling for weakly viscoelastic dilute polymer solutions is also discussed.

Symposium SF Self-assembly and Flow-induced Systems/Gels

Organizers: Eric Furst and Anne Grillet

Thursday 8:40 Commonwealth D

SF21

The effect of branching on the nonlinear rheology of wormlike micelles (WLMs) using small angle neutron scattering (SANS) with spatial and temporal resolution

Michelle A. Calabrese, Simon A. Rogers, and Norman J. Wagner

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

The nonlinear rheology and segmental alignment of a model series of WLMs is studied to determine the effect of branching on shear flow phenomena. The degree of branching in the mixed cationic/anionic surfactant (CTAT/SDBS) studied is controlled via the addition of the hydrotropic salt sodium tosylate. The shear-induced segmental alignment of the micelles is measured for local gap positions and time under large amplitude oscillatory shear (LAOS) in the flow-gradient plane using novel flow-SANS instrumentation [1] as well as temporally in conjunction with rheology in the flow-vorticity plane [2]. Our ability to resolve the microstructure via scattering projections in multiple planes of flow provides new insights into the effect of flow on the WLM microstructure under time-dependent shear flow. Local segmental orientation and alignment in the flow-gradient plane is found to be a complex function of the branching level, radial position, and time during the oscillation. Spatiotemporal SANS demonstrates that LAOS can elicit simultaneous elastic and viscous material responses depending on gap position, thereby corroborating recent theoretical predictions with experiment for the first time [3]. Furthermore, the maximum alignment in the flow-gradient plane under LAOS is found to be significantly higher than that observed in steady shear at the same instantaneous shear rate. This nontrivial hyperalignment under dynamic deformation is interpreted in terms of the dynamics of the microstructural rearrangement during LAOS. This research quantitatively links micellar microstructure and topology to the measured nonlinear shear rheology of WLM solutions, providing a more complete data set to enable interpretation of the rheology and rigorous testing of microstructure-based constitutive equations.

[1] A.K. Gurnon, et al., *J. Visual Exp.* 84 (2014). [2] C.R. Lopez-Barron, et al., *Phys. Rev. Lett.* 108 (2012). [3] J.J. Stickel et al., *Journal of Rheology* 57 (2013).

Thursday 9:05 Commonwealth D

SF22

Microstructure, temperature, aging and rheological studies of an ionic micellar structure composed by a p-p organic salt

Joshua J. Cardiel¹, Ya Zhao¹, Pablo De la Iglesia², Lilo D. Pozzo², and Amy Q. Shen¹

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In equilibrium, wormlike micelles can transition from entangled to branched structures with increasing ionic strength. Under flow conditions, wormlike micelles transition shows different behavior. In this study we consider the flow of a semi-dilute wormlike micellar solutions through microposts, with focus on its microstructural, temperature, aging and rheological evolution. The micellar solution (precursor) contains cetyltrimethylammonium bromide (CTAB) and the hydrotropic salt 3-hydroxynaphthalene-2-carboxylate (SHNC). We observe the formation of a flow induced structured phase (FISP), with entangled, branched, and multi-connected micellar bundles, evidenced by electron microscopy and small-angle neutron scattering (SANS). We also study the temperature behavior of both precursor and FISP by using SANS and gold-microheaters incorporated into the microchannel with microposts. We notice that the FISP does not completely disintegrate at high temperatures, whereas, the precursor exhibits shortening of the wormlike micelles as temperature increases. Further, we correlated the microstructure and temperature studies of both FISP and precursor to their rheological behavior by using two point passive microrheology and bulk rheology.

Thursday 9:30 Commonwealth D

SF23

Linear and nonlinear rheology of wormlike micelles with cationic surfactant and organic hydrotropic salt mixture

Ya Zhao and Amy Q. Shen

University of Washington, Seattle, WA 98195, United States

Aqueous micellar aqueous solutions of cationic surfactant cetyltrimethylammonium bromide (CTAB) and organic hydrotropic salt 3-hydroxy naphthalene-2-carboxylate (SHNC) were studied by using a combination of linear and nonlinear rheology, and dynamic light scattering (DLS) in the semi-dilute regime. The strong hydrophobicity and dual naphthalene rings present in the SHNC induce significant growth of CTAB micelles and formation of stable micellar networks, yielding versatile structural transitions under large strains and elevating temperatures. Our systematic rheological characterizations of CTAB/SHNC demonstrate SHNC as a strong and stable hydrotrope in a semi-dilute cationic surfactant systems under thermal variations, which enables further thermal enhanced oil recovery and drag reduction studies in surfactant solutions, sensing applications in a less electrolyte environment.

Thursday 10:25 Commonwealth D

SF24

The sequencing of dynamic rheological measurements

Simon A. Rogers, Michelle A. Calabrese, and Norman J. Wagner

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

A new quantitative analysis scheme is presented that is commensurate with recent studies [1, 2] suggesting that nonlinear responses to large amplitude oscillatory shear (LAOS) are due to sequences of physical processes. In addition to two 'regular' viscoelastic material parameters (moduli, viscosities, compliances, or fluidities), the new scheme includes a third term that is an entirely new concept for viscoelastic analysis. The new term accounts for yield strains and stresses, shifting equilibria, and irreversibly-acquired strain.

The new technique is used to analyze the nonlinear rheological response to LAOS of a series of mixed cationic/anionic surfactant (CTAT/SDBS) WLMs in which the level of branching is controlled via the addition of the hydrotropic salt sodium tosylate [3]. By providing temporal resolution to the analysis of viscoelastic responses, this research provides a rational pathway toward a more complete understanding of results from all oscillatory rheological tests as well as hybrid flow-microstructure experiments.

[1] S. A. Rogers et al., *J. Rheol.* 55, 435 (2011). [2] C. R. Lopez-Barron et al., *Phys. Rev. Lett.* 108 (2012). [3] B. A. Schubert et al., *Langmuir* 19, 4079 (2003).

Thursday 10:50 Commonwealth D

SF25

A suggestive rheological behaviour of branched micellar solutionsDanila Gaudino, Nino Grizzuti, and Rossana Pasquino*Università degli Studi di Napoli Federico II, Napoli, Italy*

Micelles are "living polymers", which behave very similarly to standard polymer chains. The difference stands in the fact that polymers have a rigid and covalently bonded backbone, whereas the micelles are held together by physical attractions. When deformed, the micelles have access to a wide range of ways to relieve their stresses by, for example, not only reptating as polymers but also breaking and reforming. The unique rheological behavior of worm like micellar solutions makes them useful as rheology modifiers in a very wide range of industrial products. By tuning the components of the micellar solutions, it is possible to change the microstructural morphology of the micelles, from linear to branched. Different micellar solutions have been prepared, with various anionic and non-ionic surfactants and with different kinds of salts. More specifically, we have dealt with two micellar systems, based on the following chemical components: - 24-3 (C12-14/E3, triethylene glycol dodecyl ether) and 24-7 (C12-14/ E7, heptaethylene glycol dodecyl ether) and an anionic surfactant, HLAS (Linear alkylbenzene sulphonic acid) - Cetylpyridinium chloride (CPCI), sodium salicylate (NaSal) and sodium chloride (NaCl). By tuning the relative quantities of each system components, various solutions with different morphologies have been achieved. Rheological measurements have been performed on each solution, both in linear and non-linear regime. In linear regime, creep tests have been performed with a stress controlled rheometer (Bohlin CVO120, Malvern), in a way to enlarge the frequency window to lower values, together with the classical frequency sweeps carried out with a strain controlled instrument (ARES, TA Instruments). In non-linear regime, step rates and large amplitude oscillatory measurements have been carried out. We found that branched structures (for which the microstructure have been confirmed with cryo-TEM frames) show a peculiar rheological response both in linear and non-linear regime.

Thursday 11:15 Commonwealth D

SF26

Light-activated fluidic valve by triggering the ionic gelation of a biopolymerHyuntaek Oh, Vishal Javvaji, Annie X. Lu, Reza Hashemipour, and Srinivasa R. Raghavan*Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States*

Fluids with light-tunable rheological properties (i.e., photorheological or PR fluids) have been studied in the recent past by many research groups. One advantage of light over other stimuli lies in its ability to be directed at a precise location from a remote source. A potential application for PR fluids that leverages the spatial selectivity of light is in the area of flow control within fluidic devices, e.g., to stop the flow at a precise location within a network of fluidic channels (valving action). However, despite a wide variety of existing PR fluid formulations, current fluids are not suitable for this application. Here, we report a PR fluid based on the biopolymer, alginate, that could be useful in this context. The fluid is composed entirely of commercially available components: alginate, a photoacid generator (PAG) as a photo-trigger, and a chelated complex of divalent strontium (Sr²⁺) ions (Sr-EGTA). Upon exposure to UV, the PAG dissociates to give H⁺ ions, which induce the release of free Sr²⁺ ions from the Sr-EGTA. The released Sr²⁺ ions then self-assemble with the alginate chains to give a nanostructured gel with a high gel modulus (~ 2000 Pa). To test the possibility of fluidic valving, we flow the above fluid through a microchannel and expose a specific point in the channel to UV light. At that point, alginate is converted into a strong gel in a few minutes, and we find that the resulting gel blocks the flow. When the UV light is removed, the gel is gradually diluted by the flow and the channel reopens. We have thus shown a new kind of light-activated fluidic valve; note that the above concept relies entirely on physical (non-covalent) bonds, i.e., on self-assembly, rather than on covalent crosslinking of dissolved monomers or polymers.

Thursday 11:40 Commonwealth D

SF27

Migration and alignment of anisotropic planar particles with pinned contact lines at a curved interfaceNima Sharifi-Mood¹, Lu Yao², Iris B. Liu¹, and Kathleen J. Stebe¹¹*Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA, United States;* ²*Dow Chemical, Spring House, PA, United States*

microparticles trapped at a fluid interface can distort the interface owing to the boundary conditions at their contact lines. This distortion stores energy, leading to the capillary interactions that can be harnessed for directed bottom-up self-assembly of particles for advanced material applications. On planar interface, capillary interactions between microparticles are well established, however on a curved interface these interactions are not yet well understood. Here, we study rigid particles at oil-water interface where the curvature field is imposed by molding the interface around a vertical cylindrical micropost. The shape of interface close to the micropost has zero mean curvature and position dependent deviatoric curvature. We study circular disks and elongated wafers with varying particle aspect ratio. All particles studied have sharp edges which pin the contact line when they are trapped at the interface. On planar interfaces, the particles interact very weakly. On curved interfaces they migrate to sites of high curvature. The wafer shaped particles have preferred alignments, which depend on aspect ratio. We theoretically investigated this migration and alignment utilizing both energetic and force approaches. Our analysis indicated the force on the particle is simply due to the slope variation of the disturbed interface along the contact line. We develop an asymptotic analysis to determine the disturbance field created by the particle and the associated energy landscape. Finally, we extended the theory to capture the pair interaction of planar disks at curved interfaces. Our analysis is in agreement with experimental measurement. These results have implications on tuning the structure of particle self-assemblies in particle-stabilized emulsions, interfacial gels and encapsulation of materials within particle stabilized drops.

Symposium SG Solids and Glasses

Organizers: Tom Engels and Jim Caruthers

Thursday 8:40 Commonwealth A1

SG11

Accelerated assessment of the long-term performance of engineering polymersMarc Kanters and Leon Govaert*Polymer Technology, Eindhoven University of Technology, Eindhoven, The Netherlands*

Engineering polymers are used in a multitude of load-bearing applications where structural integrity and long-term reliability are of the utmost importance. With the increasing social demand for durable products with long service life, and a gradual shift to more critical applications, e.g. involving high loads and temperatures (e.g. under-hood automotive applications, domestic hot water systems), the need for such predictive methods is even more vital. Standardized certification tests (e.g. pressurized pipe or full scale product test) are costly and time-consuming. Especially in material development this hampers material optimization. In this talk we present results of experimental protocols that are effective for fast screening of long-term performance in the plasticity-controlled and the crack-growth controlled failure regimes.

Thursday 9:05 Commonwealth A1

SG12

Aging of polymeric films used in protective glazing systemsChristopher White, Kar Tean Tan, and Donald Hunston*Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

Polymer glass laminates or window glazing, are used to protect buildings and occupants from shattered glass resulting from natural disasters (e.g., hurricanes, tornadoes, seismic events), and intentional events (e.g., robbery, terrorist attack). Glazing films, as with all other polymers, may degrade upon prolonged exposure to ultraviolet (UV) radiation, rain, snow, or extreme temperature. Such undesirable weathering will impact the performance of the materials, deteriorating the durability and shortening their useful life spans. The non-linear elastic properties show the greatest changes as a result of weathering. This is unfortunate as it is not easy to detect changes in this critical property. Typically, the end user will use yellowing of the film to indicate performance changes. Our work will illustrate how the rheological properties of these films are modified by exposure to weathering.

Thursday 9:30 Commonwealth A1

SG13

Linear viscoelasticity of soft glassy materialsManish Kaushal and Yogesh M. Joshi*Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, U.P. 208016, India*

Owing to lack of time translational invariance, aging soft glassy materials do not obey fundamental principles of linear viscoelasticity. We show that by transforming the linear viscoelastic framework from the real time domain to the effective time domain, wherein the material clock is readjusted to account for evolution of relaxation time, the soft glassy materials obey effective time translational invariance. Consequently, we demonstrate successful validation of principles of linear viscoelasticity (Boltzmann superposition principle and convolution relation for creep compliance and stress relaxation modulus) for different types of soft glassy materials in the effective time domain.

Thursday 10:25 Commonwealth A1

SG14

Particle rearrangements and rheology in a 2D glassy solid near yieldingNathan C. Keim and Paulo E. Arratia*Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States*

We present experiments on the relationship between the microscopic structure of a disordered 2D solid and its response to deformation. The material is a monolayer of mutually repulsive particles adsorbed at an oil-water interface, for which we simultaneously measure oscillatory shear rheology, and image the motion of many individual particles. We find a reversible plastic regime near the yielding transition, in which a stable population of dissipative rearrangements controls deformation. The yielding transition may be understood as a transition to irreversible flow. We describe how these behaviors change when we use particles of a single size, instead of two, making disorder rarer and more concentrated. Our results hint at the collective mechanisms underlying the yielding of soft glassy materials under oscillatory shear.

Thursday 10:50 Commonwealth A1

SG15

Evidence for deformation dependence of heat capacity in cross-linked natural rubberDavid Nieto Simavilla, David C. Venerus, and Jay D. Schieber*Chemical and biological engineering, Illinois institute of technology, Chicago, IL 60616, United States*

We present a novel Infrared Thermography (IRT) technique to investigate heat capacity dependence on deformation in polymeric materials. This phenomenon is directly related with the longstanding question of whether or not there is an internal energy contribution to rubber elasticity in particular, and to viscoelasticity of polymer liquids in general. By tracking the temperature evolution of stretched samples heated by a laser beam, we are able to measure heat capacity changes with respect to the equilibrium value as a function of elongation. We find that heat capacity increases with stretch ratio in lightly cross-linked cis 1,4- polyisoprene specimens subjected to uniaxial extension. This observed deformation dependence of heat capacity is consistent with an independent set of experiments comparing anisotropy in thermal diffusivity from Forced Rayleigh Scattering and thermal conductivity from steady-state IRT. We evaluate our results with a simple thermodynamic analysis of the internal energy contribution to tension based on classical rubber elasticity results.

Thursday 11:15 Commonwealth A1

SG16

Direct observation of the end-to-end distance between crosslinks for silica-based model-rubber networks with mono-disperse short chainsTheo A. Tervoort, Coen Clarijs, and Walter R. Caseri*Department of Materials, ETH Zurich, Zurich, ZH 8093, Switzerland*

This paper reports the synthesis and characterization of silica-based tetrafunctional model rubber networks with mono-disperse short chains between crosslinks. The networks were obtained from a simple one-pot synthesis by endlinking linear precursor chains (a, ω -alkandiol) with known length, to a tetrafunctional compound (tetramethylorthosilicate), yielding amorphous transparent monoliths of notable thickness (± 5 mm). The structure of the resulting rubbers consists of tetrafunctional SiO₄ crosslinks, separated by monodisperse network chains of 8 or 10 methylene units. Uniaxial compression testing and dynamic mechanical thermal analysis was performed to access the elastic and viscoelastic properties as a function of temperature. The high scattering contrast between the silica atoms on the one hand and the carbon, hydrogen and oxygen atoms on the other hand, allows for a direct determination of the end-to-end distance between crosslinks by measuring the Si-Si distance using X-ray scattering experiments. It was found that both the end-to-end distance between crosslinks and the rubber-elastic modulus compare well to the standard Gaussian rubber network model. In addition, the influence of deformation on the end-to-end distance between crosslinks could be analyzed in detail by performing X-ray scattering experiments during uniaxial compression testing.

Thursday 11:40 Commonwealth A1

SG17

Non-Newtonian behavior of nuclear glass melts containing insoluble PGE particlesJean Puig¹, Muriel Neyret¹, and Philippe Marchal²*¹DTCD-SECM-LDMC, CEA Marcoule, Bagnols-sur Cèze 30207, France; ²UMR CNRS 7274, Laboratoire Réactions et Génie des Procédés - GEMICO, Nancy 54001, France*

French fission products coming from the reprocessing of the nuclear fuel are immobilized in a glass borosilicate matrix. The vitrification process requires the knowledge and the modeling of nuclear glass melt rheological behavior at high temperature (around 1200°C). However, the presence of undissolved PGE particles (Platinum Group Elements) leads to tricky phenomena such as non-Newtonian behavior of the glasses, aggregation of particles and sedimentation. These evolving phenomena constitute a challenge to master the vitrification process of high level waste nuclear glasses. In this context, the aim of this work is to describe the influence of the PGE content on the rheological properties of inactive nuclear glass melts (i.e., whose radioactive elements are simulated by non-radioactive elements) during the melting procedure. For this purpose, we have developed an original device in order to perform rheological measurements at high temperature. This rheometer prototype permits to perform rheological tests in steady-state, transient and oscillatory regimes (mechanical spectroscopy). Therefore, a scenario describing the PGE particles transport in a nuclear glass melt has been proposed and confirmed using different characterization techniques (scanning electron microscopy, density measurements...). In particular, sedimentation of the PGE particles was considered to be one of the most relevant physical phenomena occurring during the tests. Sedimentation rates were then determined using various experimental conditions. Finally, a rheological structural model, accounting for the physical phenomena occurring in the melts, was established on the basis of the experimental data. This model should represent a significant advance to better describe the rheological properties of nuclear glass melt and to improve the vitrification process.

Symposium EF Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant and Sascha Hilgenfeldt

Thursday 8:40 Commonwealth A2

EF21

Buckling of particle-laden interfaces

Theo Kassuga and Jonathan Rothstein

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Particle-laden interfaces have found wide application in modern industry, particularly in the stabilization of emulsions (the so-called Pickering emulsions), and extensive research has been done on their mechanical properties and behavior, including buckling instabilities. However, the buckling of particle-laden interfaces is not yet fully understood. In this talk, we present an investigation of the buckling of an oil-water interface populated by micron-sized latex particles using a Langmuir trough. In our research, we extended results of buckling of particle-laden interfaces from the millimeter down to the submicron range while investigating the effect of a different capillary length on the wavelength of the resulting surface instability. The experimental data was compared to the existing theoretical framework. An unexpected deviation from the prediction of theory of the dominant wavelength of buckling was observed for particles smaller than one micron. Those observations suggest that there is a transition to a new buckling regime involving the formation of trilayers below one micron. Furthermore, we observed cascading of the dominant wavelength similar to that observed in thin polymer films; this had not yet been reported for particle rafts. In addition a series of transitions between wavelengths not observed in thin films was observed within the same particle raft. Lastly, the effect of compression history on the macroscopic arrangement of particles was investigated, along with its effect on the buckling wavelength.

Thursday 9:05 Commonwealth A2

EF22

Generation of stable non-spherical capsules with controlled interfacial coverage of surface-active particles

Anthony P. Kotula¹ and Shelley L. Anna²

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The complex interfaces of particle-stabilized drops and bubbles have a significant effect on the rheology of emulsions and foams. Common high-shear emulsification methods offer no direct control over the rate of droplet generation, the final droplet size distribution, or the composition of the interface, all of which directly impact the rheology of the final emulsion. In this talk, a simple microfluidic device is used to generate monodisperse droplets with independent control of droplet size, production rate, and the degree of particle loading on the interface. Droplets are formed on demand at a T-junction via pressure control of each fluid phase. The freshly formed droplets travel along the axis of a circular capillary containing a surface-active particle suspension. The residence time of the droplets within the capillary and the transport of particles in the thin films and fluid volumes between droplets determine the coverage of particles on the interface. The flow along the axis of the droplet sweeps adsorbed particles to the rear of the droplet, leading to a highly concentrated region of the interface that does not relax upon exiting the confined geometry of the microchannel. The length of the concentrated region increases with particle coverage, producing capsules with shapes from pears to maracas to cylinders. The capsules are monodisperse, can be produced at high rates, and remain stable for tens of hours after formation. Measurements of the dilatational and shear interfacial rheology help rationalize the observations of highly stable non-spherical shapes. Thus, careful control of transport in microscale devices allows for production of emulsions with tunable morphology, interfacial rheology, and bulk rheology.

Thursday 9:30 Commonwealth A2

EF23

Measuring moduli of elastic biofilms at oil-water interfaces by pendant drop method

Liana Vaccari¹, Daniel B. Allan², Nima Sharifi-Mood¹, Jian Sheng³, Robert L. Leheny², and Kathleen J. Stebe¹

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Biofilms form at oil-water interfaces to form viscoelastic layers which evolve with time to form an elastic skin. In this work, we focus on the mechanics of the elastic skin, which we characterize using a pendant drop method modified to quantify anisotropic tensions in thin film layers at the pendant drop surface. The method relies on forming a pendant drop, and allowing the biofilm to assemble on the drop surface. The drop shape is subsequently distorted from this initial state, which is treated as an unstrained base state, with shape determined by the balance of gravity and isotropic tension. The drop is then expanded or contracted, with anisotropic distortion fields and hence tension. Its shape is compared to a theoretical shape determined by integration of the Young Laplace equation for anisotropic tensions related by a constitutive model. Upon expansion, tension in the skin increases, and the drop shape becomes more spherical. Upon compression, the tension decreases, and the drop becomes extended. By comparing theoretical and experimental drop shapes, the Young modulus and Poisson ratio of the biofilm can be extracted, and departures of the biofilm mechanics from simple linear mechanical models (e.g. Hookean membranes) can be elucidated.

Thursday 10:25 Commonwealth A2

EF24

Interfacial rheology and microstructure of carbon nanotubes at an air-water interfaceSahil Vora¹, Brice Bognet², Huseini Patanwala², Francisco Chinesta³, and Anson W. K. Ma²¹*Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States;* ²*Institute of Materials Science, University of Connecticut, Storrs, CT, United States;* ³*Ecole Centrale de Nantes, Nantes, France*

Interface-driven assembly of particles has been demonstrated by a number of authors [1]. The corresponding physics is intriguing and fairly well documented for micron-size particles with a moderate aspect ratio (<10) [2]. Carbon nanotubes (CNTs) are rolled cylinders of graphene sheets with an aspect ratio exceeding 50 and their interfacial behavior remains largely unexplored. In the present work, we investigated the surface pressure, interfacial assembly, and interfacial rheology of both functionalized and non-functionalized CNTs at an air-water interface. Firstly, our findings indicated that both types of CNTs adsorbed strongly at the air-water interface, leading to an increase in surface pressure. Volmer equation of states [3] has been applied to model and understand the surface pressure data. Secondly, the CNT-decorated interface was studied both optically (*in situ*) and with electron microscopy after performing Langmuir-Schaefer deposition. Both types of CNTs showed some degree of orientational ordering upon compression. To quantify the degree of orientation for each type of CNTs, the scalar order parameters were calculated from the electron micrographs. Lastly, we will present our preliminary data on the interfacial shear rheology collected using a double-wall du Noüy ring (DDR) setup. The findings may have implications on the development of more stable emulsions and the production of CNT thin films with controllable packing density and orientational ordering. This work is supported by NSF CAREER award #1253613.

[1] Pieranski, P., Two-dimensional interfacial colloidal crystals. *Phys. Rev. Lett.*, 45(7), 569-572 (1980). [2] Lewandowski, E.P. *et al.*, Orientation and self-assembly of cylindrical particles by anisotropic capillary interactions. *Langmuir*, 26(19), 15142-15154 (2010). [3] Fainerman, V.B. *et al.*, Surface-pressure isotherms of monolayers formed by microsize and nanosize particles. *Langmuir*, 22(4), 1701-1705 (2006).

Thursday 10:50 Commonwealth A2

EF25

Flow behavior of Janus monolayersSepideh Razavi¹, Surita R. Bhatia², and Ilona Kretzschmar¹¹*Chemical Engineering, City College of the City University of New York, New York, NY, United States;* ²*Stony Brook University, Stony Brook, NY, United States*

Amphiphilic particles, so-called Janus particles, are believed to bind more strongly to interfaces and are a potential precursor to breathable interfacial skin with applications in reactive emulsions. Since emulsions have a very large surface-to-volume ratio, their stability strongly depends on the flow behavior of the stabilizing agents. In the case of Pickering emulsions the stabilizing agents are colloidal particles. Despite the vast literature on the rheology of colloidal bulk suspensions, little is known about the impact of particle amphiphilicity on the flow behavior of particle-laden interfaces and even less information is available linking the rheological measurements to studies on emulsion stability. We have investigated the flow behavior of interfaces decorated with colloidal particles to examine the impact of particle wettability and amphiphilicity on the viscoelastic nature of these interfacial films and checked for the correlation between interfacial rheology and superior emulsion stability. Our experiments have investigated the variation of the dynamic surface modulus with changing surface concentration, wettability, amphiphilicity and interaction of particles.

Thursday 11:15 Commonwealth A2

EF26

Co-continuous polymer blends with silica nanoparticles stabilized at interfaceLian Bai, Christopher W. Macosko, and Xiang Cheng*Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455-0132, United States*

We describe an approach to prepare co-continuous polymer blends with interfacial silica nanoparticles via spinodal decomposition. Blends of polystyrene oligomer and polybutene with fluorescent hydrophobic silica nanoparticles were quenched to below their upper critical solution temperature. Beyond a critical loading of nanoparticles, a micron-sized co-continuous morphology is stabilized by aggregation of nanoparticles at the interface. Real time observation of particle dynamics during the coalescence is achieved via laser scanning confocal microscopy. Through these dynamics, we revealed mechanism by which the interfacial silica nanoparticles suppress the coalescence and stabilize the morphology.

Thursday 11:40 Commonwealth A2

EF27

PIV measurement of transient fluid flow due to the adsorption of particlesNaga A. Musunuri, Pushpendra Singh, and Ian S. Fischer*Mechanical and Industrial Engineering, New Jersey Institute of Technology, Newark, NJ 07102, United States*

The particle image velocimetry (PIV) technique is used to study the physics of particle adsorption and the spontaneous dispersion of powders that occurs when particles come in contact with a fluid-liquid interface. The dispersion can occur so quickly that it appears explosive, especially for small particles on the surface of mobile liquids like water. The measurements show that the adsorption of a spherical particle causes an axisymmetric streaming flow about the vertical line passing through the center of the particle. The fluid directly below the particle rises upward, and near the surface, it moves away from the particle. The flow, which develops within a fraction of second after the adsorption of the particle, persists for several seconds. The flow strength, and the volume over which it extends, decrease with decreasing particle size. The streaming flow induced by the adsorption of two or more particles is a combination of the flows which they induce individually.

Poster Session

Symposium PO Poster Session

Organizers: John Dorgan, Seher Ozkan and Matthew D. Reichert

Wednesday 6:05 Poster

PO1

The non-monotonic torque response of a model cellulosic biomass slurry during settling and resuspension

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The conversion of biomass, specifically lignocellulosic biomass, into fuels and chemicals has the potential to provide renewable alternatives to those derived from fossil carbon sources (oil, natural gas, and coal). Biochemical conversion involves several processing steps in which aqueous biomass suspensions of varying solids content must be transported. Due to the complex morphology and surface chemistry of the biomass particles, many interesting nonlinear flow behaviors have been observed. An increased understanding of these behaviors will help engineers develop cost-effective reactor designs and slurry transport schemes.

Here we present the global rheology of non-Brownian particles (α -cellulose; 100 μm average diameter, density of 1.5 g/cm^3) in a suspending liquid (DI water) that is not density-matched. A stress-controlled rheometer equipped with a vane fixture was used to measure the nonlinear rheological behavior of the negatively buoyant particle dispersion. During the stepped velocity ramp of the vane, a bifurcation of the torque response was observed in which a critical mixing speed can be extracted. Sedimentation occurs below this speed and above this speed the suspension is homogenized. Additionally, a hysteresis in the torque signal was observed between the ramp up and ramp down of the vane speed. The hysteresis effect is highly dependent on the initial condition of the slurry (i.e., if the slurry begins in the fully-settled or fully-suspended state) and the gap spacing between the outer edge of the vane and the inner wall of the outer cylinder. Using a large-gap setup (>10 mm), the observed hysteresis is exacerbated due to a radially dependent particle concentration gradient. However, we found that the hysteresis can be eliminated by shrinking the gap spacing. The experimental observations discussed here will help validate ongoing computational fluid dynamics and kinetics modeling efforts for improved reactor design.

Wednesday 6:05 Poster

PO2

An investigation on rheological behaviour of thermally-treated digested sludge: Dependency on solid concentration

Ehsan Farno

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Municipal sludge is a suspension of agglomerated particles in a watery medium. The anaerobic digested sludge comes from anaerobic digesters exhibit shear thinning behaviour which severely depends on temperature. This study investigated the effect of temperature and duration of heat treatment on rheological properties of different concentration of digested sludge. The flow curve and the yield stress of 2%, 3% and 3.5% digested sludge have been measured before and during heat treatment at different temperatures between 20 and 80°C for different heating duration of 1, 15 and 30min. The effect of thermal history on rheology of sludge was then studied after cooling back sludge to 20°C (thermal history at 50, 60, 70 and 80°C). In addition, the effect of temperature and thermal history on solubilized chemical oxygen demand (COD) for sludge with different solid concentration was also investigated to prove the composition change of sludge during the heat treatment. The result showed that the irreversible effect of temperature was more evident at higher temperatures and concentrations. At higher concentrations (3% and 3.5%), by increasing the temperature, the yield stress decreased after an initial increase while for 2% sludge yield stress consistently decreased with increasing temperature and showed a linear relationship with decreasing particulate COD. The liquor viscosity also showed an increase in viscosity of sludge liquid medium after cooling a 30min-longer thermally-treated sludge to 20°C. The yield stress followed a great agreement with an exponential decreasing function of temperature and temperature of thermal history. A Herschel-Bulkley equation was successfully used for predicting the flow curve of sludge after, before and during the heat treatment. A modified exponential equation was successfully used to predict the flow curve of sludge with different thermal histories.

Wednesday 6:05 Poster

PO3

Phase behavior of dilute carbon black suspensions and carbon black stabilized emulsionsMichael P. Godfrin¹, Ayush Tiwari², Arijit Bose³, and Anubhav Tripathi¹¹Center for Biomedical Engineering, School of Engineering, Brown University, Providence, RI 02891, United States;²Department of Civil Engineering, Thapar University, Patiala, India; ³Department of Chemical Engineering, University of Rhode Island, Kingston, RI 02881, United States

We use para-amino benzoic acid terminated carbon black (CB) as a tunable model particulate material to study the effect of inter-particle interactions on phase behavior and steady shear stresses in suspensions and particle-stabilized emulsions. We modulate inter-particle interactions by adding NaCl to the suspension, thus salting surface carboxylate groups. Surprisingly, yield stress behavior emerged at a volume fraction of CB as low as $\phi_{CB} = 0.008$, and gel behavior was observed at $\phi_{CB} > 0.05$, well below the percolation threshold for non-interacting particles. The yield stress was found to grow rapidly with carbon black concentration suggesting that salt-induced hydrophobicity leads to strong inter-particle interactions and the formation of a network at low particle concentrations. The yield stresses of CB-stabilized emulsions also grows rapidly with carbon black concentrations, implying that inter-droplet interactions can be induced through the tuning of carbon black concentration in emulsion systems. Emulsions stabilized by ionic surfactants show no inter-droplet interactions. In contrast, oil droplets in the CB-stabilized emulsion move collectively or are immobilized because of an interconnected CB network in the aqueous phase. These results for dilute CB suspensions or CB-stabilized emulsions in salt water provide basis for aqueous particulate systems with tunable surface functionality and network structure.

Wednesday 6:05 Poster

PO4

Damping of sloshing of a liquid bath using a thin foam layerFrançois Boulogne, Alban Sauret, Jean Cappello, and Howard A. Stone

Princeton University, Princeton, NJ, United States

The dynamics of sloshing, i.e. the movement of the free interface of a liquid, is induced by variations of the velocity of the container. Such phenomenon can lead to crucial technical constraints in various applications such as the transportation of oil and liquefied gas in cargoes or the sloshing of propellants in rocket engines. Therefore, a method to damp the oscillations of the free surface is required to improve the safety of liquid transport. In this work, we study experimentally the effect of a liquid foam placed on the top of a liquid bath in a Hele-Shaw cell on the sloshing dynamics. Two methods to generate interfacial waves are considered: (1) an impulse response or (2) a continuous oscillation of the container. Using the first method, we obtain the natural frequencies of oscillations as well as the damping coefficient of the amplitude of the waves. The second method provides us the amplitude of the interface for varying frequencies of oscillations. First, we ensure that our experimental results for a single Newtonian fluid are in agreement with results from the literature. Then we generate a monodisperse 2D liquid foam on the top of the liquid bath. Taking advantage of the 2D foam, we track the motion of the foam to obtain the velocity and the strain fields for various foam thicknesses. Qualitative observations exhibit a viscoelastic response of the foam without plastic deformation. Moreover, 2 to 3 layers of bubbles already lead to a significant damping of the interfaces. For more than 5 layers of bubbles, the original vertical motion of the foam becomes mainly horizontal. We rationalize our experimental findings with a model that describes the foam contribution to the damping coefficient. Our model, based on the dissipation in Plateau borders, involves the interfacial rheology of the foamy solution. Our results suggest that thick foams constitute an easy to implement and low-cost method to minimize sloshing dynamics in liquid transport.

Wednesday 6:05 Poster

PO5

Electric field induced self-assembly of monolayers of sub-micron sized particles on flexible thin filmsKinnari Shah¹, Md.Shahadat Hossain², Edison C. Amah³, Ian S. Fischer³, and Pushpendra Singh³¹Mechanical Engineering, New Jersey Institute of Technology, Newark, NJ 07102, United States; ²Engineering Technology, City University of New York, New York, NY 11364, United States; ³Mechanical and Industrial Engineering, New Jersey Institute of Technology, Newark, NJ 07102, United States

We present a technique that uses an electric field in the direction normal to the interface for self assembling particle monolayers of sub-micron sized particles on fluid-liquid interfaces and freezing these monolayers onto the surface of a flexible thin film. The electric field gives rise to dipole-dipole and capillary forces which cause the particles to arrange in a triangular pattern. The technique involves assembling the monolayer on the interface between a UV-curable resin and another fluid by applying an electric field, and then curing the resin by applying UV light. The monolayer becomes embedded on the surface of the solidified resin film.

Wednesday 6:05 Poster

PO6

Food emulsions, interfacial properties measured with the Double Wall Ring geometryCarlos A. Gracia-Fernández¹, Aadil Elmoumni¹, Alfonso Pérez-Quintáns², and Juan Méndez-Dónega²¹TA Instruments, New Castle, DE 19720, United States; ²Aula de Productos Lacteos, University of Santiago de Compostela, Lugo, Lugo 27004, Spain

The rheological characterization of thin liquid layers at interfaces is motivated by their intensive use in a variety of industries, ranging from enhanced oil recovery, food technology to biomedical applications. The most used devices for measuring interfacial properties that can be attached to a commercial rheometer are the Du Noüy ring, disc and bi-cone geometry. The Du Noüy ring is only suitable for purely viscous interfaces. The bi-cone and disc geometries can be used for viscous and viscoelastic interfaces, but the sensitivity is limited because these devices intrinsically

possess a large area in contact with the bulk fluids. Newly developed Double Wall Ring (DWR) geometry is used with a standard rotational rheometer to characterize both viscous and viscoelastic properties of interfaces. It has the advantages of a good intrinsic sensitivity due to a small area in contact with the bulk phase and well defined flow fields that enable bulk and surface contributions to be separated. The double-wall ring geometry has a square edged cross-section and is used with a temperature controlled bottom circular channel arrangement to contain the fluid. Results on model interfaces show that the new geometry is able to measure viscous as well as visco-elastic interfaces in both continuous and oscillatory shear experiments. In this work, we used the DWR to study the interfacial viscoelastic properties of two food emulsifiers. One is a low molecular weight Monoglyceride and the other is a high molecular weight Sodium Caseinate Protein. Both are emulsifiers widely used in the food industry. One of the main applications of these emulsifiers is the stabilization of food emulsions. Analysis of their mechanical properties will be shown along with the evolution of interface formations due to the molecules' migration to the water/oil interface. Structural information of both interfaces will be compared.

Wednesday 6:05 Poster

PO7

Rheological characterization of a UV curing optical adhesive

Carlos A. Gracia-Fernández and Aadil Elmoumni

TA Instruments, New Castle, DE, United States

Ultraviolet curing (commonly known as UV curing) is a photochemical process in which high-intensity ultraviolet light is used to instantly cure or "dry" inks, coatings or adhesives. UV curing has been shown to increase production speed, reduce reject rates, improve scratch and solvent resistance, and facilitate superior bonding. Using light instead of heat, the UV curing process is based on a photochemical reaction. Liquid monomers and oligomers are mixed with a small percent of photoinitiators, and then exposed to UV energy. In a few seconds, the products - inks, coatings or adhesives instantly harden. Rheology is a valuable technique that can provide information about flow properties before the curing, Suitability of the curing cycle, Adhesive properties of the cured film, gel time, rate of Curing, shrinkage during the curing process, stiffness of the cured film.... The adhesive used in this work is a Norland Optical Adhesive 61 ("NOA 61"). This adhesive is a clear, colorless, liquid photopolymer that will cure when exposed to ultraviolet light. A high-pressure mercury lamp UV light source. Provides a broad range of spectrum from 250nm - 600nm with a primary peak at 365 nm with maximum output intensity of 300 mW/cm². A LED system that Provide single wavelength available at 365nm and 455nm with maximum output intensity of 150mW/cm² and 350mW/cm² respectively The experiments were made at room temperature. The intensities used were 0.3, 1, 15, 50 and 150 mW/cm². Gel time, and final viscoelastic modulus were measured for all the intensities and type of UV sources. UV curing adhesives are typically used in thin films, because most do not cure well in thick sections or if they do, the stress due to shrinkage becomes a problem. So, to monitorize the shrinkage behaviour during the rheological experiment is a valuable technique to get information of the final properties of the adhesive.

Wednesday 6:05 Poster

PO8

The effects of emulsifying additives on the interface of oil and water

Sarah Cotts

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Emulsions of oil and water are widely used in many industries, including personal care, food and pharmaceuticals. Although such emulsions are ubiquitous, they are thermodynamically unstable systems. Over time, the dispersion will break down via processes such as creaming, sedimentation, flocculation and coalescence. In order to stabilize emulsions of oil and water over time, amphiphilic surface-active molecules must be included in formulation.

Surfactants can act as emulsifiers by forming an adsorbed layer between the oil and water phase, decreasing the interfacial tension. The presence of surfactants at the interface makes droplets more deformable and lowers the energy needed for dispersion. Polymeric emulsifiers, typically proteins, also form an adsorbed layer at the oil-water interface. Unlike surfactants, protein emulsifiers form a viscoelastic interface that stabilizes the emulsion against coalescence.

Traditionally, bulk rheological properties have been used to evaluate the effect of emulsifiers in formulations. Recently, interfacial rheology has been used to study the effect of emulsifiers on the viscoelastic properties of the oil and water interface, excluding contributions from the bulk phases.

This work examines the properties of several commercially-available surfactants and proteins for emulsifying personal care products. In addition to the rheological properties of the emulsions, interfacial rheology is used to characterize the time scale of adsorption of the additives and the viscoelastic properties of the interface.

Wednesday 6:05 Poster

PO9

Effect of material rheology on polymer blend thin film morphology

Jillian A. Emerson, Eric M. Furst, and Thomas H. Epps, III

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

Polymer blends offer a promising and economically viable route to creating materials for a variety of applications including coatings, membranes, and optoelectronics. For these applications, the final material performance is strongly dependent on the morphology of the polymer blends. Thus, knowledge of processing effects on phase separation and the resulting blend morphology is vital to improving the viability of polymer blend materials. In this work, we use the material rheology to predict phase separation in thin films cast by spin coating blends of poly(3-hexylthiophene) [P3HT] with polystyrene [PS]. We compare the experimentally captured drying curves with spin coating models. Meyerhofer extended early flow-

based models for spin coating^{1,2} to incorporate the effect of evaporation on film thinning.³ This model describes the competition between loss of solution from the substrate (outflow) and loss of solvent (evaporation) for a given angular velocity and initial polymer concentration. The deviation of our data from Meyerhofer's model is explained in the context of phase separation during spin coating (*i.e.* the onset of phase separation changes the flow properties). Comparing the onset of phase separation with the polymer/polymer/solvent phase diagram allows us to better understand the relationship between processing conditions and equilibrium phase behavior. Control over phase separation processes during casting and final morphology may be afforded by tuning the viscosity, spin speed, and evaporation rate to promote outflow or evaporation. This work highlights the importance of understanding the material rheology in the context of phase separation during casting to control blend morphologies in thin film geometries.

[1] Emslie, A. G.; Bonner, F. T.; Peck, L. G. J. of Appl. Phys. 1958, 29, (5), 858. [2] Acrivos, A.; Shah, M. J.; Petersen, E. E. J. of Appl. Phys. 1960, 31, (4), 963. [3] Meyerhofer, D. J. of Appl. Phys. 1978, 49, (7), 3993.

Wednesday 6:05 Poster

PO10

Investigation of rheological properties of emulsified asphalts to evaluate viscoelastic behaviors

Amir Gopalipour¹ and Delmar Salomon²

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Emulsified asphalt is widely used as a pavement material used to resurface pavements and extend their useful life. They are environmentally friendly, safe and cost effective [1]. Current purchase specifications uses traditional and empirical viscosity, penetration and ductility test methods that are unrelated to their performance[2]. The rheological properties of emulsified asphalts can be used as a key performance specification and quality control parameter for manufacturers and state agencies to monitor emulsified asphalt production and performance. Therefore, in this study, rheological properties for different emulsion families (slow, medium, and rapid sets; anionic and cationic) are investigated to follow their workability, breaking and curing characteristics. To evaluate the breaking properties, Amplitude sweep test is conducted to define Linear Viscoelastic Range (LVE) of these materials. Cylindrical geometry (Bob & Cup fixture) is used to accommodate the low viscosity of emulsified asphalts and avoids any trimming of the sample compared to the use of parallel plates. Strain level is changed from 0.1% to 100% and the G' and G'' are monitored to define the most important properties such as Apparent yield point (G' starts to decrease) and Cross-over between G' and G'' (flow point). Furthermore, Thixotropy test is used to simulate spraying, setting and curing emulsions in one test. The preliminary results indicated that rheological properties can be a useful tool to predict the stability of emulsified asphalts and differentiate between the different family of emulsions. The rheological tests, designed to simulate emulsified field applications, can generate useful information to understand the breaking and setting behavior of the different emulsified asphalt applications such as chips seals, fog seals, and microsurfacing.

[1] Emulsified asphalt: A Basic Emulsified asphalt Manual, Manual Series No. 19, Third Edition, Asphalt Institute and Emulsified asphalt Manufacturers Association. [2] AASHTO T 59

Wednesday 6:05 Poster

PO11

Validation of effective time translational invariance for polymer undergoing crosslinking reaction

Manish Kaushal and Yogesh M. Joshi

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In polymeric liquids undergoing crosslinking reaction rheological properties continuously change as a function of time. Consequently, the materials do not obey the time translational invariance and therefore the principles of linear viscoelasticity. In this work we propose a methodology in which principles of linear viscoelasticity are transformed from the real time domain to the effective time domain. In the latter the readjustment of the material clock, which accounts for the time dependency, facilitates validation of the effective time translational invariance. By carrying out experiments on crosslinking PDMS, we show that material that is undergoing time evolution in the real time domain indeed validates Boltzmann superposition principle and convolution relation relating creep compliance and relaxation modulus in the effective time domain.

Wednesday 6:05 Poster

PO12

Standard and developmental methods for performing rubber rheometry

Gregory W. Kamykowski and Thomas R. Rauschman

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The rheological characterization of rubber - before, during, and after curing - has been performed by standard test procedures for many years on rheometers designed specifically for testing rubber. Uncured rubbers and rubbers that have begun curing have been characterized on Mooney viscometers to get the Mooney viscosity, stress relaxation modulus following flow, and scorch times (ASTM D1646). One way of extending knowledge of the molecular architecture of unvulcanized materials is simply to test the material over a range of speeds, e.g., 0.1 to 10 rpm, instead of the standard 2 rpm. Dynamic testing has also been performed on unvulcanized, curing, and post-curing materials. Dynamic frequency sweeps have been performed on unvulcanized materials to characterize the elastomers in this state. Curing kinetics can be studied by monitoring the Elastic Torque, S', as a function of time, and scorch times at various degrees of curing can be tabulated. Post-cure strain sweeps can then be performed. Recent advances in Large Amplitude Oscillatory Shear (LAOS) testing and reporting have extended the testing capabilities of rubber rheometers to more clearly differentiate cured materials that are similar in testing but different in production. In this poster, the general designs of rubber rheometers will be shown, as well as typical results, with common nomenclature from the rubber industry, of standard rubber testing.

Examples of how additional testing, such as viscosity versus shear rate, frequency sweeps, time-temperature superposition, and LAOS will be given.

Wednesday 6:05 Poster

PO13

Shear rheology of imidazolium-based ionic liquids with aromatic functionality

Ran Tao and Sindee L. Simon

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As a material class, ionic liquids possess attractive properties and have a wide range of potential uses. In this work, a series of imidazolium-based ionic liquids with varying functionalities from aliphatic to aromatic groups and a fixed anion were characterized using shear rheology. The empirical Cox-Merz relationship between the steady shear viscosity and the dynamic viscosity is examined. The temperature dependence of shift factors used for constructing the dynamic moduli reduced curves follows the expected WLF relationship, and the dynamic fragility is calculated and compared to the fragility obtained from calorimetry. The slope for the storage modulus $d(\log G')/d\omega$ of the ionic liquids deviates from the expected value of 2.0 for Maxwell behavior. The retardation spectra are calculated and compared for the series of ionic liquids.

Wednesday 6:05 Poster

PO14

Investigation of thermal transport in polymers using infrared thermography

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The anisotropic nature of thermal transport in flowing polymers plays an important role in the processing and the final properties of polymeric materials. In previous work we have investigated anisotropic thermal conductivity in polymers subjected to deformation using an optical technique based on Forced Rayleigh Scattering (FRS). This technique allows for the measurement of the components of the thermal conductivity tensor in different polymer systems under several types of deformations. We have found that there exists an apparently universal relationship between the thermal conductivity and stress tensors, known as the stress-thermal rule. More recently, we have developed a novel technique based on Infrared Thermography (IRT) that complements FRS and allows for the study of a wider range of polymeric materials. We validate IRT technique by comparing measurements of anisotropy in thermal conductivity on cross-linked networks against those obtained with FRS. Additionally, the study of transient IRT experiments allows us to investigate the heat capacity dependence on deformation. We find that heat capacity increases with stretch ratio in lightly cross-linked cis 1,4-polyisoprene specimens subjected to uniaxial extension. This deviation from the equilibrium value of heat capacity is consistent with an independent set of experiments comparing anisotropy in thermal diffusivity and conductivity employing FRS and IRT techniques.

Wednesday 6:05 Poster

PO15

Polylactic acid nanocomposites with improved toughness

Eda Acik¹, Nese Orbey², and Ulku Yilmazer¹

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Owing to the environmentally positive effects of biodegradable polymers and composites, it is imperative to improve the properties of polymers through the addition of nanofillers. The application of poly (lactic acid) (PLA) is mainly limited by its low fracture toughness. In the present work, the effect of using compatibilizers and nanoclays on the morphology and the rheological properties of PLA is studied. Two compatibilizers with different functional groups, namely ethylene-glycidyl methacrylate (E-GMA) and ethylene-butyl acrylate-maleic anhydride (E-BA-MAH) and three different organically modified layered silicates were used. Samples were prepared using a twin screw extruder. The rheological properties were characterized by dynamic oscillatory measurements in the melt state. The morphology of the nanocomposites was investigated by XRD and TEM. The dispersion of the nanoclay in the PLA matrix is highly affected by the type of organic modifier in the clay. Even though the nanocomposites have intercalated and exfoliated layers with some tactoids, the degree of intercalation is determined by the chemical compatibility between the polymer matrix and the modifier. Experimental methodology and the results obtained will be presented.

Wednesday 6:05 Poster

PO16

Viscoelastic behavior of zinc sulfonated EPDM- zinc stearate (ZnSt) shape memory polymers

Chongwen Huang and R. A. Weiss

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Blends of a low molecular weight fatty acid or fatty acid salt (FA) with an ionomer exhibit thermal-activated shape memory behavior¹. One shortcoming of this system is that the "permanent network" formed from nanodomains of the metal sulfonate groups, exhibits relaxes when the material is maintained in a temporary shape for a long time. This paper describes the viscoelastic behavior of blends of sulfonated poly[ethylene-r-propylene-r-(5-ethylidene- 2-norbornene)] (SEPDm) with zinc stearate (ZnSt) with and without covalent crosslinking. Specifically, the creep compliance was measured as a function of temperature and ZnSt concentration by dynamic mechanical analysis (DMA) and compared with the shape memory behavior. Time temperature superposition (TTS) was adopted to used to analyze and predict long time creep deformation. Covalent crosslinking suppresses the non-recoverable viscous deformation of the ionic network, which greatly improves the shape memory performance.

Reference: 1. Weiss, R. A.; Izzo, E.; Mandelbaum, S. *Macromolecules* 2008, 41, (9), 2978-2980.

Wednesday 6:05 Poster

PO17

Linear viscoelasticity and dielectric spectroscopy of ionomer/plasticizer mixtures: A transition from ionomer to polyelectrolyteNanqi Bao¹, Quan Chen², Jing-Han Helen Wang¹, Tyler Tunic¹, Siwei Liang³, and Ralph H. Colby¹¹*Penn State University, State College, PA, United States*; ²*Department of Materials Science and Engineering, Penn State University, State College, PA 16802, United States*; ³*Lawrence Berkeley National Laboratory, Berkeley, CA, United States*

For ionomers, unfavorable interaction between highly polar ion pairs and low polarity polymer medium drives their ionic groups to aggregate. In contrast, for polyelectrolytes, the counterions prefer solvation in the polar medium, leaving the chain with a net charge, and its conformation is strongly stretched locally due to charge repulsion. This study examined the ionomer to polyelectrolyte transition for ethylene oxide (EO) based ionomers upon introducing oligomeric plasticizer. To obtain the ionomers, sodium sulfonated styrene (SSNa) monomer and neutral methacryl-monomer having different number of EO units (EO2, EO5, and EO9) in the side chain were copolymerized via reversible addition fragmentation chain transfer (RAFT) polymerization. The mole percent of SSNa monomer was adjusted to keep the EO:SSNa ratio between 17 and 20. The ionomer with shorter EO side chains has more exposed ionic groups to aggregate, with ionic dissociation and chain relaxation more strongly delayed. Addition of sufficient amounts of oligomeric plasticizer, with 6 EO groups and cyclic carbonate end groups, negates this difference; similar relaxation rates were finally observed for samples having different side chains when these are solutions of polyelectrolytes.

Wednesday 6:05 Poster

PO18

Optical observations and Raman spectroscopy during flow-induced crystallization of polyethyleneAnthony P. Kotula¹, Angela Hight Walker², and Kalman B. Migler¹¹*Materials Science & Engineering, NIST, Gaithersburg, MD 20899, United States*; ²*Physics Laboratory, NIST, Gaithersburg, MD, United States*

The crystallization of polymer melts under flow is critically relevant to the polymer processing industry. Optical, thermal, and mechanical properties of semi-crystalline polymer products depend on the final crystallinity of the material, which depends on the structure and orientation of the initial molecular-scale crystal nuclei formed in flow. Here, we present a combination of optical microscopy and Raman scattering techniques to analyze structure formation in high density polyethylene during steady shear at low degrees of undercooling. When low shear rates ($\sim 1 \text{ s}^{-1}$) are imposed after a temperature quench to less than $10 \text{ }^\circ\text{C}$ undercooling, fibrous structures aligned parallel to the flow direction appear over a period of minutes. Raman spectra indicate that the fibers have a non-crystalline structure that is different from the melt phase. This fibrous structure is compared with structural changes in the melt phase during quiescent crystallization at similar degrees of undercooling to examine the effects of shear on polymer crystallization.

Wednesday 6:05 Poster

PO19

Modelling of synthesis and flow properties of propylene-diene copolymersChinmay Das¹, Daniel J. Read¹, Johannes M. Soulages², and Pradeep P. Shirodkar³¹*School of Mathematics, University of Leeds, Leeds LS2 9JT, United Kingdom*; ²*Corporate Strategic Research, ExxonMobil Research and Engineering Company, Annandale, NJ 08801, United States*; ³*Global Chemical Research, ExxonMobil Chemical, Baytown, TX 77520, United States*

Copolymerisation with non-conjugated dienes offers an attractive route for introducing long-chain branching in polypropylene. From a simplified set of rate equations for such copolymerisation with a metallocene catalyst, we derive the probabilities of branch formation at different stages of the reaction in a semi-batch reactor¹. Using these probabilities, we generate an ensemble of molecules via a Monte Carlo sampling. The knowledge of the branching topology and segment lengths allows us to compute the flow properties of the resins from computational rheology². We compare our model predictions with existing experimental data³, namely the molar mass distribution and small angle oscillatory shear response, for a set of resins with varying diene content. The rheology data suggests that the entanglement time τ_e depends sensitively and in a well-defined fashion on the diene content.

[1] Das, C.; Read, D. J.; Soulages, J. M.; Shirodkar, P.P.; *Macromolecules*, dx.doi.org/10.1021/ma5011205 (2014). [2] Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B.; *J. Rheol.*, **50**, 207-235 (2006). [3] Ye, Z.; AlObaidi, F.; Zhu, S.; *Ind. Eng. Chem. Res.*, **43**, 2860-2870 (2004).

Wednesday 6:05 Poster

PO20

Mechanically robust anion exchange membranes at variable hydrationsMelissa A. Vandiver¹, Benjamin R. Caire¹, Yifan Li², Daniel M. Knauss², Andrew M. Herring¹, and Matthew W. Liberatore¹¹*Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States*; ²*Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States*

Anion exchange membranes facilitate ion transport in polymer electrolyte membrane fuel cells. An AEM must have a high ionic conductivity, low gas/fuel crossover, and be chemically and mechanically stable over the lifetime of the fuel cell. Development of thin polymer films is critical to reduce membrane resistance, however as membrane thickness is decreased, maintaining membrane integrity is increasingly difficult. Additionally, humidity changes during fuel cell operation cause sorption and desorption of water in the polymer. Repeated swelling and contraction puts significant stresses on the membrane and can lead to cracks, pinholes, and eventual membrane failure. Many AEM polymers become stiff

and brittle when cationic functionalities are added to the polymer matrix, but still suffer softening and integrity loss at hydrated conditions. A new polyethylene-b-poly(vinylbenzyl trimethylammonium) diblock AEM has been synthesized that has improved stability over a range of hydrations. Extensional tests of the polyethylene diblock were performed under dry and saturated gas conditions. Other studies of the polyethylene diblock will cycle humidity while measuring modulus to determine how mechanical properties change over time in a working fuel cell. Advanced knowledge of AEM mechanical properties will aid in design of robust membranes to improve fuel cell lifetime.

Wednesday 6:05 Poster

PO21

Rheological evaluation of hydroxypropyl methylcellulose (HPMC) as a gluten replacer during a simulated baking process

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Gluten is a protein fraction endogenous to wheat flours that provides extensibility and gas cell retention in doughs of bread and other baked goods. Hydroxypropyl methylcellulose (HPMC) has been extensively used to replace gluten in gluten free bread, as this cellulosic ether polymer has a unique thermal gelation property, along with the ability to promote gas cell formation and retain moisture in baked goods. Baking bread is a dynamic process, with significant moisture loss, starch gelatinization and protein denaturation, along with flavor and texture development. A novel rheological method has been developed to better understand the functionality of gluten replacers such as HPMC and xanthan gum during the baking process, and to identify the optimal structure and chemistry of the ideal cellulosic-based gluten replacer. Our rheological studies have shown that with adding different types of HPMC, the mechanical strength (G') of the dough has increased. The elasticity of the dough has improved (i.e. $\tan \delta$ lower). In addition, the thermal gelation property of HPMC helped to improve water retention during the simulated baking process. The rheological test results have shown that the baked bread behaved much softer compare with control dough without HPMC.

Wednesday 6:05 Poster

PO22

Degradation of covalently adaptable hydrogels manipulating their chemical equilibrium

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Covalently adaptable (CA) hydrogels are important materials that can accelerate the engineering of biomaterials. These hydrogels mimic the native extracellular matrix that cells experience in vivo due to their ability to adapt to their environment. The CA hydrogels are made from hydrazone bonds and the bonds ability to break and rearrange depends on pH, elastic moduli and equilibrium constants. We use multiple particle tracking (MPT) to measure the dynamic material properties during cross-link breakage and reformation in the CA hydrogels. This technique measures the trajectories of 1 μ m diameter particles in the CA hydrogel to calculate the mean squared displacements (MSD) at different times during gel degradation. The pH values studied for the CA hydrogels were at stomach pH of 4.3 and physiological pH, 7.1. The CA hydrogel in a pH 4.3 buffer degrades over 2 days and has a smooth transition through time from a gel to a sol. The pH 7.1 progresses through the gel-sol transition in 2 days, but MPT measures breaking and reforming of bonds throughout the entire gelation reaction until day 10 when complete dissolution of the matrix occurs. Reverse time-cure superposition (RTCS) is a method of measuring the degradation of the cross-links in the hydrogel. RTSC is used to determine the critical degradation time and critical relaxation exponent which identifies the gel point and the type of network. The pH values tested gives insight on how to use CA hydrogels degradation in biologically relevant pH environments. CA hydrogels will enable unprecedented environments for cell growth because they yield to cells as they differentiate but reform bonds enabling traction during motility.

Wednesday 6:05 Poster

PO23

Effects of association strength of noncovalent bonding on viscoelasticities of supramolecular polymer gels

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Polymer gels are the most versatile soft materials and typically include melt polymer networks at the molecular level, usually containing a large amount of solvents. Precisely designed supramolecular polymer gels built up of supramolecular networks are expected to represent thermo-responsive behavior due to weak association strength of noncovalent bonding. However, thermoresponsiveness of the gels will be lost easily if the volatile solvents evaporate. To solve such a problem, we proposed the use of an ionic liquid as a nonvolatile solvent for preparation of the gels. In this research, supramolecular polymer gels were prepared by blending triblock copolymer and multifunctional cross-linker in an ionic liquid and were investigated effects of association strength of noncovalent bonding on the viscoelasticities. Supramolecular polymer gels composed of poly(4-vinylpyridine)-b-poly(3, 4, 5-trimethoxystyrene)-b-poly(4-vinylpyridine) triblock copolymer (PTP) and poly(4-hydroxystyrene) (H) in an ionic liquid (IL). The weight ratio of PTP:H:IL was varied as 10:X:90 for preparing the gels. To evaluate the effects of association strength, the blends composed of PTP, poly(4-vinylbenzoic acid) (B), and IL were also prepared for comparison. Temperature-ramp oscillatory shear measurements revealed that the storage modulus G' of most of samples was larger than the loss modulus G'' at room temperature, whereas $G' < G''$ at high temperatures, indicating those samples are thermoresponsive gels. Dynamic frequency sweeps were also run, where shift factors were estimated, against temperature when preparing master curves of G' and G'' as a function of reduced frequency. Flow activation energies, E_a , were estimated for all samples at high temperature range, revealing E_a for PTP/B gels is lower than that for PTP/H gels at the same stoichiometric ratio of Bronsted acid to pyridine. These results were attributed to the higher association constant of a benzoic acid-pyridine pair (~150) than that of a phenol-pyridine pair (~50).

Wednesday 6:05 Poster

PO24

Rheology and end-use properties of acrylic polymers for high performance elastomeric sealantsCatheryn L. Jackson¹, Johnpeter Ngunjiri¹, Prasanna K. Jog², Audrey Liss², Jennifer R. Lowe², Mark Westmeyer², Joseph Rubini², and Michael McGinnis²¹Core R&D Analytical Sci, Dow Chemical, Collegeville, PA 19426-2914, United States; ²Construction Chemicals, Dow Chemical, Collegeville, PA 19426, United States

The gap sealants used in construction applications can be polyurethane, silicone or acrylic based, but acrylic sealants can be preferred due to their low volatile organic compound (VOC) level, water based composition, plasticizer-free formulation capabilities and low cost. Other desirable properties include durability over a broad service temperature range, good adhesion, and a non-tacky surface to prevent dirt pick-up. Recent improvements in acrylic polymer design have led to sealants with better flexibility at low temperature (-30 deg C) while maintaining a low-tack surface at room temperature, properties that are often mutually exclusive. Dynamic mechanical analysis (DMA) and atomic force microscopy (AFM) have been key to characterize a family of acrylic latexes based on an innovative two-phase particle structure. This combination of soft and hard properties leads to polymers with a more constant modulus over the entire temperature use range (-30 to +60 deg C) and originates from a morphology of hard particles embedded in a continuous soft phase.

Wednesday 6:05 Poster

PO25

Rheology and microstructure of phase separating blends filled with graphene and carbon blackMuhammad Z. Iqbal¹, Ahmed A. Abdala², and Matthew W. Liberatore¹¹Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States; ²Chemical Engineering, The Petroleum Institute, Abu Dhabi, Abu Dhabi 2533, United Arab Emirates

The effects of thermally reduced graphene and carbon black on phase separation dynamics of polyethylene/oxidized polyethylene blends are studied using the melt rheology and segmental dynamics. The graphene and carbon black were incorporated in single phase material via solution blending and the composites were then allowed to phase separate in situ. The thermodynamics of the phase separation have been investigated by studying the evolution of rheological parameters as a function of temperature as the system passes through phase separation. Increasing graphene and carbon black loadings has been observed to affect the phase separation temperature. The rheological properties of the unfilled and filled blends are studied at 160°C. Furthermore, the effects of fillers on the morphology and thermal properties of the blends and composites are also reported.

Wednesday 6:05 Poster

PO26

Decomposing tensile stress during startup uniaxial extension of entangled meltsPanpan Lin and Shi-Qing Wang

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Upon startup uniaxial extension, entangled melts undergo global yielding, characterized by the emergence of a maximum in the engineering stress (Wang and Wang 2008). In this work, we carry out in situ temperature measurements of extending SBR melts by an IR imaging camera. Such observations of heat release not only provide more information about the nature of the stress response but also help us demonstrate the various types of specimen breakup (Zhu and Wang 2013) during continuous extension. Depending on the applied Hencky rate and the stage of the extension, we show that either elastic (entropic) or viscous (dissipative, frictional) component of the tensile stress can dominant.

Wang, Y. Y., and Wang, S. Q., "From elastic deformation to terminal flow of a monodisperse entangled melt in uniaxial extension," *Journal of Rheology* 52, 1275-1290 (2008). Zhu, X., and Wang, S.-Q., "Mechanisms for different failure modes in startup uniaxial extension: Tensile (rupture-like) failure and necking," *Journal of Rheology* 57, 223-248 (2013).

Wednesday 6:05 Poster

PO27

Thermal signature of a shear crystallized semiconducting polymer solutionRoddel Remy, Ngoc A. Nguyen, and Michael E. Mackay

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Spin cast polymer based solar cells are not commercially viable due to the fabrication method which is not industrially scalable, as well as the use of harmful solvents. Thus other fabrication methods and solvents must be investigated. In this study, a pre-crystallized poly(3-hexylthiophene) polymer solution is analyzed towards creating a solar paint. This paint was made via flow induced crystallization of the polymer solution. To characterize the paint, thermal analysis utilizing differential scanning calorimetry (DSC) was performed. Analysis of the glass transitions, crystallization exotherms and melting endotherms of freshly made, stored and sheared solutions were performed to develop a thermal signature for more perfect crystal formation and polymer morphology under shear. The freshly made solution and the stored solution exhibit similar thermal characteristics while the sheared solution is quite different. Increases in crystallinity and melting temperature show that shearing the polymer in a poor solvent creates more perfect crystals and a description of the structure (i.e. crystallinity, mobile and rigid amorphous phases) are given here. It is hypothesized that shear removes imperfectly incorporated chains allowing perfect crystals to form. In addition, a blend containing 50wt.% phenyl-C₆₁-butyric acid methyl ester (PCBM) was studied with similar results. The blend, however, exhibits lower crystallinity and this is due to PCBM inhibiting the crystallization of P3HT. Interestingly, PCBM itself does not crystallize in the solution. Pre-crystallizing the P3HT:PCBM solution provides a viable and inexpensive route to mass fabrication of polymer based solar cells since the photovoltaic device power conversion efficiency is quite close to those made by spin coating.

Wednesday 6:05 Poster

PO28

Stress relaxation behavior of polymer glasses in extension and compressionJianning Liu, Panpan Lin, and Shi-Qing Wang*Polymer Science, University of Akron, Akron, OH 44325, United States*

This work investigate the origin of mechanical stress by means of stress relaxation of ductile and brittle polymer glasses both prior to yielding and in post-yield regime. Tensile tests were carried out for ductile glasses such as bisphenol A polycarbonate, and compression tests were performed for polymers polystyrene (PS) and poly(methyl methacrylate) (PMMA). Results are discussed in term of our latest molecular model [1].

[1] "A phenomenological molecular model for yielding and brittle-ductile transition of polymer glasses" Wang, S. Q., Cheng, S., Lin, P., and Li, X., J. Chem. Phys. , to be published (2014).

Wednesday 6:05 Poster

PO29

Thermal-stiffening of dynamically asymmetric interfaces in polymer nanocompositesErkan Senses and Pinar Akcora*Chemical Engineering & Materials Science, Stevens Institute of Technology, Hoboken, NJ 07030, United States*

Dynamic confinement in polymer blends arises in miscible systems with components that have large glass transition temperature (T_g) differences. The dynamic coupling-decoupling with temperature in PEO-PMMA blends holds interesting mechanical promise for their nanocomposites. By mixing the PMMA-adsorbed silica nanoparticles with PEO in solution, uniform dispersion of particles is achieved in their bulk composites. Temperature sweep experiments on these blend composites show liquid-to-solid transitions around 140°C. We will present the role of dynamic asymmetry at interfaces between particles and matrix polymer on this unusual thermal-stiffening in polymer nanocomposites.

Wednesday 6:05 Poster

PO30

Mechanical and morphological characterization of thin polymer membranes under environmental controlBenjamin R. Caire, Melissa A. Vandiver, Andrew M. Herring, and Matthew W. Liberatore*Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States*

As part of a broader effort to develop novel, thin, highly conductive, and robust anion exchange membranes, creating a test fixture for mechanical characterization at relevant fuel cell operating conditions is being explored. New polymers are synthesized in small quantities and films are typically on the order of 10-100 microns thick to increase ion transport. A modified Sentmanat Extensional Rheometer (SER) is used to perform tensile-like testing on thin membranes at relevant fuel cell conditions using a humidity delivery system developed for the TA Instruments ARES-G2 rheometer to allow for testing at a range of temperatures (30-100°C) and relative humidity conditions (0-95% RH). Along with a typical tensile test, we explore a "water stress" test (similar to dynamic mechanical analysis) in which the rheometer is used to measure the tension as the humidity is cycled from dry to wet. This test gives insight into the force of water entering and exiting the membrane as well as the hysteresis of humidity cycling on the stress. The moduli from the water stress cycling will be compared with the moduli obtained from the stress-strain curve at fixed temperature and relative humidity conditions. The new instrumentation and test procedures will be benchmarked with Nafion® N115, and novel ionomers will be featured as well. In a separate effort, the morphology change of polyethylene-b-poly(vinylbenzyl trimethylammonium) and an ABCBA pentablock polymer is studied as it undergoes an extensional strain via in situ small angle x-ray scattering (SAXS).

Wednesday 6:05 Poster

PO31

Design of yield-stress fluids: A rheology-to-structure inverse problemArif Z. Nelson and Randy H. Ewoldt*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

A desired rheological property can often be achieved by multiple material classes, transcending the typical organization of the academic discipline into separate material classes. Our typical conceptual understanding leads from structure-to-rheology, but property-driven design requires the inverse. The purpose of this work, which focuses on yield-stress fluids, is to organize material structures according to the different mechanisms capable of producing this rheological property. This property-driven organization reveals trade-offs in material design, demonstrating multiple material classes that achieve the same yield stress, but with other properties that may be different. We show that the implementation of an appropriate organizational framework leads to a more creative yet focused design-space for rheologically-complex materials and inspires new material design opportunities to achieve a target yield stress.

Wednesday 6:05 Poster

PO32

Carboxymethyl hydroxyethyl cellulose (CMHEC) as a gelling agent in hydraulic fracturing applicationFeng Song, Tianhong T. Chen, Mohand Melbouci, Jianzhao Wang, and Brent Gonska*Ashland specialty ingredients, Wilmington, DE 19808, United States*

Guar and its derivatives are the most commonly used gelling agents in fracturing treatments. Carboxymethyl hydroxyethyl cellulose (CMHEC), nevertheless, has been investigated as an alternative to guar and it showed to be an excellent gelling agent with much lower residue after breaking resulting in highly retained conductivity and regained permeability. Furthermore, crosslinked CMHEC gel possesses excellent proppant transport and suspension capability, and is suitable for reservoir temperatures from 80 to 250 °F. The anionic carboxymethyl groups in CMHEC can be crosslinked with polyvalent cations (e.g. zirconium crosslinkers) that generate low solids-gelled systems while the nonionic hydroxyethyl

substituents impart improved salt tolerance and miscible organic liquids. Therefore, it is imperative to study rheology behavior of CMHEC in both linear solution and crosslinked gels in various aqueous systems. CMHEC critical overlap concentration was determined to be 0.32%, 0.32%, and 0.38% in DI water, 2% KCl, and 4.2% seawater, respectively. Seawater exhibits a significant impact on CMHEC linear gel viscosity while 2% KCl shows negligible effects. In addition, brine type plays an important role in crosslinked gel thermal stability.

Wednesday 6:05 Poster

PO33

Rheological characterization of end-clathrated polymers

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We examined the rheological behavior for the ternary aqueous solution of poly(ethylene glycol)s with adamantane (AD) moieties introduced in both chain ends (PEG-AD) and β -cyclodextrin (CD) polymers, using a stress rheometer (MCR302, Anton Paar) equipped with 25 mm (diameter) cone plate. The CD molecules, in an aqueous solution, can form clathrate compound with hydrophobic adamantane moieties, so that the formation of associated structures between PEG-AD and CD polymers can be expected. The PEG-AD was synthesized by reacting poly(ethylene glycol)s with 1-adamantanecarbonyl chlorides in pyridine. Two linear PEGs with molecular weight of 20K and 35K, and 4-arm star shaped PEG with molecular weight of 20K were used. The AD labeling ratio at the chain ends were 93% for PEG20K, 91% for PEG35K, and 98% for 4arm-PEG. The β -CD-polymer, which contains about 10 β -CD molecules cross-lined by epichlorohydrine, was purchased from Sigma-Aldrich. The molecular weight of the β -CD-polymer was determined to be $M_w = 3 \times 10^4$ with the apparatus of size exclusion chromatography equipped with light scattering detector. The zero shear viscosity of this system was dependent on the ratio of PEG-AD and β -CD polymer at a fixed solute concentration and showed a maximum when AD:CD = 1:3. In all the viscoelastic spectra (G' and G''), terminal relaxation behavior was observed. We utilized the 3-dimensional percolation model combined with the branched Rouse model to reproduce the G' and G'' spectra. However, that could not fully fit the data and the addition of the slow mode (represented by the Maxwell type single relaxation mode) was necessary to reproduce the spectrum shapes. The origin of the slow mode is possibly due to the deviation from the theoretical size-distribution-function for the aggregates predicted by the 3-dimensional percolation model and/or related to the association-dissociation process of the aggregated polymer chains.

Wednesday 6:05 Poster

PO34

Detailed analysis of linear viscoelastic behavior of poly(ionic liquids) with rheo-optical methods

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Ionic liquids are molten salts formed by a soft cation and an anion. Ionic liquids have attracted much attention because of their nonvolatility, nonflammability and high electric conductivity. For practical applications of ionic liquids, solidified ionic liquids without loss of these features may be useful. Poly(ionic liquids) are synthesized from the polymerization of ionic liquids. They retain the good properties of ionic liquids and also have common features of amorphous polymers, such as the glass-transition, viscoelasticity and good processability. Therefore, application to batteries is anticipated. In a previous study, linear viscoelastic behavior of poly(1-butyl-3-vinylimidazolium) based poly(ionic liquids) with various counter anions (PIm-X, X : counter anion) was investigated and the viscoelastic spectra in the vicinity of glass transition zone were found to be broadened with increasing of ionic size. In this study, dynamic viscoelasticity and birefringence of four kinds of PIm-X (X = BF₄, TfO, NfO or TFSI) which have different ionic size were investigated to clarify the molecular origin of viscoelastic response. Viscoelastic spectra around the transition zone were broadened with increasing of counter ionic size: PIm-BF₄ < PIm-TfO < PIm-NfO < PIm-TFSI. In addition, the glassy modulus slightly decreased with increasing the ionic size. The rheo-optical data were analyzed with the modified stress-optical rule: The complex modulus for PIm-BF₄ and PIm-TfO system was separated into two components, the rubbery and the glassy component, which were very similar to the ordinary amorphous polymers. On the other hand, for the cases of PIm-NfO and PIm-TFSI system, an additional component was necessary in addition to the two components for a reasonable separation. The frequency dependence of additional component suggested that this component could be attributed to the cooperative localized motion of polymer chain which is enhanced by increased intra-chain interaction due to the large counter ions size.

Wednesday 6:05 Poster

PO35

Importance of humidity control in the rheological characterization of foods

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In rheology there are many essential parameters which need to be taken into account in order to ensure both accurate and reliable rheological measurements. One such parameter is temperature control. It has been widely understood that temperature plays a key role in the rheological properties of a material. However, in the case of foods, the rheological properties can also be greatly influenced by both the water content as well as relative humidity. Sensory attributes such as mouth feel, crispness, and firmness can be measured using various rheological techniques, which are strongly affected by water content. As water content is a combination of both temperature and humidity, being able to accurately control these parameters is of great interest from both a production and storage stand point. In this study a series of food products were tested using the Humidity Option on a rotational rheometer, the Anton Paar MCR. An array of rheological techniques were implemented to probe the visco-elastic response as function of not only temperature, but humidity as well.

Wednesday 6:05 Poster

PO36

Rheological characterization of dough in shear and extensionMathieu Meerts¹, Ruth Cardinaels¹, Filip Oosterlinck², Christophe Courtin³, and Paula Moldenaers¹¹Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium; ²DSM Ahead B.V., RD Geleen, The Netherlands;³Laboratory of Food Chemistry and Biochemistry, KU Leuven, Leuven, Belgium

Bread is a major constituent of our daily diet. It is obtained after baking of its pre-product dough, which consists of water and flour to which salt, sugar, yeast and enzymes are added. In the bread-making process these ingredients are first mixed, subsequently sheeted and rolled and finally fermented to result in a leavened piece of dough. The dough matrix consists of a hydrated gluten network that is intertwined with starch granules. During bread making, dough is subjected to a wide range of shear and extensional deformations. Hence, the rheology of dough is an important parameter in the bread making process. Although bread making has been around for millennia, the fundamental understanding of the relations between dough microstructure and rheology is surprisingly limited. In this work, protocols have been developed for a systematic rheological characterization unfermented dough. Subsequently, the sensitivity of the different techniques to variations in dough microstructure, as induced by changes in gluten content, is explored by comparing the rheology of weak versus strong flour. Linear and non-linear viscoelastic behavior in shear are investigated by respectively oscillatory and creep-recovery experiments. Dough behavior in uniaxial extensional flow is explored by means of an extensional viscosity fixture on a rotational rheometer. Finally, properties in biaxial extension are studied with compression experiments. Dough shows a typical gel-like behavior with a small critical strain and exhibits substantial strain hardening both in uniaxial and biaxial extension. For small deformations (linear region), weak and strong flour behave similarly with no differences in the ratio of elastic to viscous contributions, network type (slope of G'), critical strain and growth of the elongational stress. Outside the linear region, the difference in flour stiffness as obtained from moduli and creep compliances increases substantially. The strain hardening behavior on the other hand is similar for weak and strong flour.

Wednesday 6:05 Poster

PO37

Flow behavior of carrot suspensions as a dispersed systemNasibeh Younessinaki and Martin G. Scanlon*Food Science Department, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

Most commercially prepared baby foods are suspensions of different kinds of vegetables, e.g., carrot. Their flow behavior is a major concern of the food industry. The performance and efficiency of food transportation and pumping as well as the texture and stability of the food products are all affected by the flow behavior. Optimizing the production process for suspensions such as these would be facilitated by reference graphs that show the dependence of product viscosity on the concentration of suspended particles for specific process temperatures. In this work, the relationship between the viscosity of suspensions with varying solid volume fraction, and the size and shape of the dispersed particles was studied as a function of temperature. Ungelatinized starch (corn and potato) was used to create model suspensions to compare with suspensions of comminuted carrot particles. All suspensions were prepared with a continuous phase of 60% sucrose solution to prevent gelatinization and particle settling under the influence of gravity. Flow behavior was studied using steady simple shear flow and dynamic oscillation (0.1-50 Hz) at 20, 50 and 80°C. Six solid volume fractions (1 to 25%) were used to represent dilute and intermediate concentration regimes. Corn and potato starch suspensions exhibited Newtonian behavior. Their relative viscosity increased with increasing starch content, but decreased with increasing temperature, possibly as a result of leaching of components into the continuous phase. Complex viscosity results from oscillation tests corroborated relative viscosity results from simple shear flow analyses. Carrot suspensions displayed markedly different flow behavior from that of model starch suspensions, being Newtonian at low solid volume fractions (= 5%) and Herschel-Bulkley at higher concentrations. Carrot suspensions had much higher relative viscosities compared to model starch suspensions, due to significant amounts of soluble materials affecting continuous phase viscosity.

Wednesday 6:05 Poster

PO38

Influence of process temperature, nanoclay and glycerol content on rheological behavior of taro (*Colocasia esculenta* (L.) Schott) flour film-forming solutionsAndresa V. Ramos¹, Veronica M. Calado², and Carlos P. Carvalho³¹UFRJ, Rio de Janeiro, RJ 21941-909, Brazil; ²Chemical Engineering, UFRJ, Rio de Janeiro, Brazil; ³EMBRAPA, Rio de Janeiro, Brazil

In this work, film-forming solutions were prepared with taro flour from vegetables. An aqueous solution containing 4% (w/v) of flour was prepared by adding glycerol as a plasticizer; nanocomposites were formed by preparing aqueous dispersions of nanoclay. The film-forming solutions were produced using a viscoamylograph and heated to process temperature for 10 min and then cooled to 50 °C. Rheological analyses were conducted, in duplicate, in a rheometer at 25 °C, with a plate-plate geometry. In order to classify the fluid behavior and assess the influence of different raw materials and process temperature on viscosity, flow and viscosity curves were generated. The Ostwald-de-Waele model was applied to the data. The glycerol and clay contents vary from 20 to 50% (w/w of flour) and from 0 to 10% (w/w of flour), respectively, and process temperature from 75 to 95°C, according to a 23 factorial design plus three central points. The effect of clay concentration was significant. Higher contents of zeolite resulted in a reduction of the apparent viscosity, especially at higher shear rates, which could be attributed to the silicate layers tendency to enter between polymer chains ordering the structure, resulting in a decrease of viscosity. More viscous solutions were obtained when processed under lower temperatures. Glycerol content had no effect in the rheological behavior of the films. The rheological data could be adequately described by power law model and all samples presented $n < 1$, confirming shear-thinning behavior. All parameters were statistically significant at 5%. Nanoclay can help decreasing the viscosity, acting as an internal lubricant agent. The fillers can easily exert the lubricant effect to the

macromolecular chains of the polymer matrix, reducing their mutual frictions and, therefore, the overall viscosity, and do not significantly hamper the flow. This result can suggest that nanoclay is, at least partially, exfoliated.

Wednesday 6:05 Poster

PO39

Thermogelation and rheological behavior of aqueous nano fibrillated cellulose suspensions

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Interest in Nano Fibrillated Cellulose (NFC) has increased significantly during the last decade due to their potential utility in a wide variety of applications. This is driven by their attractive properties which include biodegradability, low mass density, broad chemical modification possibilities and the sustainability of production of this naturally derived nanomaterial. NFC exists as long semi-flexible fibers of 4-10 nm diameter, with aspect ratios often exceeding 100. The fibers are typically prepared with negatively charged surfaces due to the introduction of carboxylate groups on the cellulose during preparation of the material. Here, we investigate the rheological properties of aqueous NFC suspensions. We observe that these systems display thermoreversible gelation with a significant hysteresis on heating and cooling. Our results show that the gelation temperature increases on decreasing the concentration of the NFC suspension. In addition, we study the effect of ionic strength and surfactant addition on the gelation and rheology of NFC suspensions. Increasing the ionic strength leads to an increase of the gel modulus which we speculate is related to electrostatic screening of the repulsive interactions between the fibers. The presence of oppositely charged surfactants induces aggregation of the fibers and a loss of suspension stability, leading to opaque suspensions. Conversely, like-charged (anionic) surfactants and non-ionic surfactants produce gels with enhanced moduli and retention of optical transparency.

Wednesday 6:05 Poster

PO40

Chemorheology of thermal-UV dual curable organic coatings: Role of thermal radical initiator on properties of automotive clearcoats in the dual curing process

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Energy saving and reduction of curing time are key issues in industrial curing processes for organic coatings. The efficiency of curing process can be enhanced by controlling curing conditions and coating materials. We focused on the development of automotive clearcoats with dual-curable binder (hydroxyl functionalized urethane methacrylate oligomer, HFUMO) by changing curing sequences (UV-thermal or thermal-UV) and crosslinkers. Especially, the role and usage of thermal radical initiator (TRI) derived from O-imino-isourea have been mainly scrutinized in the dual curing processes of various clearcoats. First, we elucidated the effect of curing sequence such as thermal-UV or UV-thermal dual curing on the rheological/mechanical properties of clearcoats. Second, the improved characteristics of conventional OEM clearcoats by the addition of a small amount of TRI have been examined by effectively lowering curing temperature. To observe the real-time curing kinetics of clearcoats, their elastic moduli were measured via SAOS test and were directly linked with the mechanical properties of crosslinked films such as indentation hardness and scratch resistance. The conversions of reactive sites in the main binder were predicted through FT-IR analysis.

Wednesday 6:05 Poster

PO41

Chemorheology of glycidyl azide polymer (GAP) - bi-propargyl succinate reactive system

Charles Dubois and Etienne Comtois

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Glycidyl Azide Polymer (GAP) is a low molecular weight energetic polymer that can be used as a binder or structural material after a proper copolymerization to a thermoset plastic or elastomer. Traditionally, this is accomplished by using an urethane-based chemistry on GAP having terminal hydroxyl groups. Recently, it has been shown that GAP can also be co-polymerized with molecules bearing at least two unsaturated bonds such as the bi-propargyl succinate (BPS), via a reaction with azide groups to lead to triazoles cycles. The kinetics of this reaction is not as well documented as the GAP-isocyanate curing process. It is however recognized that several time-dependent properties of the GAP-BPS reactive mixture, such as viscosity and diffusivity will depend on the degree of polymerization, thus affecting the processing of energetic materials formulations that may contain this binder. During the polymerization reaction, the molecular weight distribution (MWD) evolves with time. In this work, we used Monte-Carlo simulations and apparent kinetics parameters to calculate the MWD of a GAP-BPS system as a function of time. The effect of the azide / unsaturated bonds initial ratio was investigated. As a result, the time to gel point of several formulations was estimated and compared to experimental data. When coupled with rheological models based on a distribution of relaxation times, the chemo-rheology of GAP-BPS reactive blends can be approximated from the spectrum of relaxation times, themselves obtained from the simulated MWDs.

Wednesday 6:05 Poster

PO42

Impact of rheology on static friction

Frederik Wolf

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The properties of lubricated tribological systems depend strongly, among other things, on the rheological properties of employed lubricants and solids. The rheological properties - elasticity and viscosity - depend strongly on the internal structure of fluids, which can change due to e. g.

stresses or temperature. These properties in turn affect the tribological properties, transition into hydrodynamics and static friction. The contribution will show results of investigations on rheological effects, especially visco-elastic properties, and their impact on static friction properties of tribo systems. The properties of shear-sensitive, visco-elastic fluids will be highlighted. Associated rheological and tribological measurement techniques based on rheometers will be discussed, regarding their applicability and transfer of measurement techniques between rheometry and tribometry, as well as the synergy between the two measurement techniques.

Wednesday 6:05 Poster

PO43

Rheology of soft colloids across the onset of rigidity: Scaling behavior, thermal, and non-thermal responses

Ye Xu

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We study the rheological behavior of colloidal suspensions composed of soft sub-micron-size hydrogel particles across the liquid-solid transition. The measured stress and strain-rate data, when normalized by thermal stress and time scales, suggest our systems reside in a regime wherein thermal effects are important. In a different vein, critical point scaling predictions for the jamming transition, typical in athermal systems, are tested. Near dynamic arrest, the suspensions exhibit scaling exponents similar to those reported in Nordstrom et al., Phys. Rev. Lett., 2010, 105, 175701. The observation suggests that our system exhibits a glass transition near the onset of rigidity, but it also exhibits a jamming-like scaling further from the transition point. These observations are thought-provoking in light of recent theoretical and simulation findings, which show that suspension rheology across the full range of microgel particle experiments can exhibit both thermal and athermal mechanisms.

Wednesday 6:05 Poster

PO44

The effect of curcuminoids on gelation behavior of concentrated solution of methylcellulose

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Curcuminoids (Cur) are a natural lipophilic diphenol found in the turmeric rhizome with major curcuminoid being curcumin. It has been found to have antiseptic, antioxidant, antitumor, antibacterial, antiviral, and anti-inflammatory properties as well as to function as a Vitamin D receptor ligand and therefore, may be useful as a chemo-preventive agent. However, advancements in the application of Cur have been hindered by its low bio-availability as a result of its low solubility in water. This research focuses on dispersing Cur in a methylcellulosic substrate via dissolution in ethanol and examines the effect of curcumin in the rheology of curcumin/methylcellulose solution, as well as the impact of methylcellulose on the solubility of curcumin. The rheological measurements showed that curcumin suppressed the gelation temperature of methylcellulose solution and increased the gel modulus of methylcellulose solution. Thermal analysis and UV-Vis spectroscopy analysis showed that the methylcellulose polymer used in this research prevented the crystallization of curcumin and thus facilitated the aqueous solubilization of curcumin.

Wednesday 6:05 Poster

PO45

An evaluation of hysteresis in the viscosity of aluminum oxide colloidal suspension in water observed during measurements

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Several investigators have reported that colloidal suspensions of nanoparticles in base fluids (nanofluids) can exhibit beneficial enhancement in convective heat transfer over the conventional heat transfer fluids. On the other side of the debate, issues have been raised that by adding nanoparticles to base fluids would result in the adverse effects of higher viscosity. As a result of the increase in the viscous pressure drop, which increases the required pumping power for the system, this may offset the benefits of the heat transfer enhancement exhibited by nanofluids. In addition to the cost of higher pumping power, solid nanoparticles in base fluids may subject more potential of wear on the system than conventional fluids. The aforementioned tradeoffs may outweigh the benefits of the heat transfer enhancement. Before conclusive assessments can be made to address the tradeoffs of heat transfer in nanofluids, a proper fundamental understanding in the thermophysical properties of nanofluids needs to be established. In this study, measurements have been conducted to characterize the dynamic viscosity of colloidal suspension of aluminum oxide nanoparticles in water. For a volume fraction of the nanoparticles at approximately 6%, rheological characterizations have shown that the fluid exhibits Newtonian behavior at shear rates ranging in the order of 1-100 1/s. Dynamic viscosities of the colloidal suspension were characterized at different temperatures. During the heating and cooling of the fluid for characterizing the effect of temperature, the fluid exhibited hysteresis in its dynamic viscosity. The hysteresis phenomenon in the dynamic viscosity of the colloidal suspension suggests that thorough knowledge of the thermophysical properties of the fluid is essential for heat transfer applications. This study attempts to explore the contributing factors to the hysteresis observed in the dynamic viscosity during the measurements.

Wednesday 6:05 Poster

PO46

Yield stress measurements on concrete and cement pastesJan Plog¹, Francesca De Vito², and Jint Nijman¹¹Thermo Fisher Scientific, Karlsruhe, Germany; ²Thermo Fisher Scientific, Tewksbury, MA, United States

The workability of concrete is often measured by the "concrete slump test", a simplistic measure of the plasticity of a fresh batch of concrete following the ASTM C 143 or EN 12350-2 test standard. For this test a so-called "Abrams cone" is placed with the wide end down onto a level, non-absorptive surface. It is then filled in three layers of equal volume, with each layer being tamped with a steel rod to consolidate the layer. When the cone is carefully lifted off, the enclosed material slumps a certain amount, due to gravity. The slump of the concrete cone shows is a measure for the plasticity of the concrete.

While the "slump test" is widely applicable, it has been demonstrated that determining the yield stress value of the concrete offers a faster and easy alternative to measure the concrete's properties. The yield stress value correlates nicely with the slump value. As soft materials like concrete are often difficult to work with when using conventional plate/plate or concentric cylinder geometries with a rotational rheometer due to wall slip and excessive sample disruption during loading into narrow gaps, vane geometries were used in our experiments.

Our measurements, which were performed with a new QC model rheometer, clearly show that the vane method provides a quick, simple and accurate approach to measure the yield stress of cement paste and concrete.

Wednesday 6:05 Poster

PO47

Variation in concentration of non-Newtonian fluid suspensions at bifurcationsJason Maxey¹, Jeffrey F. Morris², and Phillip Nguyen¹¹Production Enhancement, Halliburton, Houston, TX 77379, United States; ²Levich Institute, City College of New York, New York, NY 10031, United States

In hydraulic fracturing stimulation operations in oil or gas bearing formations, high-pressure flows of fluids are used to induce and propagate a fracture network. The fluids also serve as carriers for proppants, selectively sized high-strength particles which remain the fracture and prevent it from closing under formation stresses after fluid pumping has ceased. In the process of inducing fractures, naturally occurring fractures are often encountered in the rock with fluid and (possibly) proppant flowing into these. Taking advantage of both induced and natural fractures creates a complex fracture network, maximizing production. Net effectiveness depends in part on how these fluids and proppant will behave at the bifurcations between intersecting fractures to allow successful placement of the proppant particulates into these more narrow fractures.

In this work, a combination of modeling, lab-scale experimentation, and large-scale testing of Newtonian, viscous, and viscoelastic fluids has been undertaken. Effects of fluid type, particle size, particle concentration, fracture width, and Reynolds number on movement of solid and fluid at bifurcations were studied. Unexpected results were observed regarding the influence of fluid type on particle movement into side channels. Jamming phenomena (bridging or screening out of particulates) were also observed at sufficiently high particle loading and high Reynolds number. A comparison of lab-scale testing and modeling with large-scale tests will also be presented.

Wednesday 6:05 Poster

PO48

Rheological behavior of wall-slip dominant polybutadiene solutionsMengchen Wang and Shi-Qing Wang

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

We employ rotational shear rheometry to investigate the transient and steady-state responses of entangled polybutadiene solutions that can be predicted to undergo massive wall slip. Wall slip behavior will be studied in both the rate-controlled and stress controlled modes. Unlike the entanglement-disentanglement transition [1], we expect the stick-slip transition (SST) to show hysteresis in an idealized setup of simple shear cell with a constant gap distance. Rotational shear rheometry does not offer such a scenario. Thus, more complex responses are described based on entangled solution that suffers little edge fracture.

[1] "Steady state measurements in stress plateau region of entangled polymer solutions: Controlled-rate and controlled-stress modes", S. Ravindranath and S. Q. Wang, *J. Rheol.* 52, 957 (2008).

Wednesday 6:05 Poster

PO49

Rheology testing method development on gypsum materialXue Chen

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Rheological behaviors of gypsum plaster pastes provide a useful tool for evaluating the applicability of these materials during preparation of gypsum products and end-user application processing. However, due to the short setting time ranging from several to around 30 minutes, it is a challenge to evaluate the rheology of the gypsum materials. The work here presents several developed rheology testing methods include multiple rheometers and high throughput methodology to study the rheological and flow behaviors of the gypsum materials. Those methods have been applied successfully to multiple examples with various water/plaster mixing ratio, the type and concentration of additives, and gypsum types, which affect the flow properties of plaster pastes.

Wednesday 6:05 Poster

PO50

Stress-input rheology for design intuition and user experienceRebecca E. Corman, Jill Godman, and Randy H. Ewoldt*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

When you squeeze a viscoelastic material, can you then draw the rheological material functions? Or vice versa: after seeing the rheological material functions, do you know what the material will feel like? The complex, function-valued properties of rheologically complex materials present a challenge in design for user experience and perception. Here we introduce a stress-amplitude Pipkin Space to connect perception to rheology. The stress-controlled paradigm can (i) correlate with human tactile perception of material properties, (ii) simplify the presentation of rheological complexity, and (iii) guide experimental characterization to be within stress amplitudes and timescales relevant to user experience. A case study of physical therapy putties, designed for a range of user experience (extra-soft, soft, medium, medium-firm, firm, extra-firm), shows that linear viscoelastic properties can correlate with human tactile perception. We show that stress-input measures, namely dynamic compliance and fluidity, are lower-dimensional descriptions of these materials compared to dynamic moduli. Although all linear descriptions are inter-related and interchangeable, we show that we can reduce the complexity of the data with stress-input descriptions and hence achieve a clearer conceptual understanding of the differences of the materials. This understanding leads to improved tactile intuition with viscoelasticity.

Wednesday 6:05 Poster

PO51

Analysis of cocoa content in chocolate using tribo-rheometry and its correlation to mouthfeelAlina K. Latshaw*TA Instruments, New Castle, DE, United States*

A large amount of resources in the food science industry are directed to understanding properties of food products such as texture and mouthfeel before, during, and after the consumption of food and beverages. These properties play a large role in consumer selection and acceptability, directly impacting the success of new formulations. Unfortunately, many sensory properties of food are difficult to characterize. Numerous studies have been shown to correlate some properties, such as firmness, fattiness, and creaminess with bulk rheological properties and recently, studies have begun to focus on thin-film tribological properties. Tribology is defined as the study of friction, wear, and lubrication between two interacting substrates in relative motion. Within the mouth alone, the number of interacting substrates is quite plentiful: teeth-teeth, tongue-teeth, tongue-palette, tongue-food, just to name a few. It is believed that tribology can be used to analyze friction properties of substrates within the mouth and food surfaces to correlate with consumer perception and mouthfeel. In this poster, the tribo-rheometry accessory in conjunction with a rotational rheometer will be described and the tribological properties of commercially-available chocolates. We will demonstrate how differences in chocolate composition, such as fat and cocoa content, affect the properties and behavior of chocolate thin films between two sliding surfaces. The coefficient of friction as a function of sliding velocity and load force will be given for the chocolate samples.

Wednesday 6:05 Poster

PO52

Tribo-rheology of personal care products: Correlation to sensory evaluationKevin Penfield*Croda Inc., New Castle, DE 19720, United States*

Key to the successful launch of a personal care product is the appeal of its sensory properties to the consumer. This is often evaluated through the use of trained sensory panels. Although these panels can provide an accurate assessment of an extensive set of properties, their use can be costly and time-consuming. Instrumental methods offer the promise of efficiently screening new formulations prior to submission to sensory panels. In this study, we examine the correlations of various rheological properties of consumer skin care products to their sensory properties as evaluated using the Descriptive Analysis protocol of Sensory Spectrum. In particular, use of the tribo-rheology geometry from TA Instruments to mimic the application of skin care products is evaluated. Results similar to Stribeck curves obtained using more conventional tribology instrumentation were obtained. Correlations to rub-out properties are presented.

Wednesday 6:05 Poster

PO53

Accurate measurement of low viscoelasticity near gelation point by electromagnetically spinning systemTaichi Hirano and Keiji Sakai*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, Japan*

We introduce a simple and sensitive measurement of low viscoelasticity of sol/gel solutions using the electromagnetically spinning (EMS) technique. The EMS technique was developed especially to characterize low-viscous fluids, and is now a commercially available viscometer. In the EMS viscometer, a temporally modulated magnetic field generates the eddy current in a metal sphere rotor, and the Lorentz interaction between the currents and the magnetic field induces torque to rotate the sphere rotor following to the rotation of the magnetic field. The rotating motion of the rotor is determined from the balance between the electromagnetically induced torque and the resisted viscous torque from a surrounding fluid, and gives the information on the rheological properties of the fluid.

Lately, we have also developed a variant EMS system, using a disc rotor floating on the surface of sample fluids. This disc-type EMS is completely free from the mechanical friction, and realizes the measurement under an arbitrary small torque, which is a great advantage over the conventional methods of rheological measurements. It is possible to distinguish whether the static state of a viscoelastic fluid is in the gel or sol state, and to clearly determine the transition temperature or time in a gelation process.

We observed the behavior of the disc-type rotor through a sol-gel phase transition, and could successfully observe that the rotation of the disc stopped just after a rapid decrease of the rotational speed at the transition temperature. The rotational motion under the torque of the step function was also investigated. The disc on the sample in the gel state showed a damping oscillation, and the oscillation behavior and the rotational angle provided us with the viscoelasticity of the sample. We will discuss the determination of the true sol-gel transition point with the observed rheological behaviors.

Wednesday 6:05 Poster

PO54

Mechano-electric transduction performance of actuation device based on liquid crystals membrane flexoelectricity

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Liquid crystal flexoelectric actuation uses an imposed electric field to create membrane bending and it is used by the Outer Hair Cells (OHC) located in the inner ear, whose role is to amplify sound through generation of mechanical power. Oscillations in the OHC membranes create periodic viscoelastic flows in the contacting fluid media. A key objective of this work on flexoelectric actuation relevant to OHC is to find the relations and impact of the electro-mechanical properties of the membrane, the rheological properties of the viscoelastic media, and the frequency response of the generated mechanical power output. The model developed and used in this work is based on the integration of: (i) the flexoelectric membrane shape equation applied to a circular membrane attached to the inner surface of a circular capillary, and (ii) the coupled capillary flow of contacting viscoelastic phases, such that the membrane flexoelectric oscillations drive periodic viscoelastic capillary flows, as in OHCs. By applying the Fourier transform formalism to the governing equation an analytical expression for the transfer function, associated to the curvature and electrical field, power dissipation elastic storage were found.

Wednesday 6:05 Poster

PO55

Adding an additional dimension to the measurement of viscosity: Using a biaxial confocal-rheoscope to study squishy materials

Neil Lin¹, Jonathan H. McCoy², Xiang Cheng³, Brian D. Leahy¹, Jacob Israelachvili⁴, and Itai Cohen¹

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While a viscosity tensor has 81 components in total, conventional rheology measurements only probe the component corresponding to shear along the flow-gradient plane. Furthermore, many nonlinear rheological behaviors including shear thinning/thickening, yielding in colloids, and strain stiffening in biological tissues, entail an anisotropic change in the mechanical properties of the sample. To probe the shear viscosity along different directions while simultaneously measuring sample inhomogeneity, we design an experiment that combines confocal microscopy with a biaxial shear cell. This cell is quite versatile enabling a variety of protocols. For example, by using oscillatory superposition-spectroscopy, where the primary-flow is used to drive the system away from equilibrium while the weaker secondary-flow is used as a probe, we can simultaneously measure the anisotropic viscosity associated with the flow-gradient and vorticity-gradient components. Finally, our biaxial confocal-rheoscope also allows us to image the 3D structure in situ. These images are especially useful for elucidating the mechanisms that underlie the nonlinear and anisotropic rheological properties of materials with visually accessible microstructure ranging from colloidal suspensions to liquid crystals and biological tissues.

Wednesday 6:05 Poster

PO56

Development of a vibrating wire rheometer

Cameron Hopkins and John de Bruyn

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Vibrating-wire devices have been used in the past to determine the viscosity of Newtonian fluids. We are investigating the use of a vibrating-wire device to measure the viscous and elastic moduli of non-Newtonian fluids. Our device consists of a small-diameter tungsten wire under tension and immersed in a fluid. When a magnetic field is applied and an alternating current is passed through the wire, it vibrates at the driving frequency. The resonance frequency of the wire can be tuned by varying its length and the applied tension, giving an accessible frequency range of 600 - 6800 Hz. A dual phase lock-in amplifier is used to measure the in-phase and out-of-phase components of the voltage across the wire as a function of frequency. For Newtonian fluids, the quality factor Q of the resonance curve depends on the fluid's viscosity η . Once the device has been calibrated using known fluids, a measurement of Q can be used to determine η . For non-Newtonian fluids the viscous and elastic moduli can be determined from the in-phase and out-of-phase components of the wire's response near the resonance frequency. In this poster we discuss the design and operation of our vibrating-wire rheometer and present results for a variety of Newtonian and non-Newtonian fluids.

Wednesday 6:05 Poster

PO57

Near-wall nanovelocimetry based on Total Internal Reflection Fluorescence with continuous trackingLoïc D'Eramo*MMN, ESPCI, Paris, France*

We have made progress in the domain of near-wall velocimetry. The technique we use is based on the tracking of nanoparticles in an evanescent field, close to a wall, a technique called TIRF (Total Internal Reflection Fluorescence)-based velocimetry. At variance with the methods developed in the literature, we permanently keep track of the light emitted by each particle while their positions and speeds are measured. A number of biases affect these measurements: Brownian motion, heterogeneities induced by the walls, statistical biases, photobleaching and limited depth of field. Their impacts are quantified by carrying out Langevin stochastic simulations, in a way similar to Huang et al. (2009). By using parameters calibrated separately or known, we obtain satisfactory agreement between experiment and simulations, concerning the intensity density distributions, velocity fluctuation distributions, and the slopes of the linear velocity profiles. Slip lengths measurements, taken as benchmarks for analyzing the performances of the technique, are carried out by extrapolating the corrected velocity profiles down to the origin along with determining the wall position with an unprecedented accuracy. For hydrophilic surfaces, we obtain 1 ± 5 nm for the slip length in sucrose solutions, and 9 ± 10 nm in water, and for hydrophobic surfaces, 32 ± 5 nm for sucrose solutions and 55 ± 9 nm for water. The errors are significantly smaller than the state-of-the-art. With the progress conveyed by the present work, TIRF based technique can be considered as a quantitative method for study fluid flow with nanometric resolution.

Wednesday 6:05 Poster

PO58

Morphology and flow behavior of multilamellar vesicles in surfactant solutionsAngelo Pommella¹, Dario Donnarumma², Antonio Perazzo³, Sergio Caserta³, and Stefano Guido³¹*Department of Chemical Engineering, Imperial College London, London, United Kingdom;* ²*Laboratoire Charles Coulomb, Université de Montpellier 2-CNRS, Montpellier, France;* ³*Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Napoli 80125, Italy*

Surfactant systems morphology is a topic of high scientific interest that has various industrial applications. However, while many studies have been addressed to the phase behavior of water-surfactants solutions, only limited information is available in literature on flow-induced morphology of such systems. The recent advances in rheo-optical techniques help now to elucidate the changes in microstructural conformation taking place in the lamellar phase during flow. The focus of this work is to develop a quantitative investigation of the flow behavior of single surfactant multilamellar vesicles (SMLVs). The fluid investigated is a solution of HLAS in water, a surfactant widely used in the detergent industry. Depending on concentration, different phases can be observed, such as planar lamellae, unilamellar and multilamellar vesicles. Vesicle shape has been quantified by image analysis techniques. Different setups allow the direct observation of the sample, either during the flow or in static conditions, by several microscopy imaging techniques including high speed, bright field, phase contrast and confocal. A simple shear flow cell, where the fluid is placed among two parallel transparent glass plates one of which is translating respect to the other, allow the sample observation both along the vorticity and velocity gradient directions, using two different setups, hence allowing the three-dimensional reconstruction of the system microstructure. The main result is that SMLVs are deformed and oriented by the action of shear flow while keeping constant volume, and exhibit complex dynamic modes (i.e., tumbling, breathing and tank-treading). Furthermore, 3D shape reconstruction of confocal images of SMLVs, was used to identify the presence of both superficial and internal defect, whose role in the deformation dynamics is discussed. A possible application of the physical insight provided by this work is in the rationale design of processing methods of surfactant-based systems.

Wednesday 6:05 Poster

PO59

Using the immobilization cell for characterization of paint upon dryingNathan Hesse and Bharath Rajaram*TA Instruments, New Castle, DE 19720, United States*

Standard rheological experiments using flow or oscillatory shear can provide important information for the characterization of paints. Although these experiments provide valuable information of parameters like, flow properties, yield stress, and thixotropy, they can't provide characterization under controlled uniform drying conditions. The immobilization cell accessory used in combination with a Discovery Hybrid Rheometer (DHR) can be used to determine rheological properties of materials during drying or filtration. This combination allows control of various parameters such as, temperature, gap, normal force, pressure and rheological deformation. Simultaneous deformation and drying kinetics can provide specific application information, which is valued in process or product optimization. In this poster, the characteristics on drying different acrylic paint formulations onto various porous surfaces will be shown.

Wednesday 6:05 Poster

PO60

Shear thinning behavior of metal meltsRiedl Elke¹, Prajakta Kamerkar², Peter Brandes¹, and Denis Schütz¹¹*Anton Paar GmbH, Graz A-8054, Austria;* ²*Anton Paar USA, Ashland, VA 23005, United States*

Iron and by extension steel is the single most important material of our civilization. It has been constantly used since 1200 BC and sporadically even before. Recently, the advent of accurate high temperature rheometers utilizing air bearings like the FRS 1600 (Furnace Rheometer System) from Anton Paar has enabled for the first time accurately describe the rheological behavior of a liquid iron/steel in a shear rate dependent fashion. Any high temperature metal melt measured utilizing these novel methods shows a clear shear thinning behavior similar to the previously measured

behavior of tin, zinc or cadmium. This effect is thought to originate within the metal bond (electron gas) itself which persists across the melting point and thus continues to exist at high temperatures until it is broken by shear. However the discussion within the literature is ongoing. Understanding the rheological behavior of metal melts is important in casting and other metallurgical processes. This poster presents shear depending viscosity values measured for metal melts by using a modern rheological instrument and briefly introduce the discussion surrounding the study of metal melts in the community now.

Wednesday 6:05 Poster

PO61

Developments in touch-screen, rotational, rheometry systems

David J. Moonay

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Customers require instrumentation with various capabilities for viscometric and rheological analyses. This paper will present and discuss rotational rheometers and viscometers having touch-screen functionality, capable of performing rotational shear viscosity and yield stress measurements either in standalone mode or with PC-compatible software for automated data acquisition and control. Software developments will be discussed. Data will be presented for various materials, in different applications.

Wednesday 6:05 Poster

PO62

Effect of sloped die lip design on operability window and frequency response in slot coating process using viscocapillary model

Won-Gi Ahn¹, Si Hyung Lee², Ho Suk Ji¹, Jaewook Nam³, and Hyun Wook Jung¹

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The final purpose of coating process is to manufacture stable and uniform coating products with thin coating thickness by controlling operating conditions and regulating disturbances. Among the many coating methods, pre-metered slot coating has been mainly applied with high precision and fast processing time. As in other processes, it is very important to establish stable operability window with various geometric changes and analyze the transient responses with respect to unexpected perturbations for enhanced processability in the slot coating. As an indicator for determining the operability window in this process, the viscocapillary model considering the various configurations of upstream and downstream slot die lips was developed and tested. It is confirmed that the viscocapillary model for many kinds of sloped die lips could predict the operability window accurately. Note that there exist recirculation regimes inside upstream and downstream coating bead regions, depending on the angles of sloped die lips, even for the stable coating flow. Also, the effect of die lip designs on the sensitivity (frequency response) has been analyzed by imposing the sinusoidal disturbances in flow rate, web speed, coating gap, and bead pressure.

Wednesday 6:05 Poster

PO63

Applications of electromagnetically spinning sphere viscometer

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Among various viscometers proposed so far, the most popular one is the rotational viscometer, in which shear deformation is introduced by a rotor, and the relation between the rotation speed and the applied torque gives the viscosity. However, less progress in mythology has been made in recent years to meet the growing user's demands, such as rapid observation, small quantity of samples, and completely closed system for the viscosity measurement. In our presentation, we introduce a newly developed viscometer employing Electro-Magnetically Spinning Sphere (EMS) technique. The EMS viscometer is based on the principle of remote driving of the probe by the electro-magnetic interaction. The probe is a metal sphere immersed in the sample liquid, to which rotating magnetic field is applied. Temporal modulation of the vector magnetic field induces eddy current in the probe and the Lorentz interaction in between the current and magnetic field applies torque to the probe to rotate following the magnetic field. The resistant force due to the viscosity of the sample liquid causes delay in the probe rotation, therefore, the difference in the rotational speed of the magnetic field and the probe gives the sample viscosity. The shear rate dependence of the viscosity can also be measured by detecting the rotational speed of the probe changing the rotation and/or the magnitude of the magnetic field. The most remarkable feature of the EMS viscometer is that the sample can be confined in an isolated sample cell and, therefore, the system is completely free from the harm of contamination. The other unique feature is that measurements can be performed under hermetically sealed condition and sample volume of 0.3 mL is enough. In addition, the viscometer achieves a wide measurement range of from 10^{-4} to 10^3 Pa·s. This novel viscometer has already been applied for the medical applications, such as rheology measurement of blood and other body fluids, in which preventing sample contamination is a key issue.

Wednesday 6:05 Poster

PO64

Oscillatory rheology at fluid-fluid interfaces: Uncoupling material and system responsesJoseph Samaniuk and Jan Vermant*Materials, ETH Zurich, Zurich, Switzerland*

Rheological measurements must account for the mechanical response of the rheometer, and uncouple that from the rheological response of the material. In bulk oscillatory rheology, for example, this is often accomplished reliably with a complex-impedance and a second-order model of the system. Oscillatory measurements in interfacial rheology however, are typically carried out with a Wilhelmy balance that has a complicated electro-mechanical response. Obtaining the response of the balance and properly decoupling it from the rheological response of the interfacial material is non-trivial, but vital, as our results indicate that the response of the balance can dominate during interfacial oscillatory measurements. We will present small amplitude oscillatory dilatation data obtained with a radial trough geometry, highlight the influence of the Wilhelmy balance response on the measurements, and explain our approach for decoupling that response from the response of the material.

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Wednesday 6:05 Poster

PO65

A new innovative method to improve process control of processed cheese via in-line viscosity measurementOlivier Reglat*Technology Mg, Krohne inc, Peabody, MA 01960, United States*

Modern transformation processes require good efficient and reliable in-line controls in order to minimize operating costs and maximize quality. In this context, viscosity is one of the major parameters to take into account. For non-Newtonian fluids, a viscosity value just by itself means nothing if it is not referred to specific corresponding flow conditions. The VISCOLINE, a process pipe rheometer, offers an innovative measurement technique based on mixing principles. The VISCOLINE is composed of a pair of low pressure drop static mixers specially designed to be distinct and obey to Metzner and Otto concept applied to pipes. The average shear rate through each static mixer is associated with a power consumption of the fluid to define the viscosity function. The instrument provides, on a continuous base, a shear thinning and a consistency indexes, as well as viscosity. An accurate flow rate measurement is obtained with the Optimass 7010T, a monopipe Coriolis mass meter. This is the ideal combination with the VISCOLINE for non-Newtonian applications. A new successful application will be presented in this poster. The VISCOLINE was installed in a process cheese plant, after the cooker, in order to assess the quality of the processed cheese. In a batch process, once cooked, the texture of the produced cheese cannot be adjusted anymore, but the next batch can be corrected. This way, successive faulty batches are avoided. The cheese is then transferred to a service tank, holding several batches, were it gets mixed with previous batches, before packaging. This way, downtime at packaging and production losses got significantly reduced, and the empirical former lab measurements are no longer used. The next step of this project consists in redesigning the whole production line to a continuous process, with in-line monitoring of the cooking of the cheese.

Wednesday 6:05 Poster

PO66

Improvements in rheomicroscopy due to stagnation plane created by counter-rotationTharanga Perera¹ and Gina Paroline²¹*Anton Paar USA, Ashland, VA 23005, United States;* ²*Anton Paar USA, Houston, TX 77032, United States*

The ability to view structural changes in materials under shear, and while conducting rheological measurements, has always been encumbered by difficulty in maintaining the structures of interest within the field of view due to the motion related to the measurement. The advent of a twin drive rheometer wherein an upper and lower motor can rotate in opposite directions to shear the sample provides a solution to this problem. The stagnation plane created provides a means to study the changes in individual small structures, such as crystals and droplets, under shear. The device, measured data, and interpretation of results are presented.

Wednesday 6:05 Poster

PO67

Orthogonal superposition measurements on thermo reversible gelsMadhu Namani*TA Instruments Waters LLC, New Castle, DE 19720, United States*

Rheological measurements in rotational rheometers are performed by applying a stress or deformation (rate) in rotational direction. In an orthogonal superposition experiment in addition to a shear deformation in the main direction, a stress or linear shear deformation (rate) is applied in a second direction, normal to the primary shear direction; for example to measure the effect of a strong shear flow on the rheological material behavior. A new test geometry which is based on a double wall concentric cylinder is used, and allows the application of a shear flow in rotational and simultaneously in axial direction. In order to avoid end effects at the top and bottom of the concentric cylinder systems, windows are cut into the inner wall of the cup allowing fluid to be displaced when the bob moves downwards and windows in the top section of the bob eliminating effects of the free liquid interface in the gap on the force measurement. For understanding gelation in thermo reversible gels, transient 2D experiments were performed at decreasing temperature after removing the history of the gels by heating past the gel transition temperatures with and without superimposed rotational shear. During the range of gel transition temperatures the samples are sheared and the viscoelastic properties are studied to get an idea on the effect of shear on the gelation process, the results in rotation and the orthogonal direction are discussed.

Wednesday 6:05 Poster

PO68

Microfluidics: A rheo-optical tool to study micro-structured emulsions and their flow instabilitiesValentina Preziosi, [Antonio Perazzo](#), Rosa D'Apolito, Giovanna Tomaiuolo, Sergio Caserta, and Stefano Guido
Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Napoli 80125, Italy

The addition of water to a solution of oil and surfactants may lead to the creation of viscoelastic mesophases, often called bi-continuous emulsion. So-obtained micro-structured phases are suitable as drug carrier or micro-reaction media. In flow processing of such systems, flow instabilities, flow-induced structures and surfactants self-organization all play a key-role and are relevant issues for industrial production and development of such systems. Microfluidics of emulsion is gaining growing interest due to compatibility with many chemical and biological reagents, precise control of droplet, and sorting in combination with fast analysis tools [1]. Moreover, microfluidics is suitable to obtain peculiar soft matter systems, i.e., micro-sized porous geometry can be exploited to get reversible or irreversible gel-like structures from a surfactant solution [2]. In this work, microfluidics has been exploited to get some insight on the flow instabilities of bicontinuous viscoelastic emulsions in different flow regimes, e.g., capillary flow and elongational flow. Hexadecane, two non-ionic surfactants and water were used to produce the emulsions. Glass micro-channels coupled with high-speed micro-visualization apparatus have been used to achieve optical sectioning of the flowing emulsion. Confocal microscopy gave also further insight on emulsion morphology, unraveling the structure of the bicontinuous phases, the surfactant vesicles produced in the stagnation points and the finest structures eventually produced. Rheological measurements have been used to characterize viscoelasticity of each phase.

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[2] Cardiel, J. J., Dohnalkova, A. C., Dubash, N., Zhao, Y., Cheung, P., & Shen, A. Q. (2013). Microstructure and rheology of a flow-induced structured phase in wormlike micellar solutions. Proceedings of the National Academy of Sciences, 110(18), E1653-E1660.

Wednesday 6:05 Poster

PO69

Rheo-optical characterization of colloidal suspensions using a novel optical device[Bharath Rajaram](#) and Aadil Elmoumni
TA Instruments, New Castle, DE 19720, United States

Structural visualization using in situ scattering, rheo-optical methods, and confocal microscopy measurements have been used extensively to gather an understanding into the flow-induced structure in suspensions. A new optical device, which works in concert with a rotational rheometer, has been developed for characterizing the structure of complex fluids under flow. It offers a rheo-optical platform with flexibility to perform bright field, fluorescence, and cross-polar microscopy. The optics train mounts underneath an open platform with a borosilicate glass plate, which acts as the lower plate for the parallel or cone and plate geometry used. This provides a transparent optical path through which the sample can be viewed. The lower glass plate is also supported by a bearing and driven by a high precision motor to counter-rotate with respect to the direction of the rheometer upper geometry, thus creating a stagnation plane and containing objects in the field of view to study their flow induced microstructures. A variety of microstructural changes under flow in suspensions such as aggregation, break up, yielding will be shown.

Wednesday 6:05 Poster

PO70

Polymer relaxation and stretching dynamics in semi-dilute DNA solutions: A single molecule study[Kai-Wen Hsiao](#), Christopher A. Brockman, and Charles M. Schroeder
Department of Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States

In this work, we study polymer relaxation and stretching dynamics in semi-dilute solutions using single molecule techniques. We fully characterize the relationship between the longest polymer relaxation time and polymer concentration in semi-dilute DNA solutions. Using this approach, we uncovered a unique scaling relation for relaxation time that falls in the regime described by semi-flexible polymer solutions, which is distinct from truly flexible polymer chains. In addition, we performed a series of step-strain experiments on polymer molecules in planar extensional flow using an automated hydrodynamic trapping system. In this way, we are able to precisely control the flow strength and the amount of strain applied to isolated polymer chains, thereby directly observing the full relaxation process for single polymer molecules in semi-dilute solutions after flow cessation. We use this approach to make connections between the nonlinear relaxation modulus in bulk rheological measurements and molecular stretch in single molecule experiments. From this perspective, our work achieves a direct link between polymer microstructure and macroscopic rheological quantities in non-dilute polymer systems from a molecular perspective. Overall, our work reports on a key advance in the field of polymer dynamics via direct observation of dynamics in semi-dilute solutions in strong flows.

Wednesday 6:05 Poster

PO71

Active fractal gels of colloidal Janus spheres[Megan E. Szakasits](#) and Michael J. Solomon
Chemical Engineering, University of Michigan, Ann Arbor, MI, United States

We find that fractal gel networks of polystyrene colloids can be broken up by active motion of Janus colloids that have been incorporated into them. We synthesized Janus particles by electron beam deposition of platinum onto one micron carboxylate modified polystyrene particles. By adding the divalent salt magnesium chloride, an initially stable suspension of Janus colloids and polystyrene colloids, present in equal proportion, underwent aggregation to yield a fractal gel. The Janus colloids were activated by the addition of hydrogen peroxide. Changes in colloidal structure and dynamics were visualized by two channel confocal laser scanning microscopy (CLSM). By means of image analysis, we calculated the mean squared displacement (MSD) and radial distribution functions (RDF) of particles before and after addition of hydrogen peroxide. The MSD

confirmed active motion of the synthesized Janus particles, and the RDF demonstrated how the addition of peroxide changed the gel structures by breaking the gel network up into clusters.

Wednesday 6:05 Poster

PO72

Microrheological investigation of a biofilm and its constituent extracellular polymers

Maresh Ganesan¹, John G. Younger², and Michael J. Solomon¹

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We report the creep compliance of a model biofilm formed by *Staphylococcus epidermidis* and its polymeric extracellular matrix (ECM) over a time range of 10^{-5} - 10^1 s, as measured by diffusing wave spectroscopy (DWS). Biofilms are biological soft matter, consisting of bacterial cells embedded within a self-produced ECM. Thus, the bulk mechanical properties of a biofilm originate due to the coupled response of cells and ECM polymers. The components of this response can be probed using microrheology. Using DWS, we track the motion of thermally driven probes in re-constructed ECM and in biofilms cultured directly in rectangular glass cuvettes. We found that the short time ($< 10^{-3}$ s) creep of the biofilm was congruent with that of the reconstructed ECM up to a finite compliance of $\sim 10^{-2}$ Pa⁻¹. This response was that of a viscous liquid with viscosity of $\sim 10^{-2}$ Pa.s. For time $> 10^{-3}$ s, we find a transition from a purely viscous to a viscoelastic response characterized by a long time plateau in creep that agrees well with results from mechanical rheometry (L. Pavlovsky et al., *Soft Matter*, 9, 2013). The transition region was found to depend on the amount of biofilm growth. The biofilm creep deformation can therefore be viewed as a viscous, polymer mediated response in parallel with a cellular suspension mediated elastic response. This study identifies the particular contributions of ECM and cells to the mechanical properties of bacterial biofilms.

Wednesday 6:05 Poster

PO73

Microrheology of a colloidal gel in a water-surfactant solution

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Colloidal gels have wide applicability ranging from commercial products to biomaterials due to their unique rheological characteristics. Multiple particle tracking (MPT) is used to determine the material properties of a colloidal gel in water-surfactant environment. The colloidal gel consists of rod-like particles, and is dehydrated with 20wt% water, similar to gels used in home care products. The osmotic gradient between solution and gel drives the expansion and contraction. MPT uses fluorescent video microscopy to capture the movement of probe particles embedded in the gel. The mean-squared displacement (MSD) is quantified from the particle trajectories. The MSD is related to rheological properties using the Generalized Stokes-Einstein Relation. The logarithmic slope of the MSD, α , determines the state of the material with $\alpha=1$ indicative of a sol and as α approaches 0 the material is a gel. Probe particle movement is tracked during expansion and contraction of the colloidal gel over six hours in a series of surfactant solutions with varying water content (0-100% water). A phase change occurs during expansion, starting as a gel and transitioning to a sol. A toolbox for the analysis of a dynamic system was successfully created for determining heterogeneity and material properties of an evolving colloidal gel. Heterogeneity of the material during dynamic expansion and contraction is quantified by comparing particle trajectories using a F-test with a 95% confidence interval to determine if movement of individual particles is statistically different. During expansion the gel experiences heterogeneous microenvironments but are homogeneously distributed throughout the field of view. The information gained by these experiments aids in the advancement of commercial goods, and the tools and techniques developed during the experiments can be used to study a wide variety of colloidal gels.

Wednesday 6:05 Poster

PO74

Relaxation of particle motion in bimodal suspensions during drying via multi-speckle diffusing wave spectroscopy

Gwi Jeong Oh¹, Ji Won Hwang¹, Seong Jae Lee², and Hyun Wook Jung¹

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The fast dynamics generated by Brownian motion of particles in suspension systems recently plays a key role in understanding colloidal physics. Multi-speckle diffusing wave spectroscopy (MSDWS) can be effectively applied to the non-ergodic drying process of particulate suspensions because of using CCD or CMOS for light detector and calculating the autocorrelation function by averaging both over time and over pixels. To quantify the diffusion of particles in the suspension, the characteristic time of relaxation was defined as the time at which the value of autocorrelation function becomes a certain value (0.6 here). In this study, we have investigated relaxation behavior of polystyrene (PS) particles in bimodal suspension systems during drying process. To compare the effect of PS size ratio on the diffusion of particles, the characteristic relaxation times of bimodal PS particles (sets of 1 μ m and 2 μ m diameters and 1 μ m and 4 μ m with different volume ratios) in suspensions have been measured using MSDWS. The diffusion of particles was also measured under different drying temperatures (30°C, 35°C, and 40°C). In the case that the portion of small particles is relatively higher under the same concentration condition, the characteristic relaxation times get lower due to the active Brownian motion of small particles. It is very interesting to see relaxation time patterns for bimodal suspension systems having particles of 1 μ m and 4 μ m diameters. Small particles in this case strongly drive relaxation times toward values for monodisperse case with 1 μ m particles. It is thought that small (1 μ m) particles actively move in the media and even freely in the rather large void space between large (4 μ m) particles.

Wednesday 6:05 Poster

PO75

Generalized work relations for polymer solution rheologyFolarin Latinwo¹, Patrick Corona², Joshua Moller², and Charles M. Schroeder²¹*Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States;* ²*Department of Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States*

We present a general framework based on Jarzynski and Crooks relations to study polymer solutions. This framework allows for the determination of a wide array of equilibrium and nonequilibrium thermodynamic properties from rheological properties. Equilibrium thermodynamic properties represent the purely elastic behavior of the polymer solutions, while the nonequilibrium properties are essential for understanding processes such as flow-induced phase transition of polymeric materials. Using Brownian dynamics simulation in conjunction with experimental analyses, we apply this general framework to individual polymer stretching trajectories in extensional and shear flows. In addition, we show that rheological properties such as extensional and shear viscosities, polymer relaxation time, and linear and non-linear elastic behavior of polymer solutions can be determined from fundamental steady-state thermodynamic properties. Overall, connecting equilibrium and nonequilibrium properties of dilute polymer solutions provides a new platform to study the dynamics of flowing soft matter systems.

Wednesday 6:05 Poster

PO76

Diffusing wave spectroscopy: A modern light scattering technique to characterize the rheological properties of soft matter systemsFrédéric Mondiot, Mathias Reufer, and Andreas C. Voelker*LS Instruments AG, Fribourg 1700, Switzerland*

Diffusing Wave Spectroscopy (DWS) is a modern light scattering technique that allows the quantitative measurement of microscopic motion in soft matter systems, from which the rheological properties can be extracted via the so-called microrheology approach. DWS applies to highly turbid media such as concentrated particle suspensions or emulsions. In such opaque mixtures, the light is scattered multiple times by solid or liquid particles. These particles perform Brownian motion, which makes the intensity of scattered light fluctuate over time. By applying the diffusion approximation, one then obtains the mean square displacement (MSD) of the particles from the correlation function of the intensity fluctuations. Moreover, the rheological properties of the medium, namely the storage (G') and loss (G'') moduli, can be derived from the particle MSD by applying the generalized Stokes-Einstein relation. Microrheology represents the main application of DWS, and can also be carried out in initially transparent (non-scattering) systems after addition of tracer particles ("tracer microrheology"). Another application of DWS is particle sizing, which uses the particle MSD and the standard Stokes-Einstein relation to calculate the mean hydrodynamic radius of particles in Newtonian fluids. We here demonstrate the abilities of the modern instruments (DWS RheoLab, LS Instruments AG, Switzerland) in utilizing DWS microrheology to accurately characterize the rheological properties of colloidal materials like Xanthan-stabilized emulsions in a very large frequency range, and to precisely determine the gel point of gelling systems such as gelatin solutions. In addition to DWS microrheology, we show that DWS is also able to measure the size of particles or droplets in optically dense dispersions with an accuracy larger than previously assumed ($\pm 5\%$). The last feature, referred to as DWS sizing, was successfully applied to the monitoring of Ostwald ripening taking place in a concentrated oil-in-water emulsion.

Wednesday 6:05 Poster

PO77

Monitoring phases and phase transitions in two phosphatidylethanolamine monolayers using active interfacial microrheologySaba Ghazvini¹ and Prajnaparamita Dhar²¹*Bioengineering, The University of Kansas, Lawrence, KS 66045, United States;* ²*Chemical Engineering, The University of Kansas, Lawrence, KS 66045, United States*

Surface rheological properties of 1,2-Dimyristoyl-sn-glycero-3-phosphoethanolamine (DMPE) and 1,2-Dilauroyl-sn-glycero-3-phosphoethanolamine (DLPE) monolayers have been studied in different phases and been compared with detailed grazing incidence X-ray diffraction available in the literature. DLPE has a wide Liquid Expanded (LE) phase while DMPE has a short LE and wide Liquid Condensed (LC) and solid (S) phases. Although surface viscosity measurements could be an indicator of phase transitions from LE to LC to S, it is hard to detect surface viscosity in the LE phase. Nickel nanorods have been used as a sensitive tool to actively study the viscoelasticity of DLPE and DMPE monolayers in the different phases. We find that the surface viscosity does not change significantly in the LE region for a surface pressure change from 10 mN/m to 35 mN/m, proving that the LE phase in phospholipids do not have a measureable surface viscosity. On the other hand, phase transition from LE to LC could be easily detected due to the significant increase of surface viscosity. This first order phase transition has also been detected with a sharp change in the surface compressibility modulus (or isothermal two-dimensional bulk modulus). The surface viscosity in the LE-LC coexistence region is not a single value, due to the heterogeneity of emerging lipid domains. In contrast to the LE region, the LC region shows exponential increase in surface viscosity with increase in surface pressure. We were unable to detect any significant elasticity until both monolayers go through a LC-S transition. Onset of a measureable surface elasticity in the solid phase suggests a change in molecular ordering of lipid headgroups possibly accompanies the LC to S transition, which is not always reflected in isotherms or in grazing incidence X-ray diffraction. In conclusion, active interfacial microrheology may be a sensitive tool to detect phase transitions as well as headgroup order in phospholipid monolayers.

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PO78

Active microrheology studies of colloidal suspensionsSebastian Hurtado Parra¹, Ryan T. Stull¹, Xin Du², Eric R. Weeks², Roseanna Zia³, and Piotr Habdas¹¹*Department of Physics, Saint Joseph's University, Philadelphia, PA, United States;* ²*Department of Physics, Emory University, Atlanta, GA, United States;* ³*Department of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States*

We present an experimental one-particle active microrheological study of colloidal suspensions at low and moderate volume fractions. As opposed to conventional rheology, which requires large samples of material, microrheology interrogates small samples at the microscopic level. In active microrheology, a colloidal probe is driven through a complex fluid and its motion studied in order to infer material properties of the embedding medium. Mean probe motion reveals the microviscosity¹, while fluctuating probe motion gives force-induced diffusion². More recent work proposes that the stress tensor is a linear combination of microviscosity and microdiffusivity³. This suggests that knowledge of system properties, such as osmotic pressure and normal stress differences, can be attained by simply tracking the motion of a forced probe through a bath of particles, providing rich insight into the system. We drag magnetic probes with a range of velocities through colloidal suspensions of several volume fractions. The effective viscosity of the suspension, diffusivity, and normal stresses are determined from the mean and mean-square motion of the probe. Results are compared to theoretical predictions.

¹ A.S. Khair & J.F. Brady, *J. Rheol.* **49**, 1449 (2005). ² R.N. Zia & J.F. Brady, *J. Fluid Mech.* **658**, 188 (2010). ³ R.N. Zia & J.F. Brady, *J. Rheol.* **56**, 1175 (2012).

Wednesday 6:05 Poster

PO79

Experiments to interrogate polyurethane foam bubble growthCasper O. Brady, Grant Soehnel, Melissa M. Soehnel, Bion Shelden, Christine C. Roberts, and Lisa A. Mondy*Sandia National Laboratories, Albuquerque, NM 87185, United States*

Information about bubble growth, coalescence, and collapse is needed to populate engineering models to predict polyurethane foam expansion into a mold. Polyurethane foams are blown by a chemical reaction between isocyanate and water, producing carbon dioxide gas. Foam density and bubble sizes depend on the temperature and pressure of the reaction, as well as the starting material chemistries. Here, optical views of bubbles at a transparent wall of a narrow, temperature-controlled channel are recorded during the foaming reaction. These images are analyzed using an automated bubble identification and sizing algorithm implemented in MATLAB. Sizes of bubbles near the wall are compared to scanning electron microscope images of the final, cured samples to elucidate wall effects such as shear or local temperature gradients on the bubble growth. Diffusing wave spectroscopy is also used to determine the average bubble size across the width of a channel as the bubbles change with time. These data will be used to create predictive models for bubble size and density of polyurethane foams reacting in more complicated mold geometries.

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

Wednesday 6:05 Poster

PO80

Inferring molecular information by determination of the fitting parameters to nonlinear oscillatory shear data

Piyush K. Singh and Randy H. Ewoldt

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Rheologists have long dealt with the problem of inferring molecular properties from macroscopic linear shear rheology. For example, various techniques are available for determining relaxation spectra from oscillatory linear viscoelasticity (LVE) data (McDougall et al. 2014). Here we explore best practices for fitting nonlinear oscillatory data, specifically fitting the experimental data on the four asymptotically-nonlinear material functions with medium-amplitude oscillatory shear (MAOS), $[e1]$, $[e3]$, $[v1]$, $[v3]$. Available constitutive models for MAOS material functions typically have a single nonlinear fit parameter associated with them, some of which can be related to molecular information (Bharadwaj and Ewoldt). The problem of fitting asymptotic nonlinearities is non-trivial due to the multiple options available for fitting. In addition, these nonlinearities may change sign which adds to the complexity of the problem compared to the linear data. We present a case study to fit the experimental data on a 1,4-polyisoprene polymer using the Giesekus model to develop the best strategy for such fitting. The nonlinear fit parameter can vary substantially depending on whether we fit only a few or all of the nonlinearities together and the range of experimental data we use. We show that the parameter obtained by fitting a single nonlinearity, especially one without sign change, results in the best fit for this data set. The framework can be used to tackle other inverse problems with different material systems, for example, inferring structural information like persistence length from the macroscopic measurements of material functions under MAOS.

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Wednesday 6:05 Poster

PO81

Small and large amplitude oscillatory shear analysis of ballistic witness materialsJonathan E. Seppala¹, Yoonae Heo², and Gale A. Holmes¹¹Material Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8542, United States; ²Montgomery College, Gaithersburg, MD 20899, United States

Ballistic witness materials (BWMs) are a class of materials used to measure the severity of backface deformation (armor deflection) during ballistic events on protective armors. Oil-based clay or polymer composite BWMs deform plastically providing a permanent record of backface deformation, the depth of which is commonly used as part of pass/fail metrology for body armor conformity assessments based on standards or specifications. The current oil-based clay BWM used in the United States has two critical disadvantages: the material is thixotropic, stiffening after being worked into the ballistic testing apparatus and only has the desired mechanical properties when elevated above room temperature. To resolve these issues, the testing community is seeking a replacement material, usable at room temperature, with minimal thixotropy. To help achieve that goal we evaluated rheological methods for characterizing BWMs using small and large amplitude oscillatory shear. Measurements were made using several handling protocols resulting in significant differences in mechanical properties based on handling method, confirming history dependent mechanical properties. Slip was evident at moderate strains requiring the use of serrated parallel plates. Strain dependent breakdown of mechanical properties was observed above 1 % strain, and the time scale for recovery at 0.1 % strain was on the order of weeks. Breakdown was further characterized by fitting the intra-cycle decay in stress at each strain level. Finally, the linear and nonlinear properties of several candidate BWMs were analyzed and compared. At low strains (< 1 % strain) the modulus varies greatly, however, as strain was increased the moduli approach a constant value across all candidate materials studied. In the nonlinear regime the BWMs studied had a similar behavior with only minor deviations that correlate with the stiffness in the linear regime.

Wednesday 6:05 Poster

PO82

Investigating rheological properties of wheat flour dough at different stages of farinogram using LAOSGamze Yazar¹, Ozlem C. Duvarci², Sebnem Tavman³, and Jozef L. Kokini²¹Food Science, Purdue University, West Lafayette, IN 47906, United States; ²Purdue University, West Lafayette, IN 47907, United States; ³Ege University, Izmir, Turkey

Soft red winter wheat flour (12.17% moisture, 23.9% wet gluten, 56.6% water absorption) obtained from Siemer Milling Company (Hopkinsville, KY) was used to prepare dough samples in this study. Dough samples were prepared using Farinograph (Brabender, Germany) according to the AACC method No 54-21 (AACC, 2000). The samples were obtained at 4 different stage of the farinograph measurement: 1) at peak point, 2) 1 min after the peak point, where the curve starts to decrease instantaneously, 3) 5 min after the peak point, which shows the mixing tolerance index of the dough, 4) 12 min after the peak point, which is a sign of softening value. The rheological properties of the dough samples were determined with HR3 Rheometer (TA Instruments, USA) using LAOS in order to be able to understand the mixing behavior of dough in non-linear region. The measurements were carried out at 25 °C, 1 rad/s frequency value and between the strain values of 0.01 and 500%. The non-linearity started to be observed after $\gamma=0.06\%$ strain value. The variation of G^* , G' , and G'' with respect to strain (%), the variation of γ^* , γ' and γ'' with respect to strain rate, and the Chebyshev coefficients (e_3 , e_3/e_1 , v_3 and v_3/v_1 , S and T) of each sample with respect to strain were evaluated. All the samples showed strain stiffening (S) and shear thinning (T) behavior in large strains. S values were measured as 0.32, 0.31, 0.29, and 0.26 at the strain value of 522% for the dough samples obtained from the 1st, 2nd, 3rd, and the 4th phase of the farinogram, respectively. The peak point of the farinogram indicates the point where gluten network starts to form in the dough. In the progressive phases, the viscosity starts to decrease gradually due to the mechanical force the dough is exposed during mixing. γ' values obtained at $\gamma=500\%$ also supports this phenomenon.

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PO83

Comparison of the LAOS characteristics of four structured foods consisting of a concentrated emulsion (mayonnaise) , a concentrated suspension (tomato paste) and a viscoelastic network (hard and soft dough) products using LAOSOzlem C. Duvarci¹, Gamze Yazar², and Jozef L. Kokini¹¹Purdue University, West Lafayette, IN 47907, United States; ²Food Science, Purdue University, West Lafayette, IN 47906, United States

Four different structured foods (tomato paste, mayonnaise, hard and soft dough) were investigated using Large Amplitude Oscillatory Measurements (LAOS). Tomato paste (Hunt) and Mayonnaise (Heinz) were used as they are received. Dough samples were prepared according to the AACC method No 54-21 (AACC, 2000). The samples were studied from 0.01% to 200% strain at 24 progressively increasing strains and at frequencies ranging from 0.5 rad/s, 1 rad/s, 5 rad/s, 10 rad/s and 15 rad/s. All samples showed strain thinning behavior considering strain sweep tests regardless of the applied frequency. The nonlinearity begins at 0.4% of strain for tomato paste, 7% for mayonnaise, 0.1% for both soft and hard wheat flour dough. More detailed and insightful structural information were observed when the variation of the parameters extracted by LAOS. Tomato paste which is a concentrated suspension (solid particles in aqueous medium) showed a slight strain softening ($S\sim-0.06$ at 1.7% of strain) when it enters the nonlinear region and followed by progressively increasing strain stiffening ($S\sim 1.1$ at 214% of strain) as strain was increased. Mayonnaise, o/w emulsions in a protein network, showed a wider linear viscoelastic behavior than other products mentioned here. A slight strain softening ($S\sim-0.07$ at 152% of strain) followed by a sharp increase in strain stiffening ratio ($S\sim 0.96$ at 217% of strain) was observed. This might be attributed to have more gel like structure. Both tomato paste and mayonnaise showed a shear thickening behavior with a decreasing

trend at larger strains. Soft and hard dough showed strain stiffening and shear thinning behavior associated with 3D network of hydrated proteins and pseudoplastic behavior, respectively. Hard dough has lower S and higher T values due to stronger structure.

Wednesday 6:05 Poster

PO84

Comparison of conventional rheology and FT rheology analysis for commercial toothpaste formulations

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The utilization of Fourier Transform (FT) Rheology with Large Amplitude Oscillatory Flow data (LAOS) for determining the relationship between sensorial perception and rheological parameters is a fairly new method in the Personal Care industry, specifically within Oral Care. Lissajous curves of LAOS data provide a very effective visual aid to differentiate formulations via "fingerprinting" them, but there is insufficient data to interpret these material "fingerprints" in the context of consumer perception. In this study, full and 1:1 and 2:1 dilutions of ten commercial toothpaste formulations were characterized using dynamic oscillatory flow, steady torsional flow, continuous shear rate ramp, and compression / extension tests without suppressing wall slip. Diluted formulations were centrifuged and the supernatant fluid static surface tension values were measured. Shear and extensional viscosity indices were also characterized by a microcapillary rheometer. All samples were tested with the LAOS method without suppressing wall slip and FT analysis was applied to calculate material parameters besides their "fingerprints". All results were correlated using principle component analysis (PCA) to map out the relationships between conventional measurement parameters and LAOS analysis results.

Wednesday 6:05 Poster

PO85

Spray droplet size predictions using microfluidic extensional rheometry

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Spraying low viscosity polymeric solutions is a common practice for many industrial applications such as food processing, cosmetics, pharmaceutical manufacturing, agricultural and coatings. In these applications, dilute solutions are exposed to a wide range of shear and extension rates associated with short relaxation times. Even a dilute amount of polymer can alter the character of capillary break-up during droplet formation since the polymer will uncoil when it is placed in an extensional flow with a strain rate exceeding the slowest molecular relaxation. The existence of capillary, inertial, elastic and viscous effects on small length and time scales experienced during the spraying process complicates the prediction of spray droplet sizes using conventional rheological measurements. Therefore, it is important to be able to measure the extensional viscosities at relevant shear rates with appropriate sensitivity, avoiding gravitational and evaporation effects. In this study, a series of dilute (0.1% w/w) aqueous solutions of commercial polymers with different chemical structures, molecular weights and functional groups were utilized as model systems. These polymers included polyethylene oxide (PEO), hydroxypropyl (HP) guar, hydroxypropyl cellulose (HPC), polyvinyl pyrrolidone (PVP) and hydrophobically-modified polyacetal-polyether (HM-PAPE) copolymers. A microfluidic device, with a hyperbolically-shaped contraction/expansion flow channel geometry that can apply relatively high shear rates, was used to measure apparent extensional viscosity indices to overcome the inertial effects and potential evaporation. Their reduced extensional viscosity indices are calculated by normalizing these values with the apparent extensional viscosity index for water. Their shear viscosity values at high shear rates were measured using straight rectangular flow channel geometry. Since filament break-up and droplet formation is a function of the balance between viscous stresses and surface tension, the static surface tension values were also measured. Capillary numbers of the solutions (Ca) at the narrowest point of the spray nozzle were calculated using both shear and extensional viscosity indices to correlate with the mean droplets sizes measured using a laser diffraction system. Linear regression analysis was used for correlations. Results show that Ca numbers calculated from extensional viscosity data show good correlation with mean droplet sizes while shear viscosity was not an effective parameter. Increasing molecular weight increases droplet size within the same polymer family with a constant surface tension. For different polymeric structures, the presence of hydrophobic functional groups and polymer flexibility contribute to droplet formation due to changes in the surface tension and extensional viscosity values at high shear rates.

Wednesday 6:05 Poster

PO86

Suspensions of solid particles at thermoclines

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Widespread implications of settling particles in stratified fluids call for accurate assessment of a suspension of particles at pycnoclines. We perform direct numerical simulations of motion of particles based on a distributed Lagrange multiplier technique to quantify the effect of density stratification on the settling velocity and microstructure of a suspension of rigid particles. The flow field around particles is fully resolved and a statistically steady-state condition is obtained after a transient acceleration of particles. Based on the simulation results, we propose a correlation for the mean settling velocity of the suspension as a function of solid volume fraction and background density gradients in a fluid column. The effect of the stratification on the microstructure of the suspension is also investigated by direct comparison of the pair correlation function between homogeneous and stratified fluids. It is shown that the presence of the background density gradient enhances the formation of horizontally aligned clusters in the fluid column.

Wednesday 6:05 Poster

PO87

Modeling interactions in carbon nanotube suspensions: Transient flowsGiovaniantonio Natale¹, Julien Ferec², Gilles Ausias², Marie-Claude Heuzey¹, and Pierre J. Carreau¹¹Chemical Engineering, École Polytechnique de Montréal, Montréal, Québec, Canada; ²Mechanical Engineering, Université de Bretagne du Sud, Lorient, France

Transient flow data of untreated CNTs dispersed in a Newtonian epoxy matrix have been analyzed. A sequence of shearing and rest steps was applied to characterize the transient responses of the suspensions. Stress overshoots appeared at very small deformations during forward and reverse flow measurements, and their intensity increased with rest time between two consecutive flows, during which the suspensions structure was reconstructed. The transient behavior of the CNT suspensions is explained with the help of a recently proposed model¹. The CNTs are described as rigid rods dispersed in a Newtonian matrix and the evolution of the system is controlled by hydrodynamic, rod-rod interactions and Brownian motion. Flexibility is here neglected since the interactions are assumed to play a more important role for these concentrated suspensions. The force due to the interactions is modelled as a non-linear lubrication force, which is a function of the relative velocity at the contact point, and is weighted according to the contact probability. The total stress tensor is evaluated calculating the well-known fourth order orientation tensor and a new fourth order interaction tensor. The Fokker-Planck equation is numerically solved for simple shear flows using a finite volume method avoiding the need of closure approximations. The model predictions show that the overshoots are mainly due to interactions between rods and for the first time, the effect of shear rate is directly accounted by the model.

Natale G, Heuzey MC, Carreau PJ, Ausias G, Férec J. Rheological modeling of carbon nanotube suspensions with rod-rod interactions. *AIChE Journal*. 2014;60(4):1476-1487.

Wednesday 6:05 Poster

PO88

Nanoparticle dispersion in a polymer matrix: Scientific problem and technological opportunityJosef Jancar*CEITEC, Brno Univeristy of Technology, Brno, Czech Republic*

Depending on the system thermodynamics and preparation protocol, nanoparticles (NPs) in the polymer matrix can aggregate, uniformly disperse or cluster. The specific mechanisms and kinetics of polymer nanocomposite (PNC) morphogenesis have not been discovered, yet. Here we report on effects of NP shape, volume fraction and PNC preparation protocol on the state of NP dispersion in an amorphous polymer exhibiting strong particle-chain attraction. We found that composition and size of mechanically percolating clusters was controlled by NP shape. We observed dramatic stiffening for dispersed and clustered states; several fold toughness increase for the clustered state compared to dispersed state, and, the dispersed system exhibiting significantly lower dynamic fragility compared to the clustered one. The observed behavior is ascribed to the altered spatial distribution of segment dynamics, degree of correlated motion and packing frustration related to the state of NP dispersion. We show that hierarchical PNCs with desired balance of stiffness and toughness can be prepared by controlling the kinetics of the hierarchical NP assembly.

Wednesday 6:05 Poster

PO89

Pair-particle trajectories in Bingham shear flowHassan Fahs¹, Guillaume Ovarlez², and Xavier Chateau²¹IFSTTAR Nantes, Université Nantes Angers Le Mans, Nantes, France; ²Laboratoire Navier, Université Paris-Est, Champs sur Marne, France

Using numerical simulations we discuss the hydrodynamic interactions of two particles suspended in a Bingham fluid subjected to linear shear flow. The computations are based on the fictitious domain method with distributed Lagrange multipliers. Most of our simulations are for two equal radii cylinders in two dimensions but some examples are given for two spheres in three dimensions. Fluid and particle inertia are not taken into account ($Re = 0$). Three different contact models (smooth particles, Glowinski model and Cunha-Hinch model) have been implemented. We calculate the change between the initial and final streamlines caused by roughness as a function of the initial separation of the particles, the Bingham number and the roughness size. We put into evidence that Bingham number has a strong impact on the asymmetry of the trajectories: larger the Bingham number larger the net displacement across streamlines caused by a collision. We also show that Glowinski and Cunha-Hinch roughness models have similar effect on the collision for well chosen Glowinski model's parameters. To conclude shear-induced microstructure in non-Brownian dilute suspensions of rough particles is computed which allows to determine the pair distribution function.

Wednesday 6:05 Poster

PO91

Rapid colloidal self-assembly through periodic variation of inter-particle potentialsSumedh R. Risbud and James W. Swan*Department of Chemical Engineering, Massachusetts Institute of Technology, Boston, MA 02139, United States*

We study the self-assembly of Brownian particles driven by a short-range attractive interaction. Although the equilibrium state is expected to be crystalline for high strengths of attraction, formation of a kinetically arrested gel is typically observed. Crystals form for weaker strengths of attraction, but their nucleation kinetics are slow. Under only a narrow range of conditions can crystals be self-assembled effectively. We demonstrate computationally that if the attractive potential is switched on and off periodically in time, the envelope for self-assembly is broadened considerably. Our kinetic theory calculations as well as Brownian dynamics simulations show that the rate at which particles cross energy barriers is accelerated by the pulsed potential. In the context of colloidal self-assembly, barrier crossing is the rate limiting step and responsible for both

gel formation and slow nucleation. Through pulsing the inter-particle potential these physical processes are accelerated, and fine control over the rate of self-assembly is possible. Examples of switchable potentials include those due to magnetic or electric fields, those due to photo-switchable ligands, and those that are thermally responsive mediators such as DNA-coatings. Our theoretical analysis of barrier crossing with a pulsed potential, suggests that there exists an optimal frequency of switching for which a self-assembled state is attained fastest. The optimal frequency is related to the time required for particles to diffuse over the range of the attractive interaction. This allows for the release of kinetic constraints that would lead to gelation instead of crystallization. Our simulations of self-assembly in a pulsed potential reveal the formation of crystalline domains via nucleation and subsequent Ostwald ripening. These results confirm the existence of optimal switching frequency for self-assembly.

Wednesday 6:05 Poster

PO92

Model for the shear viscosity of solutions of star polymers and other soft particles

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We propose a model to describe the concentration dependence of the viscosity of soft particles. We incorporate in a very simple way the softness of the particles into expressions originally developed for rigid spheres. This is done by introducing a concentration-dependent critical packing, which is the packing at which the suspension loses fluidity. The resultant expression reproduces with high accuracy the experimental results for solutions of star polymers in good solvents. The model allows to explain a weak increase of the viscosity observed in the case of diblock copolymer stars suggesting that the reason for this peculiar behavior is mainly a consequence of the softness of the particles. In the semi-dilute regime, solutions of star polymers are modeled using the Daoud-Cotton picture to complete the description in the whole concentration regime.

Wednesday 6:05 Poster

PO93

Jammed soft-particle suspensions: Spatial correlations, rheology and diffusion

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Suspensions of soft particles (like emulsions, micro-gels) exhibit a remarkable bifurcation at the random close packing volume fraction (ϕ_c). There is a yield stress above ' ϕ_c ' but not below, and the flow curves at various ' ϕ_c ' have been shown to collapse onto a universal scaling function near this point. As the long-range hydrodynamic interactions are thought to be negligible in the dense regime, the particle level contact deformations are taken into account to model the elastic and drag forces. We have considered two variants of Durian's bubble model in simple shear -- (1) Mean drag, where viscous force is proportional to the relative velocity with the background flow and (2) Pair drag, where viscous force is transmitted locally by the neighboring particles only. We show that both the approaches give consistent result for the yield stress and single particle diffusivity in the quasi-static regime but at finite shearing rate, they each exhibit Herschel-Bulkley rheology but with different exponents. The rate dependent diffusion coefficient shows an analogous dependence on the drag law. We show that these differences arise from distinct spatial structure of the correlated particle rearrangements at finite rate in the two models.

Wednesday 6:05 Poster

PO94

Secondary-flow behavior of non-Newtonian fluids with Carreau-Yasuda model in curved rectangular microchannels

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Serpentine curved geometry becomes an essential tool in microfluidic systems to attain improved performance. Even though microflows are really low Re number flow, the inertial force in curved channel plays a role in arising secondary flow, which is different from straight passages. A secondary Dean flow in curved rectangular microchannels is investigated by applying a finite volume scheme with a SIMPLER (semi-implicit method for pressure-linked equations reversed) algorithm for the pressure-driven transport. This framework is based on the theoretical model with coupled equations of Poisson-Boltzmann, Cauchy momentum with the constitutive model of electrolytic Carreau-Yasuda fluids, and the Nernst-Planck principles of net ionic charge conservation. Particular attention is focused on the effect of non-Newtonian rheological properties on the secondary flow pattern with variations of power-law indices and time constants. We consider the prototype channels having aspect ratio (i.e., ratio of the channel height to the channel width) $H/W = 2/3$ with hydrophobic polydimethylsiloxane (PDMS) surfaces. As a general trend regarding power-law index, the electroviscous effect plays a more important role in shear thinning fluids compared to the Newtonian fluid. Due to very small Dean numbers, inward skewness was observed in axial velocity profile with a secondary motion. Non-Newtonian fluid represents lower vorticity than Newtonian fluid, presenting negligible improvement of mixing. Our results provide a fruitful insight into the accurate manipulation of electrolytic non-Newtonian fluids with microfluidic devices.

Wednesday 6:05 Poster

PO95

Molecular scale simulation of shear, parabolic, and extensional flow: Implementation and findings

Nichoals A. Rorrer and John R. Dorgan

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The COMOFLO Algorithm is an adaptation of the Cooperative Motion Algorithm which simulates polymers as coarse grained segments on a fully occupied lattice between to athermal walls. The algorithm cooperatively rearranges the segments through small closed loops of cooperative

motion, and under quiescent conditions captures the crossover from Rouse to reptation like dynamics. Flow is simulated by biasing the displacement of polymer segments depending on their location on the lattice. By implementing this biasing shear, parabolic, and extensional flow profiles can be obtained. In the case of extensional flow, a hyperbolic flow profile similar to that found in a four roller mill is implemented. The crossover from the unentangled to entangled state is once again captured in the scaling of the zero shear viscosity when the polymer melts are subject to shear flow. In addition, when the polymer melts are subject to extensional flow the extensional viscosity profile can be obtained. At low extension rates, the extensional viscosity is three times (3x) the zero shear viscosity, agreeing with experimental results and theoretical postulates. Polydispersity has been implemented into the simulations and is found to affect the rheological properties of mixtures. Polydisperse melts demonstrate a cross flow migration behavior when subject to parabolic flow. Finally the algorithm proves to be capable of capturing the molecular scale details of slip. When subject to parabolic flow, all polymers exhibit signs of slip and when subject to shear flow the polymer melts exhibit signs of cohesive failure at high shear rates. The COMOFLO algorithm proves to be capable of capturing the correct rheological properties of polymer melts and offers fundamental insight into the molecular scale details of elusive phenomena, such as slip and cross flow migration.

Wednesday 6:05 Poster

PO96

Dynamics of deformable and orientable objects in electric field and fluid flow gradients

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Experiments and theory have shown that electric field gradients can stretch deformable objects and their electrophoretic mobility depends on the conformation. We have developed a coarse-grained Brownian dynamics simulation model that incorporates the change in electrophoretic mobility of rigid as well as flexible objects with conformation. The model incorporates the effect in a computationally efficient way, and has been validated by comparison with experiments using double-stranded DNA. Further, we have applied our new model to perform simulations of deformable polymers and rigid objects in a combination of electric field and fluid flow in different microfluidic geometries. We quantified the conformation and residence time of these objects in such systems. The coupling of the electrophoretic mobility and conformation, along with the interplay of the physical differences in the electric field and fluid flow, leads to new ways to trap and manipulate rigid and deformable biomaterials. Manipulating and separating objects based on differences in deformabilities is important, for example, in separating regular versus sickled red blood cells and proteins which can acquire different folded conformations.

Wednesday 6:05 Poster

PO97

Numerical study of the three-dimensional effects of drop deformation as consequence to an imposed two-dimensional elongational flow with vorticity

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The issue of this work is to observe the history of drop deformation that is immerse in another flow. Drop deformation is an effect of the flow imposed in the continuous fluid. The family of planar flows used, the velocity is characterized by a parameter α , which specifies the rate of vorticity and the rate of strain in the flow Reyes, Minzoni and Geffroy (2011)³. Those kind of flow are similar to the family of flows used by Bentley and Leal (1984)¹. The boundary element method (BEM) in three-dimensions has been used to regard the deformation in the cross section when its imposed a two-dimensional flow. According to Hinch and Acrivos (1978)² the cross section is not circular. The analysis of the drop is over the section of major deformation (deformation of Taylor) and the cross section. We characterize modifications suffered by the cross section of the drop. We observed that cross section suffer a modification form circular to non-circular when the flow increases their magnitude of strain and the Capillar number increases.

¹ Bentley, B.J. and Leal, L.G., (1986b). An experimental investigation of drop deformation and breakup in steady two-dimensional linear flows, *J. Fluid Mech.*, 167:241. ² Hinch, E.J. and Acrivos, A., (1979). Steady long slender droplets in two-dimensional straining motion, *J. Fluid Mech.*, 91:401. ³ Reyes, M.A.H., Minzoni A.A., Geffroy E., (2011). Numerical study of the effect of nonlinear control on the behavior of a liquid drop in elongational flow with vorticity, *Journal of Engineering Mathematics*, 71(2):185.

Wednesday 6:05 Poster

PO98

Active probe rheology of polymer melts from molecular simulations: Investigation of the non-linear regime

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Over the last two decades, experimental linear active and passive particle rheology has been demonstrated as a powerful tool for capturing local viscoelastic properties of complex soft materials over a wide range of frequencies. In previous work, we showed that molecular simulations can be used to extend this approach for investigating the nanoscale linear viscoelastic properties of an unentangled polymer melt. Extension of particle rheology to the non-linear regime i.e. regime involving larger medium perturbations, is of both practical and fundamental interest. The most important challenge in this analysis will be relating the material response to its rheological properties due to the complexities in the flow field and microstructure around the probe. This is especially the case since the traditional Stokes-Einstein relationship will no longer be applicable in this regime. In this computational study, we address some of these issues by focusing on the steady pulling of a model nanoparticle through an unentangled polymer melt over a wide range of values of the Peclet number. We capture the nature of the flow field around the probe in the non-linear regime along with the potential presence of structural asymmetries which are considered to be responsible for the non-linear rheological

behavior of the complex fluids. The timescales of force induced chain relaxations and reorientations have important ramifications in this analysis. We will present a comparison of these timescales with the chain-diffusion time scales.

Wednesday 6:05 Poster

PO99

Mesodynamic simulation of drug molecule distribution in lipids surfactants

Leela Rakesh

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Mesodynamics simulation is used to model the distribution of drug molecules in various drug carriers of lipids surfactant particles (LSP). Simulation results showed that drug molecules are absorbed on the surface of the carrier. Moreover, depending upon the surfactant quality various morphological structures such as spherical, hexagonal and cylinders are emerged. Also, release performance of the LSP is predicted based on simulation structure.

Wednesday 6:05 Poster

PO100

Rheology of dispersions in the ionic liquid [Bmim][BF4]

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Shear-thickening dispersions of colloidal particles in ionic liquids (ILs) are being developed to improve ballistic, puncture and abrasion resistance for space suits and micrometeorite and orbital debris (MMOD) shielding of spacecraft. ILs are chosen for the solvent phase because of their thermal stability and low volatility. However, simulations and experiments have shown that high ionic strength in ILs effectively shields the electrostatic repulsion between silica particles, leading to significant particle aggregation. In this work we examine the role of solvation forces and solvent structuring as a means to stabilize nanoparticles and colloids in ILs. In particular, stable silica dispersions up to 65 wt % in [Bmim][BF4] are created by chemically coating the surface with 1H, 1H, 9H-hexadecafluoro-1-nonanol, and shear-thickening behavior is observed. A combination of techniques, including rheology, dynamic light scattering (DLS), electron microscopy, and small angle neutron scattering (SANS) are employed to determine the mechanism of colloidal stability. We propose solvation layers are initiated by hydrogen bonds between anion [BF4]⁻ and the fluorinated group on the surface coating, separating and stabilizing the silica particles. Analysis of SANS spectra across a broad range of particle concentrations allows us to quantitatively determine the inter-particle interactions including the thickness of solvation layer. The solvation layer thickness is approximately 5 nm at room temperature and is confirmed by independent rheology and DLS measurements. The addition of water dramatically decreases the IL viscosity but surprisingly, increases the relative viscosity of concentrated suspensions. However, assuming that the water partitions selectively to the particles enables rationalizing this behavior. This work also has potentially important implications for environmental and energy engineering as ILs are candidates for remediation, separation, and recycling of nuclear waste.

Wednesday 6:05 Poster

PO101

Long-time transient responses of branched wormlike micelles under nonlinear shear flows

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The nonlinear rheology and microstructure of a model series of wormlike micelles (WLMs) are measured by rheology and flow small angle neutron scattering (SANS) [1,2] to ascertain whether transient material responses are affected by micellar branching. The degree of branching in the mixed cationic/anionic surfactant (CTAT/SDBS) system is controlled by adding sodium tosylate. With increasing branching, we observe differences in the development of the shear stress and shear-induced segmental alignment of the micelles under the startup of shear and large amplitude oscillatory shear (LAOS) in the flow-gradient and flow-vorticity planes. The evolution of the macroscopic stress during shear startup for a nearly linear WLM system exhibits an overshoot and a short transient response (<60s) in the shear banding regime. The segmental alignment of the WLMs in the 1-3 plane, however, evolves very slowly (400s) to steady state. This discrepancy between rheology and alignment factor corresponds with shear band formation and disappears at lower shear rates where shear banding is not present. For highly branched WLMs where banding is not observed, both alignment factor and shear stress evolve toward steady state rapidly. A different behavior is observed under LAOS, where the stress response of nearly linear WLMs reaches steady alternance within several cycles and remains stable. In branched samples at similar De and Wi numbers, the measured stress overshoot and segmental alignment factor evolve very slowly over the course of five hours. This highly repeatable and unique aging under LAOS and recovery upon cessation of shear is interpreted as a stress relief mechanism driven by branch rearrangement. This research quantitatively links micellar microstructure and topology to the measured transient and steady shear rheology of WLM solutions, providing insight into the formation of flow instabilities and shear induced microstructures.

[1] A. Kate Gurnon et al. *JoVe*, (2014). [2] C. Lopez-Barron et al. *PRL*, (2012).

Wednesday 6:05 Poster

PO102

Rheological behavior of silica nanoparticles measured by small angle x-ray scatteringJonghun Lee¹, Suresh Narayanan¹, Xiao-Min Lin², and Alec R. Sandy¹¹X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, United States; ²Nanoscience and Technology, Argonne National Laboratory, Lemont, IL 60439, United States

The viscosity of colloidal suspensions varies depending on the shear rate. Particularly, at high particle volume fraction, its viscosity abruptly increases beyond the critical shear rate, which is known as shear thickening. Even though this non-Newtonian fluid behavior has long been known, the mechanism of shear thickening still remains unclear. It is proposed that colloids would form hydroclusters based on the low particle volume fraction solution, or the colloids would jam by shearing. Direct probing colloidal dynamics during shear is a promising method to understand the mechanism of shear thickening. Here, we studied the dynamics of silica nanoparticle solution under shear based on small angle x-ray scattering (SAXS) and x-ray photon correlation spectroscopy (XPCS). X-ray is a suitable light source to probe nanoparticle dynamics with high spatial and temporal resolution as it is capable of probing dynamics over 100 nm to 10 nm length scales and millisecond to 1000 sec time scales. By measuring intensity-intensity autocorrelation function, we examined the dynamics of the silica nanoparticles. These combined x-ray spectroscopic and rheometric results provide a general perspective on shear thickening.

Wednesday 6:05 Poster

PO103

Rheology of sulfonated polystyrene ionomersSergey Vorontsov, Arkady I. Leonov, and R. A. Weiss*Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301, United States*

Rheology and Rheo-SAXS experiments on sulfonated polystyrene ionomers neutralized with different cations were used to study time-dependent behavior and to develop a physical picture of the morphology changes that occur during the deformation in the melt. The experiments showed that the materials were sensitive to deformation and thermal histories, and a pre-shear treatment is necessary to obtain repeatability and consistency of the experimental data. The rheological behavior was dependent on the rate of deformation. Rheo-SAXS experiments provided evidence for microstructure changes during melt deformation. Those observations led to the following explanation: at low shear rates, the ionomers behave similar to non-ionized polymers. Stress overshoot occurred at shorter times than for the parent polystyrene and the shear stresses were also higher for the ionomers. "Ion-hopping", which facilitates flow of the ionomer began at some critical value of stress. For a constant shear rate, the "ion-hopping" process was not fast enough to allow the polymer to deform and the ionic aggregates begin to break up. Flow instabilities in "cone-plate" geometry occurred at lower shear rates compared with the parent polymer. That behavior was manifest as a decrease of the stress with increasing time. Destruction of the ionic aggregates was confirmed by the Rheo-SAXS experiments. The characteristic ionic peak, broadened, lost intensity, and eventually disappeared with increasing strain. The low- q upturn in the SAXS curve, however was unaffected by the deformation. Reliable experimental data for ionomers requires that a sufficient aging time is provided after deformation to allow the microstructure to reform.

Wednesday 6:05 Poster

PO104

Identifying the mechanisms of shear-induced clustering in polymer-colloid mixtures using 3D rheo-SANS measurementsJuntae Kim and Matthew Helgeson*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106-5080, United States*

The formation of shear-induced aggregates in polymer-colloid mixtures has been hypothesized to arise from polymer normal stresses, due to vorticity-aligned clusters observable in the flow-vorticity plane. To comprehensively test this hypothesis, we have made shear flow measurements of fully 3D microstructure with simultaneous small angle neutron scattering (flow-SANS). As a model system, we use oil-in-water nanoemulsions in the presence of polyethylene glycols, which form non-aggregating viscoelastic networks. The steady shear rheology of these fluids exhibit strong shear thinning, during which significant flow-induced anisotropy develops in the droplet microstructure. Flow-SANS measurements from two shear planes provide spatial resolution of the 3D microstructure within the flow geometry during shear thinning. Specifically, previously observed butterfly scattering appears in the flow-vorticity plane at shear rates corresponding to the stress plateau, with projected orientation in the vorticity direction. However, significant anisotropy develops in flow-gradient plane with oriented structures along the compression axis of shear. To visualize the shear-induced structure, we employ reverse Monte Carlo (RMC) simulations to rationalize the 3D microstructure with neutron scattering data. The resulting structures suggest that hydrodynamic interactions play an important role in the formation of shear-induced clusters, and allows for collapse of the shear thinning response over a number of different viscoelastic parameters through a modified Peclet number. Overall, this structural information provides mechanistic means to control the rheology of non-aggregating polymer-colloid mixtures.

Wednesday 6:05 Poster

PO105

Extensional FlowSANS at the NIST Center for Neutron ScienceKathleen M. Weigandt*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, United States*

Extensional flows are commonly observed in nature and industry, but still poorly understood when compared with shear flows. This is due to inherent experimental difficulties in making precise structural and mechanical measurements of fluids undergoing extensional strain. In recent years, there have been a number of groups using microfluidic devices to accurately measure the extensional rheology and birefringence of various viscoelastic fluids. However, the relatively minimal available tools to probe the structure of complex fluids under extensional flow is in stark

contrast to the variety of techniques used for similar materials in shear flow. For instance, at NIST we have a complementary suite of tools used to access the structure of complex fluids under shear relative to the 1-2, 1-3, and 2-3 shear planes. In an effort to address this unmet need we have recently designed a new modular flow cell for neutron scattering that will allow us to measure the structure of complex fluids in non-shear flows including extensional flow. Currently, we are using a cross slot geometry so that we can now quantify nanostructural changes that occur in complex fluids that are undergoing extensional deformation near a stagnation point. In addition to the structural measurement, the new flow cell has additional access ports that enable the simultaneous measurement of pressure at each inlet and outlet which gives further insight into the mechanical properties of the fluid during the SANS measurement. Recently, we have begun the process of optimizing the cross-slot geometry for both flow and neutron measurements. In this talk we will describe the new flow cell and we will present the results of recent investigations into the structure of wormlike micelles solutions undergoing extensional flow at a stagnation point.

Wednesday 6:05 Poster

PO106

Gelation of patchy rods

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Colloidal suspensions of rod-like particles (viruses, nano-wires, nano-tubes, etc.) can be stabilized and, under appropriate conditions, undergo a gelation to form a rigid, system spanning network with finite low frequency shear modulus and yield stress. However, the interactions that govern this organization at the particle scale are not well understood in all material systems. In this work, we study a model colloidal suspension of attractive rods via Brownian dynamics simulations. We show that, counterintuitively, increasing the net attraction between rods can significantly suppress the tendency to form networks. In particular, we find that at relatively high aspect ratio and low volume fraction, strong, but uniform, attraction leads to the formation of compact clusters, while a patchy attraction, with a lower binding energy per unit length, can lead to robust rigid networks at the same volume fraction. This suggests that recently reported network formation might rely on patchy surface interactions. We also study the mechanical properties of the networks that do form at various levels of surface coverage and show that, again counterintuitively, the yield stress depends non-monotonically on the surface coverage of inter-rod binding sites.

Wednesday 6:05 Poster

PO107

Origin of shear thickening in semidilute wormlike micellar solutions

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The origin of shear thickening in a semidilute wormlike micellar solution of cetylpyridinium chloride and sodium salicylate was investigated in this work by using Couette rheometry, flow visualization and capillary Rheo-particle image velocimetry. The use of the combined methods allowed the discovery of gradient shear banding flow occurring from a critical shear stress and consisting of two main bands, one isotropic (transparent) of high viscosity and one structured (turbid) of low viscosity. Mechanical rheometry indicated macroscopic shear thinning behavior in the shear banding regime. However, local velocimetry showed that the turbid band flowed at constant shear rate and increased its viscosity along with the shear stress. This shear band is the precursor of shear induced structures that subsequently give rise to the increase in viscosity or shear thickening.

Wednesday 6:05 Poster

PO108

Effect of curvature on shear banding of wormlike micelles in Taylor-Couette flow

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Shear banding of wormlike micelles (WLMs) involves spontaneous separation of a flow field into separate regions with distinct velocity gradients upon shear, and is typically attributed to mechanical instability due to a non-monotonic constitutive curve. The details of steady state banding, including an apparent stress plateau between an envelope of lower and upper critical shear rates, and the simple "lever rule" followed by the location of the interface between bands, have been thoroughly studied for narrow gap Taylor-Couette flows that approach simple shear. However, it is currently unclear how these signatures change as the flow type and geometry are changed from simple shear toward more realistic processing flows. As a first step to study the possible effects of geometry on banding, we report velocimetry measurements in a Taylor-Couette device with systematically varying curvature (i.e., the ratio of gap size to cylinder radius). We use WLMs of different categorical types to determine the generality of our observations. In WLMs where the mechanism of banding is presumed to be purely mechanical, we show that increasing curvature (i.e., stress gradient along the gap) leads to an expansion of the envelope of critical shear rates for banding, as predicted by models. However, we also observe that the banding interface deviates significantly from the "lever rule" with increasing curvature, especially close to the critical shear rates. Furthermore, in some WLMs, significant apparent wall slip develops for small curvature, but is absent for larger curvatures. We test the ability of the Vasquez-McKinley-Cook model to describe the data in order to highlight the qualitative features of this behavior that are not captured by contemporary constitutive models.

Wednesday 6:05 Poster

PO109

Multiphase waxy crude oils rheo-optical characterizationSergio Caserta, Antonio Perazzo, and Stefano Guido*Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Napoli 80125, Italy*

Multiphase fluids, such as emulsions, where an oil phase is coexisting with an aqueous phase, are particularly relevant in upstream operations, being involved in many physical and chemical phenomena occurring during the various stages of the processes. For example shale gas/oil extraction can be modeled as multiphase flow in porous media, where oil-water-gas fluids flow through confined channels. The flow can induce bubble or droplet deformation, break-up, coalescence, pattern formation or phase separation [1, 2, 3]. Selection and optimization of surfactant mixtures based on suitable rheological and interfacial properties (e.g., interfacial tension, wettability) is needed to increase extraction productivity and ensure stability of well operations. Heavy crude oil transportation is a key step and is strongly affected by oil rheological properties because of its viscoelasticity. Particles, asphaltenes, and low molecular weight fatty acids acts as surface active molecules, influencing drop deformation, coalescence and aggregation. Wax deposition during pipeline flow is a common problem [4], affected by the oil composition, water cut, oil temperature, temperature difference between the bulk oil and the ambient, velocity, flow pattern, pipe material. In order to propose new solutions for flow assurance, it is necessary a full comprehension of the physico-chemical phenomena underlying wax deposition in multiphase fluid flow. In this work we investigated both waxy oils rheological properties by means of rheometry and waxy oil confined shear flow. The latter can be realized by using a parallel plate rheo-optical apparatus. Fluid morphology in flow can be quantified by image analysis techniques.

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Wednesday 6:05 Poster

PO110

Effect of droplet stiffness on the dynamics of dense emulsionsXiaojun Di, Zhen Shao, and Chinedum Osuji*Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, United States*

Particulate systems such as colloidal suspensions and emulsions exhibit glassy behavior at high volume fractions. It has been found that the softness of the particle can affect the glassy dynamics, specifically, the fragility of the system. However, systematic quantitative investigations of the relationship between the modulus of the dispersed phase and the dynamics of the suspension have not been advanced to date. This is in part due to the difficulty associated with reliable preparation and characterization of micron-scale droplets/colloidal particles with well-defined and controllable mechanical properties. In the current work, we employ emulsion droplets of worm-like micelles, dispersed in an inert continuous fluid. The worm-like micelles exhibit a well-defined temperature-dependent viscoelasticity with a single relaxation time that is exponentially dependent on temperature, i.e. Maxwell behavior. As a result we can systematically vary the mechanical properties and relaxation time of the dispersed phase as a function of frequency and temperature. We investigate the effect of droplet stiffness on the dynamics of the emulsion and correlate the viscoelasticity of the droplet to the rheology of the suspension.

Wednesday 6:05 Poster

PO111

Transient yield in reversible colloidal gels: A micro-mechanical perspectiveBenjamin Landrum¹, Lilian C. Johnson², William B. Russel¹, and Roseanna Zia²*¹Chemical and Biological Engineering, Princeton University, Princeton, NJ 08540, United States; ²Department of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States*

In this second part of a study of the nonlinear rheology of reversible colloidal gels, we investigate via dynamic simulation their age- and flow-induced structural evolution, with a view toward understanding transient yield. The gel network comprises microscopic, spherical particles that interact via a hard-sphere repulsion and a short-range attraction. The strength of attractions is on the order of a few kT and leads to a bi-continuous, space-spanning network that exhibits elastic and viscous behaviors and continues to evolve structurally over time due to thermal fluctuations. Upon start-up of an imposed strain rate, the transition from rest to steady stress response is characterized by one or more "overshoots" in the shear stress. Prior studies, in which the onset strain and height of such overshoots depend on gel age, strain rate, volume fraction, and attraction strength, suggest that the underlying microstructural origin is a two-step process of cage breaking and bond breaking. However, our detailed studies of the microstructural evolution challenge this view. We present a new picture of the connection of macroscopic yield and micro-mechanics.

Wednesday 6:05 Poster

PO112

Manipulating particle shapes: Deformation and solidification of molten wax drops at an immiscible liquid interfaceShilpa N. Beesabathuni¹, Seth Lindberg², Chris Wesner², Marco Caggioni², and Amy Q. Shen¹*¹Mechanical Engineering, University of Washington, Seattle, WA 98105, United States; ²Process and Engineering Development, Procter and Gamble, West Chester, OH 45069, United States*

The controlled generation of varying shaped particles is important for many applications: food processing, consumer goods, adsorbents, drug delivery and optical sensing. In this paper, we investigated the deformation of millimeter size molten wax drops as they impacted an immiscible liquid interface. Spherical molten wax drops impinged on a cooling water bath, then deformed and as a result of solidification were arrested into

various shapes such as ellipsoids, mushrooms, spherulites and discs. The final morphology of the wax particles is governed by the interfacial, inertial, viscous and thermal effects, which can be studied over a range of Weber, Capillary, Reynolds and Stefan numbers. By systematically varying the initial temperature and viscoelasticity of the molten drop, drop size, impact speed, viscosity and temperature of the bath, and the interfacial tension between the molten wax and bath fluid, we constructed cursory phase diagrams for the various particle shapes that resulted. We solved a simplified Stefan problem for a spherical drop and estimated the time required to initiate a phase transition at the interface of the molten wax and water after impact. We correlated this time with the drop deformation history and final wax particle shape to understand the influence of rate of solidification of molten wax on the final shape.

Wednesday 6:05 Poster

PO113

Microfluidics based conducting polymer polyaniline particles for glucose sensing

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Polyaniline is a widely used conductive polymer known for its stability, high conductivity, and favorable redox properties. Monodisperse micron-sized polyaniline spherical particles are synthesized using two-phase droplet microfluidics from Aniline and Ammonium persulfate oxidative polymerization in an oil-based continuous phase. The morphology of the polymerized particles is porous in nature which can be used for encapsulation as well as controlled release applications. The properties of the polyaniline (PANI) particles are characterized by using UV-Vis spectroscopy, SEM and conductivity measurements to understand the relationship between their microstructures and stability. Glucose oxidase enzyme is encapsulated inside PANI particles for glucose sensing.

Wednesday 6:05 Poster

PO114

Analysis of flow-induced structure in CTAB/NaSal aqueous solution using polarization imaging

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Wormlike micelles in aqueous solutions show flow-induced structures, FIS, under fast shear flow. Since FIS have the spatial distribution of stress or shear rate, it is difficult to analyze them in detail using conventional rheometer. Imaging methods are effective to characterize FIS. In previous studies, steady shear band structure in a Couette cell was mostly reported. However, detailed observation of FIS in cone and plate fixture has not been utilized, probably due to unstable structure. In this study, we observed FIS of the wormlike micelles of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) in aqueous solutions under various shear rates in a glassy cone and plate fixture using the polarization imaging camera. This camera has the photonic crystal in front of CCD image sensor, and the spatial distribution of birefringence and extinction angle can be obtained by analyzing each set of four adjacent picture elements detecting respectively the four polarization component (0, 45, 90, 135°). At high shear rates, some concentric rings indicating the high birefringence region were observed and these rings moved to the center with time. Thus, the observed concentric rings structure was not steady and rather close to the dissipative structure repeating generation and disappearance. Averaged intensity of birefringence in the whole region oscillated with time and shear stress and the first normal force difference also oscillated. Their periods showed a good coincidence.

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PO115

Micro-mechanics and nonlinear rheology of reversible colloidal gels: Creep and delayed yield

Benjamin Landrum¹, William B. Russel², and Roseanna Zia¹

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In this first part of a study of the nonlinear rheology of reversible colloidal gels, we investigate via dynamic simulation their age- and stress-induced structural evolution, with a view toward understanding creep and delayed flow under step shear stresses. The gels are formed from dispersions of Brownian spheres that interact via a hard-sphere repulsion and a short-ranged attraction. The reversible attractions allow the system to develop a bi-continuous, space-spanning network that exhibits elastic and viscous behaviors and continues to evolve structurally over time with thermal fluctuations. When subjected to step shear stresses, the structure undergoes creep, followed by viscous flow. This macroscopic "delayed flow" is consistent with previously proposed models of competition between breakage and formation of particle bonds among static load-bearing structures. Our findings suggest, however, that the load-bearing structures evolve, and that the gel's resistance to delayed flow depends upon this structural evolution and reinforcement.

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PO116

Shear thickening fluid (STF) – nanocomposites for improved hypervelocity impact protection against micrometeoroids and orbital debris

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Concentrated colloidal dispersions exhibit a rich shear rate-dependent rheology that includes shear thickening at higher shear rates as a result of large lubrication stresses between particles. Composites based on such field-responsive materials are finding increasing commercial use in personal protective equipment against ballistic, stab, and needle puncture threats. The demonstrated ability of shear thickening fluid (STF) to improve the puncture and ballistic resistance of engineering textiles suggests their potential application for use in the extra-vehicular activity (EVA) suit worn

by astronauts. In low-earth orbit, astronauts and spacecraft are exposed to the perils of micrometeoroids and orbital debris (MMOD). While generally less than a centimeter in size, these MMOD particles can travel tens of thousands of miles per hour, rendering them highly energetic. In a collaborative effort with NASA scientists from the Hypervelocity Impact Testing Facility (HITF) at Johnson Space Center, we have conducted hypervelocity impact (HVI) testing at White Sands Remote Hypervelocity Test Laboratory (RHTL) on a prototype lay-up containing STF-Kevlar® that was lighter in mass than the existing EVA suit. We identified the ballistic limit up to 7 km/s and found the results to be comparable to existing available suit data. An energy balance on the projectile and target provides a rational method to understand the observed HVI performance and motivates the need to better understand the rheology of STFs at ultrahigh deformation rates where inertial effects are important. These EVA suite prototype materials are scheduled to be placed on MISSE-X external test station of the International Space Station in the coming months to investigate the effects of the low-earth orbit environment on their stability and MMOD resistance.

Wednesday 6:05 Poster

PO117

Non-equilibrium depletion interactions in colloidal dispersions

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While equilibrium depletion interactions in suspensions are well-understood, much less is known about such interactions when an imposed flow distorts the particle microstructure. Such interactions arise when a pair of colloidal 'probes' of size a is driven at a velocity U through a dispersion of colloids of size b . Probe motion distorts the configuration of background particles; the degree of this distortion is set by the separation distance between the probes, the orientation of the applied force to their line of centers, and the relative strength of the particle motion to the entropic restoring force of the bath, $Pe=U(a+b)/D$, where D is the diffusion coefficient of a lone bath particle. Recent theoretical, computational, and experimental studies have examined such non-equilibrium depletion interactions with limited success, due primarily to their difficulties in solving a three-body Smoluchowski equation. We have solved the 3-body Smoluchowski equation directly in toroidal and bispherical coordinates utilizing a combination of asymptotics and numerical methods and, from this, utilized the statistical mechanics theory to determine the non-equilibrium interactive force between two probes translating at arbitrary separation and arbitrary orientation to their line of centers through a Brownian suspension, for $0=Pe=1,000$. In contrast to the dilute equilibrium picture, the non-equilibrium depletion force may be attractive, repulsive, or transition from one to the other with changes in probe separation and flow strength Pe .

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PO118

Diffusion and rheology in a suspension of hydrodynamically interacting colloids enclosed by a spherical cavity

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We study diffusion and rheology of a suspension of hydrodynamically interacting colloidal spheres enclosed by a spherical cavity, utilizing the Stokesian Dynamics framework to account for long-range many-body and pairwise lubrication interactions between the particles and between particle and enclosure. Previous studies of 1D- and 2D-confined suspensions have revealed that boundaries exert a pronounced qualitative influence on microstructure, dynamics, and rheology. While studies of the motion of a point particle in a cavity have been reported, the neglect of finite size sacrifices significant qualitative information, resulting in an incorrect coupling between torque and velocity, among others. We have derived new hydrodynamic mobility functions for finite-size particles confined by a spherical boundary that faithfully capture the physics of the boundary and its influence on particle dynamics. We obtain the full grand-mobility matrix and, from these, the position-dependent short-time self-diffusivity for an isolated particle and the dynamics of a hydrodynamically interacting pair suspended in the cavity. Both of these are studied over a range of particle-to-cavity size ratios.

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PO119

Structure and rheology of binary Pluronic block copolymer mixtures in the protic ionic liquid ethylammonium nitrate

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The structural and rheological properties of a model series of binary Pluronic block copolymer mixtures dissolved in a protic ionic liquid are studied as a strategy to modulate and control the soft solid behavior of amphiphilic block copolymers in ionic liquids. The properties of the soft solids are controlled via tuning the mixture composition of Pluronic block copolymers P123 and F127 self-assembled in deuterated ethylammonium nitrate (dEAN). Equilibrium microstructures are studied by linear viscoelasticity and small angle neutron scattering (SANS), while the shear induced microstructures are probed by in situ rheo-SANS in the radial direction (1-3 plane of flow) under steady and oscillatory shear flow using recently developed time resolved methods [1, 2]. Solutions with total Pluronic composition of 27.5 wt% and 50/50 mass ratio of P123/F127 in dEAN form closed packed micellar phases similar to those formed in parent homopolymers [3]. The application of shear flow in a Couette geometry leads to layering of the closed packed phases. It was also observed that relatively low amplitude oscillations induces slightly different ordering than steady shear. This study points out a strategy for modification of the structural, and hence rheological, properties of Pluronic block copolymers in ionic liquid solvent, providing insights useful for comparing the properties of self-assembled amphiphilic block copolymers in molecular versus ionic liquid solvents under rest as well as steady and dynamic oscillatory shear flows.

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PO120

X-ray photon correlation spectroscopy studies of structural irreversibility in a colloidal gel subjected to oscillatory shear flow

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X-ray photon correlation spectroscopy (XPCS) is used to probe the microscopic structural reversibility in a colloidal gel subjected to oscillatory shear flow. Silicon dioxide particles in decalin aggregate into a gel structure as a result of depletion interactions associated with dissolved polystyrene molecules. XPCS studies on aged quiescent gels show negligible structural dynamics on time scales of tens of seconds. Such samples were subjected to oscillatory shear with varying strain amplitude using a rheometer installed in the XPCS beam line and x-ray capable polycarbonate fixtures; this enable simultaneous rheological measurements during the XPCS experiment. In the presence of unidirectional shear flow, the decay of the XPCS autocorrelation function is dominated by the convective motion induced by the applied deformation. In oscillatory shearing of samples in the absence of significant structural relaxation, the autocorrelation function becomes periodic, returning to its initial value once every oscillation period. At higher strains, irreversible motions at the microscopic level lead to decay in the 'echos' of the autocorrelation function. Interestingly, structural irreversibility is detected by XPCS only at strains that are significantly higher than those at which nonlinearity in rheological behavior first appears. At small strains for which the autocorrelation function is found to be strictly periodic, there is considerable variability in the shapes of the periodic waveform. None of these shapes agree with the shape of the correlation function calculated under the assumption of affine deformation of microstructure. This suggests that the microscopic deformation, while reversible, may be quite complicated.

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PO121

The use of the mathematical model of Volterra in the aggregation of deoxy-hemoglobin S molecules in sickle cell anemia

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Rheology is the study of the flow and deformation of matter under constraints. Considering blood as a rheological fluid, we review the basic rheological properties of blood and more importantly the ones for the polymerization of deoxy-hemoglobin in sickle cell anemia. We present the nonlinear dynamical model of the polymerization of deoxy-Hemoglobin S molecules and show that the use of a cumulative braking term homogeneous to a time dependent shear, transforms the evolution equation of the dynamical variable into an integro-differential equation of Volterra. However, it is well known that the solutions of the Volterra integro-differential equations can only be put into parametric forms. Nevertheless, using the original idea of Chasse J.L. et al. to obtain the solution on an explicit form by adequate approximations, we proved in this work that the mathematical model allows a correct description of the stationary and non-stationary rheological behaviors of the gel of Deoxy Hemoglobin S molecules. The mathematical model and its approximations reveal an excellent descriptive quality for the interpretation of numerical data.

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PO122

Wave propagation and blood rheology

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Rheology is a science dealing with the deformation and flow of matter. Blood rheology is one of the most interesting topics in medical, pharmaceutical and biochemical field. Indeed, there has been countless research on the study of blood rheology. Specifically, modified mathematical models have been used to analyze many properties of blood such as blood's velocity, viscosity, and wave propagation. In this research, we will review physiological and analytical concepts in blood flow. Most importantly, the wave propagation phenomenon in blood flow will be discussed. We will look at the Euler's and Lambert's models, Windkessel theories as well as non-Newtonian properties of blood flow and the related Navier-Stoke equation. Additionally, we will examine Lamb's work and other contemporary models of blood flow as well.

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PO123

Development of a viscosity-pressure drop correlation model for predicting physical behavior in medical tubing

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The physical behavior of liquids, gels, and suspensions flowing through a flexible tube is a fundamentally important concept, appearing in many everyday applications. In the pharmaceutical industry, medical devices such as those used in enteral feeding rely extensively on controlled fluid flow. An infusion pump is used in conjunction with a feeding tube to properly deliver a drug to the patient. In successfully designing and developing these drug delivery systems, a variety of material (e.g. rheological properties of drug, tubing rigidity), geometric (e.g. tubing diameter and length),

environmental (e.g. temperature), and operational (e.g. flow rate) factors must be considered in order to provide timely drug administration while ensuring that the device operates normally. This includes keeping the back pressure inside the tube at a reasonable level during flow. In this work, a model was developed for predicting the pressure drop across the length of a tube involving non-Newtonian fluids (namely gels). Pressure predictions were generated for specific temperatures and compared against independent experimental measurements made under steady state flow as well as pulsed flow conditions that are typical for an infusion pump. In both cases, the results exhibited a slight deviation from the model prediction at high flow rates. This deviation was shown to be attributed to tubing flexibility allowing a slight increase in diameter with increasing pressure. After applying an appropriate correction, the results and model showed excellent agreement, even for the case of pulsed flow involving the pump. This work demonstrates that the model can offer a practical means for estimating the back pressure in tubing during flow and can help guide the development and improvement of drug/medical device combination products.

Wednesday 6:05 Poster

PO124

Bacterial biofilms can increase their stiffness by making more of a soft biopolymer

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Bacterial biofilms are communities of bacteria held together by a biopolymer matrix, and they are responsible for most chronic bacterial infections. In the body's attempts to clear these biofilms, they are subjected to mechanical forces exerted by phagocyte defenders, which exert forces of the order of kiloPascals. *Pseudomonas aeruginosa* is an opportunistic human pathogen which readily forms biofilm infections. Recent work by Huse, Whiteley, and co-workers has shown that long-term infections of *P. aeruginosa* evolve to increase the expression of one biopolymer, named PSL (2013 PLoS ONE). PSL is one of four biopolymers that are major constituents of the *P. aeruginosa* matrix. Here, we show that increased PSL expression can stiffen the biofilm by about a factor of two. This is surprising, since increased expression of other biopolymers acts to soften biofilms. We speculate that the stiffening effect of PSL may result from long-ranged interactions that allow bacteria to act as cross-linking structural elements in the biofilm. We further speculate that some of the fitness associated with increasing PSL expression in long-term infections may come from increasing biofilm stiffness and resistance to mechanical clearance.

Wednesday 6:05 Poster

PO125

Numerical and experimental modeling of blood sedimentation

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One of the major parameters that changes the viscosity of blood is Red Blood Cells (RBCs) aggregation. This work describes the development of a computational fluid dynamic model that considers RBCs and aggregated RBCs as the poly-dispersed phase in a base fluid (blood plasma). This model is used to simulate RBCs aggregation while sedimenting due to gravity. The aggregation rate was assumed to have a linear relation with hematocrit. The numerical aggregation rate coefficient is set up in order to agree with the RBCs aggregate sizes of our experimental results. Experiments are done using a microscope with a horizontal lens to be able to observe human blood in a vertical "U" shape PDMS chip. Then the aggregate size distributions are estimated using image processing. Complete numerical modeling of blood using poly-dispersed model is the aim of this research, and this work is done as the first step towards this goal. Future work will investigate the application of this model to a Couette flow, with the introduction of a dependency between the aggregation rate coefficient and the shear rate.

Wednesday 6:05 Poster

PO126

Random walk simulation and one-particle tracking of fibroblast cells

Clare Maristela V. Galon and Rommel Bacabac

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Particle-tracking methods, which probe local mechanical properties, are well suited to test existing hypothesis derived from in vitro models of reconstituted cytoskeleton networks. We present in this paper the theoretical results, through simulation using labVIEW, the trajectories of a particle in Brownian motion. For a 2.0-micron polystyrene bead attached to the walls of fibroblast cells, we track its movements through time using video microscopy in which Rytrack software geared with algorithms, is used to extract the trajectories of the particles. The time-lag dependence mean-squared displacement (MSD) of each fibroblast cell, which is computed from the time-dependent coordinates of that cell, reveals the viscoelastic nature of the microenvironment in the immediate vicinity of each cell. From the experiment and through simulations of random walk, we have found out that as time increases, MSD also increases. Observing from our computed MSDs, we could say that the medium presents some viscoelastic properties because the tracers are having sub-diffusive mean trajectories and the mechanical properties of the cytoplasm of fibroblast cells are spatially variable and depend on timescales. There are deviations seen with increasing slopes due to the specifically chaotic mechanism which was a long time considered to be a property of living or at least organic matter and due to the rate of diffusion of the cell which is affected by its properties and its surrounding solution. We can also attribute it to cell attachments because it entails a very good contact of our beads to our cells for us to track the motions correctly. Other main sources of uncertainty resulting from image-fitting approaches are due to noise and camera exposure. The protocols we followed in our laboratory with regards to the sample preparation were safe and efficient because we were able to attach correctly the fibronectin-coated polystyrene beads unto our cell and were able to track its trajectories.

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PO127

A visual scripting interface for human red blood cells' osmotic characteristicsClare Maristela V. Galon and Rommel Bacabac*Physics, University of San Carlos, Cebu City, Cebu 6000, Philippines*

The mammalian red blood cell (RBC) plasma membrane is very permeable to water, and osmosis across the red blood cell plasma membrane occurs very rapidly. Therefore, mammalian red blood cells (RBCs) are sensitive to osmotic pressure gradients and their viability depends greatly on the amount of salt in the surrounding medium. Furthermore, the osmotic fragility of Human RBCs is not uniform and the number of cells undergoing hemolysis depends on the degree of tonicity of the extracellular medium. Hence, we tested whether the salinity of the medium used in washing RBCs affect their surface morphology. We designed a machine vision system, using National Instruments Vision Assistant (NIVA, Austin, USA) for automatically counting the number of RBCs present in a hemocytometer. We have found out that there are less RBCs present and less crenation or deformation on their shape when washed during preparation using a medium with 0.89% Sodium Chloride (NaCl) concentration compared with Phosphate Buffer Saline (PBS) solution (Calbiochem, Baltimore, Maryland, USA). The same results occurred with washing using media of salt concentrations less than 0.89% NaCl. Furthermore, cells that appeared blurry under the microscope were present when subjected to 0.46% and 0.36% NaCl media. These cells are suspected to have swollen due to hypotonic medium conditions. Thus, the RBC count correlated with the salt content of the washing medium. However, with media of concentrations higher than 0.89% NaCl, we observed the presence of several crenated RBCs. These findings support observations relating salinity in blood with RBC count in physiological conditions. The use of a machine vision system for cell counting is recommended for minimizing human error and enhancing methods that require high throughput characterization.

Wednesday 6:05 Poster

PO128

Numerical study of the influence of the swimming microbot's morphology in a blood analogue fluid flowSergio Martinez-Aranda, Francisco J. Galindo-Rosales, and Laura Campo-Deaño*Centro de Estudos de Fenómenos de Transporte, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal*

In the recent years, the use of bio-inspired micro and nanobots to operate through the human body has become a challenge for science and technology [1]. The future application of these new devices will represent a huge improvement in recent medical treatments such as detecting cerebral aneurysms or drug delivery. Many experimental and numerical studies have been carried out concerning micro-flows behavior [2, 3] or microbots fabrication, propulsion and control [4, 5]. However, rarely the non-Newtonian behavior of biological fluids as blood is taken into account in these studies. In this work we present a 2D numerical study focused on the influence of the shape of a swimming microbot through a human body channel, considering the viscoelastic properties of blood. For the microbot, four different shapes are analyzed: an sphere, a cubic block and two ellipsoids with aspect ratios $\frac{1}{2}$ and $\frac{1}{4}$ respectively. Parameters proposed by Campo-Deaño [6] for a multimode simplified-PTT model were considered for mimicking the shear-thinning behavior and elasticity response of blood. Simulations were developed using the open source code OpenFOAM together with the viscoelasticFluidFoam solver [7]. Results showed that the higher the flow rate is, the longer the wake becomes downstream of the rear stagnation point. However, the magnitude of the negative wake decreases as flow rate increases.

Authors would like to acknowledge financial support from FCT, COMPETE and FEDER through project EXPL/EMS-TRA/2306/2013 and grants IF/00148/2013 and IF/00190/2013.

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Wednesday 6:05 Poster

PO129

Numerical study of the flow of a shear thickening fluid expelled out from a cellSergio Martinez-Aranda, Laura Campo-Deaño, and Francisco J. Galindo-Rosales*Centro de Estudos de Fenómenos de Transporte, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal*

In the last decade Shear Thickening Fluids (STFs) have been incorporated into other materials for the fabrication of passive dissipative devices[1-2]. The addition of STFs to the porous media increases their energy absorption capabilities, due to the contribution of the viscous work done by expelling the fluid from inside the cells of the porous medium, which is added to the energy dissipated due to the elastic, plastic, and buckling modes that occur during compression. Stabilized suspensions of cornstarch with a high loading fraction of particles are a typical example of a discontinuous and eco-friendly STF, and it has been reported that these suspensions enhance their shear thickening behavior when sheared under confinement[3]. The dynamic response of STFs is greatly affected by the applied deformation rates, which depend directly on the local geometry and the applied forces. In this work, we have developed a 2D numerical study of the flow of a cornstarch aqueous suspension expelled out from a single cell at different radial velocities, mimicking the effects of different impact energies. The ad-hoc model by Galindo-Rosales et al[4,5] was considered as generalized Newtonian model for the constitutive equation of the fluid. The numerical simulations were developed at steady state based on finite volume method. The geometry consisted of a sudden contraction-expansion which represents the path followed by the STF when expelled from one cell towards the continuous one.

Authors would like to acknowledge financial support from FCT, COMPETE and FEDER through project EXPL/EMS-TRA/2306/2013 and grants IF/00148/2013 and IF/00190/2013.

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Wednesday 6:05 Poster

PO130

Velocity profile measurements of blood in PDMS bifurcating microchannels using micro-particle image velocimetry

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Microcirculation is the range of blood vessels with diameter around 100 μm or less. Understanding the dynamics of the blood at the micro scale is important in the research of the vascular diseases development and in the design of micro-artificial organs. Blood is a non-homogeneous fluid, and its complex composition and environment make the characterization of blood at the micro scale challenging. The purpose of this experimental work is to study the influence of the microchannel bifurcation on the microhemodynamics. In particular to study the velocity profile and evaluate the change in the shear rate at the wall. High shear stress can damage red blood cells and activate platelets resulting in anemia or thrombus, while low shear rate allow RBCs to aggregate and increase the blood viscosity. In addition, in the microcirculation, processes such as medicine uptake, nutrient and gas exchange between blood and body cells are shear-dependent. AutoCAD program, Soft lithography and microfabrication are used to design the mold to build the proposed microchannels network. Polydimethylsiloxane (PDMS) is used to build square cross section straight microchannels with dimension of $20\mu\text{m} \times 20\mu\text{m}$, and network with bifurcating angle 35 or 75 degree. Using Micro-particle image velocimetry (μPIV), which is a particle-based flow visualization technique, the velocity profiles of flow in microchannels has been measured. The velocity profile is used to deduce the maximum velocity at the microchannel center, flow rate in the microchannel, and shear rate at the microchannel wall. The velocity profile is a function of the blood flow rate, percentage of red blood cells, shape and material of the microchannel. In future work, gas transfer as a function of the microchannel geometry, in relation with the local hemodynamics, is going to be investigated. This study will contribute to characterize blood flow in microcirculation network and lead to improve the design of several micro-artificial organs or lab-on-chip.

Wednesday 6:05 Poster

PO131

Correlating protein-protein interactions and solution viscosities at high concentration

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Therapeutic monoclonal antibodies are effective due to their ability to bind tightly and selectively to the drug targets. However, high doses are necessary for the effectiveness of these proteins. Currently there are two methods of drug administration; intravenous, large volume at dilute condition and subcutaneous, small volume at high concentration.[1] The subcutaneous route of drug administration is preferred due to its convenience and the possibility of patient self-administration. However, high concentrations lead to undesirable solution behaviors such as increases in viscosity, aggregation, and protein instability.[2] Improved understanding the cause of such undesirable behaviors may lead to new strategies to alleviate current difficulties when formulating and manufacturing mAb products.

Recent research has attempted to understand the relation between viscosity changes at high concentrations with measurements of protein-protein interactions (PPI).[3] This poster will focus on initial work conducted using *alpha*-chymotrypsinogen A (aCgn), where we have experimentally determined PPI and viscosity over a broad range of protein concentration. Static and dynamic light scattering (SLS and DLS), were used to measure PPI over a range of ionic strengths and pH conditions. The osmotic second virial coefficient (B_{22}) and the Kirkwood-Buff integral (G_{22}) were used to quantify PPI in dilute and concentrated regimes, respectively. Viscosity of aCgn solutions was measured using multiple particle tracking microrheology. The results of these experiments will be presented and discussed in terms of its application in elucidating the connection between PPI and pronounced increases in viscosity that are sometimes observed at intermediate to high protein concentrations.

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Wednesday 6:05 Poster

PO132

A novel method to characterize the creep recovery of soft biomaterials

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Understanding the mechanical behavior of soft materials ranging from biological tissues to foods is of a great interest in regards to biomaterial design and processing. Although creep recovery test is considered as an important measurement to assess elasticity and structure recovery of biomaterials, the low force resolution and displacement sensitivity under a compressive stress test may limit the application of a non-destructive testing protocol. In the current study a new method was developed to measure the recoverable strain of gels (agar) by using a high-speed, high accuracy Laser Displacement Sensor (LK-G82, Keyence Corporation, USA) with a 1000 Hz sampling rate. Agar gels of different concentrations (0.4% - 1%) were exposed to a constant stress (30-1500 Pa) for 30 seconds and displacement was recorded for 30 seconds after removing the applied stress by using a Matlab/Simulink model through dSpace Controller Desk. Total recoverable deformation changed from 2-91% of maximum deformation depending on the agar concentration and applied stress. Compression tests were performed at a displacement rate of 0.005 mm/s in order to set the suitable parameters for recovery test and stress vs strain curves were linear up to 10% deformation for all concentrations studied that refers to a maximum 9.1 % true recoverable strain. Also, recovery predictions were performed using relaxation times obtained from

oscillatory tests and were in a good agreement with the results obtained from the proposed method. Presented data is expected to serve as a scaffold for further theoretical and experimental studies in the field of biomaterial rheology.

Wednesday 6:05 Poster

PO133

Slip and flow dynamics of thin polymer films

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We investigate the slip of tridisperse mixtures of nearly monodisperse polystyrene samples on Teflon-coated silicon wafers using dewetting experiments. Tridisperse samples with a fixed weight-average molecular weight but different number-average molecular weight were prepared. Thin films of ca. 200 nm were spun cast on mica from polymer solutions and transferred on Teflon substrates. Hole growth rate and rim profile of samples with and without annealing were examined at different temperatures above the glass transition temperature of samples. Slip properties and flow dynamics were then examined and compared. We found that the rim morphology and slip of polystyrene blends on Teflon is independent of the molecular weight distribution. On the other hand, flow dynamics is significantly affected by the presence of short chains in mixture. This was attributed to lower glass transition temperature of short chains.

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Plenary Lectures and Award Presentation

- Monday, October 6**
8:30 AM, Millennium Hall
The wall slip of polymer melts: The rule or the exception?
Savvas G. Hatzikiriakos
Chemical and Biological Engineering, The University of British Columbia
- Tuesday, October 7**
Bingham Lecture
8:30 AM, Millennium Hall
Rheology revealed - Measuring the atomistic-to-micron scale structure and dynamics of complex fluids and soft matter under flow with neutrons
Norman J. Wagner
Chemical and Biomolecular Engineering, University of Delaware
- Wednesday, October 8**
8:30 AM, Millennium Hall
Microfluidic tools for the manipulation and analysis of macromolecules, vesicles, capsules, and suspensions
Susan J. Muller
Chemical and Biomolecular Engineering, University of California, Berkeley
- Thursday, October 9**
Metzner Award Presentation
8:00 AM, Millennium Hall
Low-dimensional material functions for describing asymptotically-nonlinear viscoelasticity
Randy H. Ewoldt
Mechanical Science and Engineering, Univ. of Illinois at Urbana-Champaign

Social Program

- Sunday, October 5**
Industry/Faculty/Student Forum: *Rheology in the Real World*
4:00 PM – 6:00 PM Washington C
Sponsored by AIP and The Dow Chemical Company
- Welcoming Reception**
6:30 PM – 8:30 PM 33rd Floor of Loews Philadelphia Hotel
Hosted by TA Instruments
- Tuesday, October 7**
Rocky Rheology Run
6:45 AM Loews Philadelphia Hotel Lobby
- Society Business Meeting**
12:05 PM – 1:30 PM Commonwealth D
- Awards Reception**
7:00 PM – 8:00 PM Millennium Prefunction Area
Sponsored by Xpansion Instruments
- Awards Banquet**
8:00 PM Millennium Hall
- Wednesday, October 8**
Poster Session Reception
6:05 PM – 8:00 PM Millenium Hall
Sponsored by Anton-Paar USA

*The Society gratefully acknowledges the generous support of
Anton-Paar USA, Malvern Instruments, TA Instruments, Xpansion Instruments
American Institute of Physics, The Dow Chemical Company
Department of Chemical and Biomolecular Engineering and
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