



# THE SOCIETY OF RHEOLOGY

## 89<sup>TH</sup> ANNUAL MEETING PROGRAM AND ABSTRACTS

Embassy Suites Denver Downtown  
Denver, Colorado  
October 8 - 12, 2017

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Matthew Liberatore (chair)

*The University of Toledo*

Andy Kraynik

*Consultant*

Joseph Samaniuk

*Colorado School of Mines*

Nathan Crawford

*ThermoFisher*

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*National Renewable Energy  
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Abstract Book Editor and Webmaster:

Albert Co, *University of Maine*

# Meeting Schedule

## Monday, October 9, 2017

	<i>CYA</i>	<i>CYB</i>	<i>CYC</i>	<i>CEA</i>	<i>CEB</i>	<i>ASP</i>
8:30			R. T. Bonnecaze (PL1) - <i>CCB</i>			
9:20			Coffee Break			
9:50	EF1	SM1	SC1	NF1	IM1	CR1
10:15	EF2	SM2	SC2	NF2	IM2	CR2
10:40	EF3	SM3	SC3	NF3	IM3	CR3
11:05	EF4	SM4	SC4	NF4	IM4	CR4
11:30	EF5	SM5	SC5	NF5	IM5	CR5
11:55			Lunch Break			
1:30	EF6	SM6	SC6	NF6	IM6	CR6
1:55	EF7	SM7	SC7	NF7	IM7	CR7
2:20	EF8	SM8	SC8	NF8	IM8	CR8
2:45	EF9	SM9	SC9	NF9	IM9	CR9
3:10			Coffee Break			
3:45	EF10	SM10	SC10	NF10	IM10	MM1
4:10	EF11	SM11	SC11	NF11	IM11	MM2
4:35	EF12	SM12	SC12	NF12	IM12	MM3
5:00	EF13		SC13	NF13	IM13	MM4
5:25			End			
6:30			Monday Evening Reception			

## Tuesday, October 10, 2017

	<i>CYA</i>	<i>CYB</i>	<i>CYC</i>	<i>CEA</i>	<i>CEB</i>	<i>ASP</i>
8:30			J. A. Kornfield (PL2) - <i>CCB</i>			
9:20			Coffee Break			
9:50	AM1	SM14	EF14	CR10	GS1	MM5
10:15	AM2	SM15	EF15	CR11	GS2	MM6
10:40	AM3	SM16	EF16	CR12	GS3	MM7
11:05	AM4	SM17	EF17	CR13	GS4	MM8
11:30	AM5	SM18	EF18	CR14	GS5	MM9
11:55			Lunch Break / Society Business Meeting			
1:30	AM6	SM19	SC14	NF14	GS6	MM10
1:55	AM7	SM20	SC15	NF15	GS7	MM11
2:20	AM8	SM21	SC16	NF16	GS8	MM12
2:45	AM9	SM22	SC17	NF17	GS9	MM13
3:10			Coffee Break			
3:45	SG1	SM23	SC18	NF18	GS10	MM14
4:10	SG2	SM24	SC19	NF19	GS11	MM15
4:35	SG3	SM25	SC20	NF20	GS12	MM16
5:00	SG4	SM26	SC21	NF21	GS13	MM17
5:25			End			
7:00			Awards Reception - <i>CCF/SLF</i>			
8:00			Awards Banquet - <i>CCB</i>			

## Wednesday, October 11, 2017

	<i>CYA</i>	<i>CYB</i>	<i>CYC</i>	<i>CEA</i>	<i>CEB</i>	<i>ASP</i>
8:30			K. Anseth (PL3) - <i>CCB</i>			
9:20			Coffee Break			
9:50	BB1	SM27	SC22	GS14	NF22	SG5
10:15	BB2	SM28	SC23	GS15	NF23	SG6
10:40	BB3	SM29	SC24	GS16	NF24	
11:05	BB4	SM30	SC25	GS17	NF25	SG8
11:30	BB5	SM31	SC26	GS18	NF26	SG9
11:55			Lunch Break			
1:30	BB6	SM32	SC27	GS19	NF27	SG10
1:55	BB7	SM33	SC28	GS20	NF28	SG11
2:20	BB8	SM34	SC29	GS21	NF29	SG12
2:45	BB9	SM35	SC30	GS22	NF30	SG13
3:10			Coffee Break			
3:45	BB10	SM36	SC31	GS23	NF31	SG14
4:10	BB11	SM37	SC32	GS24	NF32	SG15
4:35	BB12	SM38	SC33	GS25	NF33	SG16
5:00	BB13	SM39	SC34	GS26	NF34	
5:25			End			
6:30			Poster Session & Reception - <i>CCB</i>			
6:30			Gallery of Rheology Contest - <i>CCF</i>			

## Thursday, October 12, 2017

	<i>CYA</i>	<i>CYB</i>	<i>CYC</i>	<i>CEA</i>	<i>CEB</i>
8:00			A. S. Khair (AP1) - <i>CYC</i>		
8:40	SG18	SM40	SC35	GS27	NF35
9:05	SG19	SM41	SC36	GS28	NF36
9:30	SG20	SM42	SC37	GS29	NF37
9:55			Coffee Break		
10:25	SG21	SM43	SC38	GS30	NF38
10:50		SM44	SC39	GS31	NF39
11:15		SM45	SC40	GS32	NF40
11:40			SC41		NF41
12:05			End		

## Session and Room Codes

AM = Active, Motile, and Field Responsive Materials  
 AP = Award Presentations  
 BB = Biomaterials and Biological Systems  
 CR = Computational Rheology  
 EF = Emulsions, Foams, and Interfacial Rheology  
 GR = Gallery of Rheology Contest  
 GS = Gels and Self-Assembled Systems  
 IM = Inverse Problems and Material Design

MM = Microrheology and Microfluidics  
 NF = Non-Newtonian Fluid Mechanics  
 PL = Plenary Lectures  
 SC = Suspensions, Colloids and Granular Systems  
 SG = Solids, Glasses, and Composites  
 SM = Polymer Solutions and Melts

*ASP* = Aspen  
*CCB* = Cripple Creek Ballroom  
*CCF* = Cripple Creek Foyer  
*CEA* = Crestone A  
*CEB* = Crestone B  
*CYA* = Crystal A  
*CYB* = Crystal B  
*CYC* = Crystal C  
*SLF* = Silverton Foyer C

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## Monday Morning

### Symposium PL Plenary Lectures

Monday 8:30 Cripple Creek Ballroom

PL1

#### **Energy, entropy and structure of soft particle glasses**

Roger T. Bonnecaze

*McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

Suspensions of soft particles, such as microgels, micelles and emulsions, form so-called soft particle glasses (SPGs) at high concentration. These suspensions have wide application including coatings, 3D printing, and personal care products, often for their rheological properties which range from solid- to liquid-like. At high concentrations the particles are jammed together and their structure and interesting rheological properties are predominantly due to elastic interactions. Because of this, thermodynamic state functions like energy and entropy are shown to be useful to describe and correlate the rheological properties of these SPGs. Ultimately, these state functions are shown to be determined by the microstructure of the SPGs connecting the particle scale interactions to the macroscopic properties. Remarkably for a dissipative system, the rheology is shown to be derivable from an energy function, analogous to the extraction of stress from the strain-energy function in elasticity theory. This provides an alternative perspective and methodology to model and describe these materials.

### Symposium EF Emulsions, Foams, and Interfacial Rheology

Organizers: Nicolas Alvarez and Vivek Sharma

Monday 9:50 Crystal A

EF1

#### **A radial Langmuir trough design for simultaneous microscopy and dilatational deformation of a complex fluid-fluid interface**

Joseph R. Samaniuk

*Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States*

The viscoelastic properties of monolayers of amphiphilic molecules at a fluid-fluid interface determine, in part, the stability of the foams and emulsions found in cosmetics, pharmaceutical formulations, foodstuffs, and petroleum refining. In addition to foam and emulsion stability, the mechanical properties of fluid-fluid interfaces are relevant to the study of biological membranes, especially lipid bilayers, where viscoelastic properties affect the transport of molecules tangentially through the membrane, and mechanical properties provide biological cells with requisite structural integrity. Unlike most bulk fluids, fluid-fluid interfaces are highly compressible and display a rich variety of viscoelastic behavior that depend on the area-density of the interfacial molecules. As a consequence of compressibility, a complete rheological description requires measurements of both shear and dilatational properties; thus, interfacial rheological devices are typically designed to generate either pure shear deformations, or pure dilatational deformations. However, isolating purely dilatational deformations in an apparatus amenable to microscopy has always been an experimental challenge. This work includes the design of, and data from, a miniaturized radial Langmuir trough that generates purely dilatational deformations with a 9:1 compression ratio, and operates on the platform of a conventional fluorescence microscope.

Monday 10:15 Crystal A

EF2

#### **Responsive foams for nanoparticle delivery**

Christina Tang<sup>1</sup>, Chang Tian<sup>2</sup>, and Robert K. Prud'homme<sup>3</sup>

*<sup>1</sup>Virginia Commonwealth University, Dept. Chemical and Life Science Engineering, Richmond, VA 23284, United States; <sup>2</sup>Dept. Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States; <sup>3</sup>Dept. Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States*

Foams are attractive vehicles to deliver therapeutics since they can effectively distribute nanoparticles over a large surface area using minimal liquid. We have developed three responsive foam systems for nanoparticle delivery. The foams are easy to make, stable at room temperature, and can be engineered to break in response to temperature or moisture. Temperature-responsive foams are based on the phase transition of long chain alcohols from solid to liquid. The solid wax particles act as Pickering emulsifiers. Polyethylene glycol (PEG)-based nanoparticles or PMMA latex nanoparticles were loaded into Tween 20 foams and the particle size was not affected by the foam formulation or foam breaking. The moisture responsive foams break by a surfactant dilution and destabilization of the foam interfaces. The third foam is based on carbon dioxide evolution when water is introduced into a dispersion of calcium carbonate and citric acid in a non-aqueous liquid phase. The delivery of therapeutic nanoparticles into the colon are followed by introducing lanthanide inclusions in the nanoparticles and using ICP-MS to quantitate NP delivery and clearance.

Monday 10:40 Crystal A

EF3

**Contrasting drainage and stratification in horizontal vs. vertical micellar foam films**Subinuer Yilixiati<sup>1</sup>, Ewelina Wojcik<sup>1</sup>, Yiran Zhang<sup>2</sup>, and Vivek Sharma<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States;* <sup>2</sup>*Department of Chemical & Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States*

Liquid foams consist of bubbles separated by thin liquid films. Understanding and controlling the drainage kinetics of freestanding thin films is an important problem that underlies the stability, lifetime and rheology of foams. In foam films formed with micellar solutions, the surfactant is present as interfacially-adsorbed layer at both liquid-air interfaces, as well as in the bulk as self-assembled supramolecular structures called micelles. We experimentally follow the drainage kinetics of foam films using imaging and color science. Interference between light reflected from two surfactant-laden surfaces that are ~ 100 nm - 10 micron apart leads to thickness-dependent iridescent colors in the visible region. As film thins below 100 nm, films appear to be progressively darker shades of grey. Furthermore, ultrathin micellar films exhibit stratification due to confinement-induced structuring and layering of micelles that contributes non-DLVO supramolecular oscillatory structural force contribution to disjoining pressure. Stratification in micellar foam films is manifested as stepwise thinning over time, and it leads to the coexistence of flat domains with discretely different thicknesses. In this contribution, we use Interferometry Digital Imaging Optical Microscopy (IDIOM) protocols to visualize and analyze thickness transitions and variations associated with stratification in micellar foam films made with sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB). We contrast the drainage and stratification dynamics in horizontal and vertical foam films. We experimentally study the emergence of thickness fluctuations near the borders and within thinning films, and study how buoyancy, capillarity and gravity driven instabilities and flows, are affected by the variation in bulk and interfacial physicochemical properties, that are effectively dependent on the choice of constituents, including added electrolytes.

Monday 11:05 Crystal A

EF4

**Surface forces, flows and fluxes underlying nanoridge formation and instabilities in stratifying, micellar freestanding films**Yiran Zhang<sup>1</sup> and Vivek Sharma<sup>2</sup><sup>1</sup>*Department of Chemical & Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States;*<sup>2</sup>*Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

Controlling and predicting the stability and lifetime of freestanding films, including foam and emulsion films, is crucial for many industrial and biological applications. Freestanding films (thickness < 100 nm), stabilized by surfactants above the critical micelle concentration, exhibit stratification or stepwise thinning. Stratification proceeds by formation of thinner domains that grow at the expense of surrounding films. In this article, we address several longstanding challenges related to the experimental characterization and theoretical description of thickness variations, forces, fluxes and flows underlying stratification. We show that nanoridges form and grow at the moving front around expanding domains, and we visualize their shape evolution using interferometry, digital imaging and optical microscopy (IDIOM) protocols with an unprecedented spatio-temporal resolution (thickness < 10 nm, time < 1 ms). We develop a theoretical model for drainage via stratification under the influence of supramolecular oscillatory surface forces arising from the confinement-induced layering of micelles, and we show that the nanoridge growth and domains expansion dynamics can be modeled quantitatively. Using IDIOM protocols, we also visualize the break-up of these nanoridges into mesas and describe how instability growth and evolution is determined by the interplay of capillarity and disjoining pressure.

Monday 11:30 Crystal A

EF5

**Effects of elastic flow instabilities on oil displacement in regular and irregular porous networks**Indranil Sinha<sup>1</sup>, Shweta Narayan<sup>2</sup>, Xueda Shi<sup>1</sup>, Cari Dutcher<sup>2</sup>, and Gordon F. Christopher<sup>1</sup><sup>1</sup>*Mechanical Engineering, Texas Tech, Lubbock, TX 79409, United States;* <sup>2</sup>*Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States*

Polymer flooding is an enhanced oil recovery technique used after both primary and secondary recovery have been exhausted and can often produce 30-60% of a wells output. Although, initially it was believed increased viscosity was the mechanism of enhancement, recent studies of porous elastic flows have indicated that displacement is improved by the changes to flow patterns caused by instabilities.

In this work, we demonstrate oil displacement by polymer flooding is improved in comparison to Newtonian fluid due to flow patterns caused by elastic instabilities at critical Mach numbers, and not due to increased excess pressure drops. This primarily appears due to the ability of the elastic instabilities to overcome capillary pressure in locally trapped oil bridges between solid surfaces and to better penetrate trapped regions of oil through normal velocities. Furthermore, we find that the nature of the porous network has a pronounced effect on the efficacy of this mechanism. Using square packed cylinder grids, hexagonally packed cylinder grids, and mock sandstone geometries, it is observed that polymer flooding is benefited by non-regular porous networks, which allow the normal velocities created by instabilities to better displace flow. Finally, we observe the effect of fractures in the geometries on the ability of polymer flooding to displace oil. Above critical Mach numbers, polymer flooding is able to better penetrate denser networks than Newtonian fluids due to the normal flow velocities that develop.

## Symposium SM Polymer Solutions and Melts

Organizers: Suraj Deshmukh and Reza Foudazi

Monday 9:50 Crystal B

SM1

### **Force-based theory for center-of-mass dynamics in ring polymer liquids**

Zachary E. Dell<sup>1</sup> and Ken S. Schweizer<sup>2</sup>

<sup>1</sup>*Dept. Polymer Science and Engineering, University of Massachusetts, Amherst, MA, United States;* <sup>2</sup>*Dept. Materials Science, University of Illinois at Urbana-Champaign, Urbana, IL, United States*

Recent simulations of concentrated non-concatenated ring polymer liquids have found they form collapsed globules on the macromolecular scale but still significantly interpenetrate to a degree that grows with molecular weight. In contrast to entangled chains, their internal modes relax relatively quickly compared to the center-of-mass (CM) diffusion time scale. In the spirit of approaches to understanding soft colloid suspensions, we formulate theories to describe the equilibrium structure and CM dynamics of ring liquids. An analytic intra-ring structure factor is constructed that has two fractal scaling regimes (globule-like on macromolecular scales, chain-like on smaller scales), which is then employed as input to calculate segment-scale inter-ring packing correlations using polymer integral equation theory. Imposing that the ring equation-of-state is qualitatively the same as for chain liquids, the computed inter-ring pair correlation functions and number of nearest neighbors as a function of degree of polymerization (N) are found to be consistent with simulations. For the CM dynamics, a segment-scale theory is developed with the primary assumption that the time-dependent effective intermolecular forces are determined by ring packing correlations. The theory is first analyzed by assuming inter-ring caging forces are relaxed via intra-ring dynamical fluctuations. The long time diffusion constant is predicted to scale as the inverse square of N beyond a crossover value that is significantly larger than the chain analog, in accord with simulations. A fully self-consistent treatment of intermolecular forces and ring CM dynamics predicts a glass-like localization transition on the macromolecular scale as N becomes large enough. In reality, this signals a crossover to activated hopping transport. How this phenomenon changes as some rings are randomly pinned is studied, and the results contrasted with recent simulations.

Monday 10:15 Crystal B

SM2

### **Probe rheology simulation technique: Polymer melts vs. polymer solutions**

Pouria Nourian, Dinesh Sundaravadivelu Devarajan, and Rajesh Khare

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

Over the past two decades, probe microrheology has emerged as a reliable experimental technique for extracting the microscale viscoelastic properties of complex fluids. The technique involves the determination of viscoelastic properties of soft matter by measuring probe particle motion in it. Recently, we have created a simulation technique that is analogous to the probe microrheology technique. Our probe rheology simulation technique combines molecular dynamics (MD) simulations with inertial generalized Stokes-Einstein relation (IGSER) to extract the viscoelastic properties of a complex medium. In previous work from our group, we applied this technique in both passive and active modes to determine the viscoelastic properties of unentangled and weakly entangled polymer melt systems. The probe rheology simulation results for viscoelastic moduli so obtained were in good agreement with those obtained from nonequilibrium MD (NEMD) simulations and the Green-Kubo formalism. In this work, we have tested the applicability of the probe rheology simulation technique for determining viscoelastic properties of polymer solutions. The success of the technique depends on the ability of the medium to act as a "continuum". The analysis of probe motion as determined by simulations is governed by an interplay of several length scales such as probe size, chain mesh size, chain size, and the wavelength of the shear wave. The technique is applied to a number of polymer solution systems covering a range of concentrations and polymer chain lengths. These results will be used to compare the applicability of the probe rheology simulation technique to polymer melts and polymer solutions.

Monday 10:40 Crystal B

SM3

### **Nonequilibrium molecular dynamics simulations of entangled polymer solutions undergoing planar elongational flows**

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

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

Experiments have shown that concentrated solutions of polymer chains in small molecule solvents exhibit different flow dynamics when subject to elongational flows from polymer melts and polymer solutions that use short chain oligomers as the solvent. This difference has been attributed to the monomeric friction reduction induced by the anisotropic environment around the polymer chains at high extension rates that occur in polymer melts and polymer solutions that which oligomeric solvents. Molecular simulation of these liquids offers a complementary perspective of individual molecule dynamics under flow.

In this work, we performed nonequilibrium molecular dynamics simulations of entangled linear polyethylene solutions subject to planar elongational flows. Through this study, we investigate how flow dynamics is affected by the architecture of the solvent and its interaction with polymer molecules. To achieve this, we used benzene as a small molecule solvent and C<sub>16</sub>H<sub>32</sub> as an oligomeric solvent in two different sets of simulations. Rheological, structural, and topological (entanglement network) properties of the systems are studied as functions of extension rate. Specifically, segmental orientation and stretch of polymer molecules, as well as solvent oligomers, are examined within a wide range of Weissenberg numbers. We will also discuss steady state in elongational flows from a molecular perspective.

Monday 11:05 Crystal B

SM4

**Brownian dynamics of wall tethered polymers in shear flow**Amir Saadat, Tiras Y. Lin, and Eric S. Shaqfeh*Stanford University, Stanford, CA 94305, United States*

The dynamics of a wall tethered polymer in shear flow is studied using a Brownian dynamics technique. Simulations are performed with bead-spring chains, and the effect of hydrodynamic interactions (HI) is incorporated through Blake's tensor with a finite size bead correction. We characterize the configuration of the polymer as a function of the Weissenberg number  $Wi$  by investigating the regions the polymer explores in both the flow-gradient and flow-vorticity planes. The fractional extension in the flow direction, the width in the vorticity direction, and the thickness in the gradient direction are reported as well, and these quantities are found to compare favorably with the experimental data of Yu et al.[1]. The cyclic motion of the polymer is described through the auto- and cross-correlation of the coordinates of the end bead, and we find the characteristic time scale of the cyclic motion as a function of  $Wi$  and chain length. We describe the collision process of each bead with the wall as a Poisson process and extract an average collision rate with the wall, which in general varies along the backbone of the chain. In comparison to the free-draining case, the addition of HI for a tethered polymer near a wall is found to have a significant effect. In particular, HI is found to decrease the fractional extension of a polymer as it is pushed away from the wall in the gradient direction, which is consistent with observations reported in the literature. Moreover, the average rate of collision with the wall is found to be reduced. We anticipate that results from this work will be directly applicable to, e.g., the design of polymer brushes or the use of DNA for making nanowires in molecular electronics.

[1] G. Yu, A. Kushwaha, J. K. Lee, E. S. G. Shaqfeh, and Z. Bao, (2010). *ACS nano*, 5, 275.

Monday 11:30 Crystal B

SM5

**The role of small amplitude oscillatory shear in solvent-diffusion through amorphous polystyrene in the melt state**Wissam Nakhle and Paula Wood-Adams*Mechanical, Industrial, Aerospace Engineering, Concordia University, Montreal, Quebec H3G2B7, Canada*

Current diffusion measurement techniques are constrained by a narrow range of accessible diffusion systems. Incomplete existing knowledge further motivates the use of a rheological tool, to study various aspects of diffusion in molten polymers. Diffusion of 1, 2, 4-trichlorobenzene (TCB) in molten polystyrene (PS) is studied at 150°C to 190°C using a rotational rheometer under small amplitude oscillatory shear (SAOS), and the diffusion coefficient is measured at various oscillation frequencies. Under SAOS, polymer molecules are in quasi-equilibrium, and the measured torque remains constant during time sweep measurements at a constant frequency on homogeneous samples. Solvents plasticize molten polymers, which causes the measured torque to decrease as solvent diffuses into polymer. The SAOS torque curve for concentric binary samples, with TCB at the center and PS as the outer material, is thus dependent on the concentration gradient, and reflects the diffusion process. A Fickian diffusion model, the free volume theory, and the theory of linear viscoelasticity (LVE) are used to determine the diffusion coefficient from the experimental torque curve. Free volume parameters are determined separately to diffusion experiments from LVE properties of homogeneous solvent-polymer mixtures, and a single parameter fitting is then used to determine the diffusion coefficient. We found that SAOS accelerates diffusion of TCB in molten PS by comparing the measured diffusion coefficient of systems subjected to continuous SAOS and those subjected to intermittent-type oscillations.

## Symposium SC Suspensions, Colloids and Granular Systems

Organizers: Cari Dutcher and Lilian Hsiao

Monday 9:50 Crystal C

SC1

**Non-Newtonian fluid behavior of dense suspensions in simple shear and extensional flows**Ryohei Seto and Giulio G. Giusteri*Mathematical Soft Matter Unit, Okinawa Institute of Science and Technology, Onna, Okinawa 904-0495, Japan*

Dense suspensions are non-Newtonian fluids which exhibit strong shear thickening and normal stress differences. Such rheological responses are determined by the microstructure built under flows and the interactions between particles. A simulation for quasi-static dynamics of particles in a viscous liquid is used to explore the microstructure formation and to estimate the importance of different interactions. Our particle simulation can impose simple shear and planar extensional flows. This allows to see how local rheological responses depend on the flow type. Taking into account these simulation results, we discuss about constitutive modeling for dense suspensions.

Monday 10:15 Crystal C

SC2

**The importance of extensional flow in determining the shear rheology of viscoelastic suspensions**Mengfei Yang, Jonas Einarsson, and Eric S. Shaqfeh*Stanford University, Stanford, CA 94305, United States*

The processing of viscoelastic suspensions is important in many engineering applications, including oil recovery, additive manufacturing, and pharmaceutical formulations, hence the bulk rheology of such suspensions is of practical interest. Due to the non-Newtonian nature of the

suspending medium, the rheology is complicated by nonlinear particle-fluid interactions. Previous theoretical work in the limit of low Weissenberg number ( $Wi$ ) using the second-order fluid as a model for the suspending medium showed that the suspension also behaves as a second-order fluid but with fluid properties that depend on the volume fraction. However, most industrial applications occur at finite  $Wi$  where such approximations are no longer valid. For example, experiments of suspensions in Boger fluids show shear-thickening of the viscosity and normal stress that do not obey the scaling laws of existing low  $Wi$  theories. This work aims to develop an understanding of the mechanism of shear-thickening at finite  $Wi$  and explain the roles of fluid rheology and particle-particle interactions. First, we perform direct numerical simulations of dilute suspensions to determine the regions of particle-fluid coupling that most contribute to the suspension shear-thickening and show that these lead to a linear scaling of the shear-thickening behavior at finite values of  $Wi$ . We identify the importance of the Lagrangian, time-dependent extensional flow within closed streamlines in generating the large fluid stresses that lead to the aforementioned thickening. Hence, we find it is crucial to quantify the extensional behavior of the suspending fluid to accurately predict the shear rheology of Boger fluid particulate suspensions. Furthermore, we perform new multi-particle simulations using the Immersed Boundary Method to show that particle-particle interactions are relatively unimportant for predicting the shear-thickening of the viscosity but are important for accurately predicting the zero-shear viscosity as a function of particle volume fraction.

Monday 10:40 Crystal C

SC3

### **Polyelectrolyte – particle flocculation in complex suspensions with mixed hydrodynamic fields**

Athena Metaxas, Nikolas Wilkinson, and Cari Dutcher

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

Water-soluble polymers with ionizable groups, or polyelectrolytes, are used in a number of applications, such as drinking water treatment, to form mesoscale structures ('flocs') with solid particulates in solution. Studying assembly kinetics and floc microstructure is particularly complex for systems with anisotropic particulates, such as clays, due to the variety of solution-dependent clay aggregate sizes and morphologies. Here, we explore assembly dynamics of anisotropic Na-bentonite clay particles with cationic polyacrylamide, a polymer commonly used in water treatment, in a variety of chemical solution conditions using a new Taylor-Couette cell setup. Taylor-Couette (TC) flows are ideal for study of mixing and composite material assembly due to their wide variation in controlled hydrodynamic flows. However, traditional TC cells are limited in their ability to examine initial mixing stages of an assembly process while the cell is operating. A TC cell with the novel ability to radially inject fluid into the annulus will be used to study how the hydrodynamics affect assembly and structure of these materials during the flocculation process. This work sheds more light on the complexities of polymer-anisotropic particle flocculation, towards improving dosing and treatment optimization for more efficient water treatment.

Monday 11:05 Crystal C

SC4

### **Does confinement screen hydrodynamic interactions in colloidal suspensions?**

Christian Aponte-Rivera and Roseanna N. Zia

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

We study hydrodynamic entrainment in spherically confined colloidal suspensions of hydrodynamically interacting particles as a model system for intracellular and other micro-confined biophysical transport. Modeling of transport and rheology in such soft materials requires an accurate description of the microscopic forces (e.g. external, entropic and hydrodynamic) that drive particle motion, and of boundary interactions. Experimentally, information about the rheological properties of micro-confined biophysical systems is often measured via two-point microrheology, where particle entrainment is assumed to behave as it does in unbound domains; confining boundaries are thus typically neglected. In the present work, we carry out dynamic simulations of colloidal motion in concentrated, spherically confined suspensions with a focus on the effect of 3D confinement on entrainment and rheology, and aim to determine whether the boundary "screens out" the effects of hydrodynamic interactions. We begin with a careful definition of "hydrodynamic screening", and show that entrainment between two tracer particles exhibits qualitatively different dependence on inter-particle separation compared to unbound suspensions. However, we find these changes in entrainment do not screen the effects of many-body hydrodynamic interactions. To provide evidence for the importance of many-body hydrodynamic interactions, we develop a scaling theory that collapses the concentrated mobility of spherically confined suspensions for all volume fractions and particle to cavity size ratios onto a master curve. Many-body hydrodynamics interactions with intervening particles result in a suppression of pair mobility, and are thus essential to predict transport and rheology in confined suspensions. For widely separated particles, we find the master curve is predicted by the pair mobility of point particles-a Green's function- in the confined domain. This suggests a more accurate framework for two-point microrheology in confined systems such as cells.

Monday 11:30 Crystal C

SC5

### **Effect of confinement on colloidal suspension rheology**

Meera Ramaswamy<sup>1</sup>, Christopher Ness<sup>2</sup>, Neil Lin<sup>1</sup>, Brian Leahy<sup>1</sup>, Andrew Fiore<sup>3</sup>, James W. Swan<sup>3</sup>, and Itai Cohen<sup>1</sup>

<sup>1</sup>*Department of Physics, Cornell University, Ithaca, NY, United States;* <sup>2</sup>*Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, United Kingdom;* <sup>3</sup>*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

Confined colloidal suspensions are ubiquitous in nature. Understanding the rheology of these confined suspensions is important in systems ranging from flow in microtubules and capillaries to petroleum extraction in the oil industry. However, studying confined suspensions is challenging because most commercially available rheometers do not reach gaps that are comparable to the particle diameter. Here we use a custom built confocal rheoscope to image the particle configuration in a suspension of silica microspheres while simultaneously measuring its stress response

at high Peclet numbers. With our devices we can cover gaps ranging from 30 to 2 particle diameters (60 - 4 microns). Further, we compare our experimental results to those from simulations, which enables us to determine the contributions of the different stresses (hydrodynamic and contact stresses) to the suspension rheology. These results provide new insights to the origin of the unique rheological behavior of confined suspensions.

## Symposium NF Non-Newtonian Fluid Mechanics

Organizers: Paulo Arratia and Chris Dimitriou

Monday 9:50 Crestone A

NF1

### **Effect of fluid elasticity on vortex formation in a planar elongational flow field**

Noa Burshtein<sup>1</sup>, Zografos Konstantinos<sup>2</sup>, Amy Q. Shen<sup>1</sup>, Robert J. Poole<sup>2</sup>, and Simon J. Haward<sup>1</sup>

<sup>1</sup>*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan;* <sup>2</sup>*School of Engineering, University of Liverpool, Liverpool L69 3GH, United Kingdom*

Recently it has been shown that flow of Newtonian fluids in cross-slot channels results in a steady spiral vortex instability as the Reynolds number,  $Re$ , is increased above a modest critical value  $Re_c$  (SJ Haward et al, Phys Rev E 93: 031101, 2016). In this work we study how the onset and development of the spiral vortex is influenced when fluid elasticity is increased by the addition of high molecular weight poly(ethylene oxide) (PEO) over a wide range of concentrations  $0.0001 < c < 0.1$  wt%. The effects of fluid relaxation time  $\lambda$  and viscosity ratio  $\beta$  are decoupled by using solvents of various viscosity. Flow visualization is performed using quantitative micro-particle image velocimetry, from which vorticity fields in the cross-section of the spiral vortex are computed. The vorticity in the centre of the spiral serves as a suitable bifurcation parameter to characterize the intensification of the instability with increasing  $Re$ . Our sensitive experimental set-up allows us to observe a significant change in  $Re_c$  at polymer concentrations as low as 0.0001 wt%, i.e. the concentration regime associated with polymer drag reduction (PS Virk & H Baher, Chem Eng Sci 25: 1183, 1970). Our results show that as the polymer concentration is increased,  $Re_c$  and the intensity of the vortex are reduced. At sufficiently high polymer concentrations  $c > 0.1$  wt%, we observe no vortex formation, but we encounter flow asymmetries due to the dominance of elastic effects at high Weissenberg numbers ( $Wi$ ). Our data can be collapsed to describe a stability boundary in dimensionless  $Wi-Re-\beta$  parameter space. Our results are qualitatively supported by numerical simulations and constitute new data on stability of low to moderate elasticity fluids in elongational flow fields. Our experimental configuration allows direct and prolonged examination of a single steady vortex, providing new insight into the effects of drag-reducing concentrations of polymer on vortex formation and dynamics.

Monday 10:15 Crestone A

NF2

### **Elastic instability and secondary flow of wormlike micellar solutions in cross-slot flow**

Michael Cromer and Arthur Kalb

*Rochester Institute of Technology, rochester, NY 14618, United States*

Recently, there has been intense experimental investigations about the development of an asymmetric instability in the flow of viscoelastic liquids in a cross-slot. The instability has been observed in both polymer and wormlike micellar solutions. In addition, a lip vortex upstream of the corners has been observed in experiments of these materials. To date, numerical investigations into the elastic instability have focused on polymeric models. Some of these models predict a constant shear viscosity, while others predict shear thinning. A feature common to the models studied is an increase in extensional viscosity with increasing extension rate. This extensional thickening occurs near the hyperbolic stagnation point in the cross-slot, feeding back on the flow, and causing the symmetric flow to become asymmetric. Unlike polymer chains, wormlike micelles (WLMs) continuously break and reform. This behavior causes a major difference in the extensional rheology. In particular, because of the chain breakage, wormlike micellar solutions typically exhibit strong extensional thinning. Despite this difference with polymers, the elastic instability is still observed. We will discuss this instability in the context of a model, the VCM model, that accurately describes the flow of WLMs. The VCM constitutive model (Vasquez, McKinley and Cook (2007)) is a two species, microstructural network model, which incorporates breakage and reforming of two micellar chains. The model predicts the typical WLM rheological trends of shear thinning and extensional thinning. Using the open-source CFD library OpenFOAM, we show that the VCM model predicts the formation of an asymmetric elastic instability. In addition, the VCM model predicts the formation of recirculation zones just upstream of where the inlet and outlet channels meet. In this talk, we focus on the role breakage and reforming play on the instability and secondary flow. Finally, the computational results are compared with experimental observations.

Monday 10:40 Crestone A

NF3

### **Probing the flow and nanostructure of viscoelastic fluids in tunable, complex deformation fields**

Patrick T. Corona<sup>1</sup>, Nino Ruocco<sup>1</sup>, Korbinian Strohm<sup>2</sup>, Chandi Sasmal<sup>1</sup>, Gary Leal<sup>1</sup>, and Matthew E. Helgeson<sup>1</sup>

<sup>1</sup>*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93117, United States;* <sup>2</sup>*Technical University of Munich, Munich 80333, Germany*

Industrial processing of viscoelastic fluids involves a wide range of flow histories that change the material's nanostructure and, therefore, the properties of the final product. Current means for measuring flow-induced nanostructure have focused primarily on measurements in purely shearing or extensional deformations, which fail to capture the highly nonlinear behavior of soft materials under more realistic flows. To address this, we have developed a new fluidic four roll mill (FFoRM) device, based upon the earlier work of Muller and coworkers, for measurements of

flow-induced structural changes under flows involving arbitrary near-2D deformation fields. The FFoRM was previously shown to achieve such flows for Newtonian fluids. Here, we determine its suitability for achieving arbitrary controlled deformations in a range of non-Newtonian fluids. Using a combination of flow visualization experiments and computational fluid dynamics (CFD) simulations, we assess the device's ability to produce nearly uniform flows of several viscoelastic fluids, and how these flows are altered by elasticity and shear thinning. Results are compared to 3D viscoelastic CFD simulations and a general stability criterion to be considered when designing devices for generating homogeneous flows of viscoelastic fluids in complex deformation fields.

Monday 11:05 Crestone A

NF4

### **Rheological and alignment transitions in rod-like micelle solutions**

Steven Hudson<sup>1</sup>, Javen Weston<sup>2</sup>, and Katie Weigandt<sup>3</sup>

<sup>1</sup>MSED, NIST, Gaithersburg, MD 20899, United States; <sup>2</sup>NIST, Georgetown University, Gaithersburg, MD 20899, United States;

<sup>3</sup>NIST Center for Neutron Research, Gaithersburg, MD 20899, United States

Recent RheoSANS experiments reported a sharp alignment transition in semi-dilute rodlike micelle solutions. At higher shear rates a peak in the alignment factor is observed and followed by a reduction of average micelle alignment. The alignment peak coincides with a rheological transition in the slope of the shear-thinning region of the fluid's flow curve. These measurements of structural and flow transitions are corroborated and extended by measurements in another flow geometry:  $\mu$ RheoSANS, which is a slit rheometer sample environment for SANS of samples undergoing pressure-driven flow, in which data analysis isolates the scattering from the high shear, near-wall region of the flow cell. In both flow geometries, the rheological transition and peak in micelle alignment coincide. Temperature strongly affects the behavior of the fluid and can be used to shift the critical shear rate where the transition occurs. Here, we present work investigating the cause of the observed transitions in fluid structure and rheology and how various factors affect that transition in order to provide insight into the structure-property relationship in the high shear rate regime for this commercially-relevant system. Understanding the visco-elastic properties and flow induced structure of these micelles is beneficial for their use in personal care, oil recovery, and other applications. The system studied here is a useful model, since the micelle alignment is relatively easy to interpret and the formulation is similar to commercial consumer cleansers.

Monday 11:30 Crestone A

NF5

### **Fluctuations of wormlike micelle fluids in pressure driven capillary flow**

Paul Salipante<sup>1</sup>, Steven Meek<sup>2</sup>, and Steven Hudson<sup>1</sup>

<sup>1</sup>MSED, NIST, Gaithersburg, MD 20899, United States; <sup>2</sup>Montgomery College, Gaithersburg, MD 20899, United States

We investigate the stability of shear banding wormlike micelle solutions in pressure driven capillary flow, with a focus on the effect of entrance geometry on the fluid fluctuations. The flow is measured at different points in the capillary using particle image velocimetry while simultaneously measuring the pressure drop across the entire capillary. In a capillary with a tapered constriction, we observe large persistent fluctuations above a critical flow rate. The fluctuations are characterized by rapid decreases in the pressure drop with corresponding increase in flow rate followed by a longer period of recovery where pressure increases and flow rate decreases. In an abrupt contraction, smaller fluctuations are observed above the same critical shear rate. The velocity field in the tapered entrance shows large flow circulations while the abrupt contraction results in smaller transient fluidized jets forming upstream of the constriction. The transition to unstable flow is shown to be initiated above critical shear and extension rates for the fluid systems. In the unstable flow regime, we measure characteristic timescales of the pressure and flow rate fluctuations.

## **Symposium IM Inverse Problems and Material Design**

Organizers: Ron Larson and Florian Nettesheim

Monday 9:50 Crestone B

IM1

### **"Psychorheology": Quantifying the human perception of viscosity through discriminability and perceptual bias in visual and haptic modalities**

Jeffrey Martin and Matjaž Jogan

*Johnson & Johnson Consumer, Inc., Skillman, NJ 08558, United States*

Viscosity is one of the salient properties of our more liquid-like consumer products. Through experience and by design, our consumers have developed viscosity preferences for products they use. Any violation of these expectations, e.g. due to reformulation, could lead to discontinuation of use. Consumers' perception of viscosity is however limited by the capacity of their perceptual system. It is therefore crucial to understand what is the minimum amount of change in viscosity that leads to a noticeable variation in the perceptual experience of a product.

In this work, we measured the minimum amount of change in viscosity that leads to a noticeably different perceptual experience of a product in visual and haptic domains, and the bias that a change in visual appearance of a product induces on the perceptual experience of its viscosity. In the haptic experiment, participants were asked to stir the test and reference fluids, Newtonian silicone oils of differing viscosity that were hidden from view, with their gloved index fingers. In the visual experiment, participants compared videos of test and reference fluids being stirred at a constant rate by a glass rod, and being pumped from a typical bottle pump dispenser. Using the method of constant stimuli, we determined perception thresholds and Weber fractions as a function of viscosity for five different reference viscosities ranging from 500 to 16,000 mPa.s, and

for both opaque and transparent fluids (dispensing only). Perceptual bias due to change in appearance was determined from observations of pairs with one opaque and one transparent stimulus.

The resulting perceptual thresholds and biases can be directly applied to consumer technical models to simplify reformulation of products with aesthetics that are inevitably different but still perceived the same by the consumer, and to aid in development of novel formulations that meet consumer expectations.

Monday 10:15 Crestone B

IM2

### **Extending yield-stress fluid paradigms for design**

Arif Z. Nelson<sup>1</sup>, Rafael Bras<sup>2</sup>, Jingping Liu<sup>2</sup>, Brittany Rauzan<sup>3</sup>, Ralph Nuzzo<sup>3</sup>, and Randy H. Ewoldt<sup>1</sup>

<sup>1</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Wm. Wrigley Jr. Company, Chicago, IL 60642, United States;* <sup>3</sup>*Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We report experimental measurements of high extensibility of several yield-stress fluids, demonstrating a behavior completely outside the standard paradigm of model materials and constitutive equations for yield-stress fluids. We designate "highly" extensible materials from uniaxial tension tests with values of strain-to-break larger than predictions of the tensorial Herschel-Bulkley model, and larger than experimental observations with some of the most heavily studied 'model' materials including aqueous microgel particle suspensions (Carbopol), and aqueous clay suspensions (Laponite and Bentonite). Real materials including a printing resin, chewing gums, and food products, have a yield stress but are able to survive extremely large extensional deformations.

The purpose of this work is to demonstrate the range of 'high' extensibility seen in model and application-relevant (commercial products, biomaterials) yield-stress fluids and generate a design space for materials selection and design of extensible yield-stress fluids. We also introduce model materials for expanding the extensibility design space of model yield-stress fluids and for identifying crucial extensibility performance targets in design for applications such as 3D printing.

Monday 10:40 Crestone B

IM3

### **Architectural paints: From hierarchical structure to rheology**

Tirtha Chatterjee<sup>1</sup>, Antony K. Van Dyk<sup>2</sup>, Valeriy V. Ginzburg<sup>3</sup>, and Nakatani I. Alan<sup>1</sup>

<sup>1</sup>*Core R&D, The Dow Chemical Company, Collegeville, PA 19426, United States;* <sup>2</sup>*Dow Coatings materials, The Dow Chemical Company, Collegeville, PA 19426, United States;* <sup>3</sup>*Core R&D, The Dow Chemical Company, Midland, MI 48674, United States*

Since their invention in the 1970s, hydrophobically modified ethoxylated urethane (HEUR) associative thickeners are widely used to modify the rheology of waterborne paints. Surprisingly, while much is known about their structure and rheology in water, the mechanism of their action in formulated paints is still not fully understood. Using small-angle neutron scattering (SANS), we studied the interaction of HEURs with model acrylic latex particles, and showed that the thickeners strongly adsorb onto the latex surfaces. On the mesoscale level, fractal aggregates are formed where latex particles are connected through transient HEUR bridges. These aggregates evolve under shear and the energy dissipation from drag on transient latex aggregates is the predominant mechanism of viscosity creation. Further, we demonstrate that in HEUR-based paints the first normal stress difference (N1) is controlled by two factors: (a) adsorption of HEUR molecules on latex particles and (b) ability of non-adsorbed HEUR to form transient bridges between particles with HEUR shells. By controlling these two effects, one can design a paint formulation with targeted N1 behavior (positive or negative N1 under high shear). Finally, a simplified phase diagram will be presented connecting formulation composition-microstructure- and N1 behavior. The results would serve as guidelines to formulate paints to meet the specific customer needs.

Monday 11:05 Crestone B

IM4

### **Multiscale modeling of polymer-colloid networks for design of latex coating rheology**

Ronald G. Larson, Hossein Rezvantlab, Elnaz Hajizadeh, Shi Yu, and Shihu Wang

*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States*

We describe methods of integration of a set of simulation methods to allow prediction of the rheological properties of colloid-polymer networks with application to latex coatings. A linkage is built between three levels of modeling, starting from a coarse-grained implicit solvent model of the polymer and colloid surfaces to Brownian Dynamics simulation of polymer chains binding to colloidal particles based on finitely extensible springs, which is then further simplified to a hybrid population balance/Brownian Dynamics model for networks of colloids bridged by polymer molecules. The limitations of each approach in predicting detailed polymer-colloid dynamics and interactions are discussed, and an efficient methodology is developed to map the rheological properties of these levels onto each other. This coarse-graining can establish a paradigm for modeling many other complex materials and multi-scale transport processes. It also provides an example of the use of multi-scale modeling for the design of rheological properties of coating materials.

Monday 11:30 Crestone B

IM5

**Toward co-design of surface textures and Non-Newtonian fluids for decreased friction in lubricated viscous sliding**Jonathon K. Schuh<sup>1</sup>, Yong Hoon Lee<sup>1</sup>, James T. Allison<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup><sup>1</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Industrial and Enterprise Systems Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We show experimentally in laminar flow that using surface textures and polymer additives together can reduce friction more than each acting independently. Motivated by this, we describe and solve a range of constitutive models, from simple to complex, that can be used for posing optimization problems for co-designing the fluid rheology and the surface texture to achieve optimal friction reduction. We have previously developed and validated a flow solver for Newtonian fluids against careful experiments at small gaps using a tribo-rheometer setup [1]. This model was then used to find optimal, generalized surface topography for surface texturing, resulting in spiral-like valleys across the disc domain [2]. To include Non-Newtonian effects, we consider a range of models with varying fidelity, from a systematic expansion about Newtonian behavior (second order fluid expansion with the 3-D flow theorem of Giesekus) up to fully nonlinear models (Giesekus) with the full 3-D Cauchy momentum equation. We describe our computational implementation of these models and present optimization results in the context of trade-offs: simpler models apply more generally for different material formulations, but for limited deformation conditions (limited range of the Pipkin map), whereas fully nonlinear models apply up to large Weissenberg and Deborah numbers, but cannot apply for all types of rheologically-complex material formulations. This represents a general challenge to design and optimization of non-Newtonian behavior.

References [1] J. K. Schuh, Y. H. Lee, J. T. Allison, and R. H. Ewoldt, "Design-driven modeling of surface-textured full-film lubricated sliding: validation and rationale of non-standard thrust observations," *Tribology Letters*, vol. 65, 2017. [2] Y. H. Lee, J. K. Schuh, R. H. Ewoldt, and J. T. Allison, "Enhancing full-film lubrication performance via arbitrary surface texture design," *Journal of Mechanical Design*, vol. 139, no. 5, pp. 053401-1-13, 2017.

## Symposium CR Computational Rheology

Organizers: Jim Swan and Rekha Rao

Monday 9:50 Aspen

CR1

**i-Rheo GT: Transforming  $G(t)$  obtained from molecular dynamics simulations into the materials' linear viscoelastic properties without artefacts**

Manlio Tassieri

*Division of Biomedical Engineering, University of Glasgow, Glasgow G12 8LT, United Kingdom*

I present a new analytical tool for deducing the materials' linear viscoelastic (LVE) properties from (atomistic and quasi-atomistic) molecular dynamics simulations (MDS) describing the temporal behaviour of the materials' shear relaxation modulus  $G(t)$ . The new tool allows the evaluation of the materials' complex shear modulus  $G^*(\omega)$  over the widest range of experimentally accessible frequencies, without the adoption of *preconceived* models, such as a generalised Maxwell model. This is achieved by means of the analytical method introduced by Tassieri *et al.* [*New J. Phys.* **14**, (2012); *J. of Rheology* **60**, (2016)] to evaluate the Fourier transform of raw data describing the temporal behaviour of  $G(t)$ . The analytical method has been implemented into a new open access executable named i-Rheo GT, enabling its use to a broad scientific community. The effectiveness of the new rheological tool has been corroborated both by analysing the dynamic response of a model system (i.e., a single Maxwell mode) and by direct comparison with bulk-rheology experimental data. i-Rheo GT offers the opportunity to gain new insights into the materials' LVE properties, especially at high-frequencies (i.e., in the glassy region and beyond); where (i) conventional tools (e.g., Reptate or Iris) struggle to *interpret* the data and (ii) MDS actually provide the most accurate predictions of  $G(t)$ . Interestingly, these frequency regions are commonly *unexplored* by the rheology community. Nevertheless, having access to atomistic and quasi-atomistic MDS represents both a challenge and a springboard for theoreticians to develop comprehensive models able to predict the materials' LVE properties over the widest range of experimentally accessible frequencies; hence, the importance of the new rheological tool.

Monday 10:15 Aspen

CR2

**Active learning of the constitutive relation by local mesoscopic simulations for continuum computations of non-Newtonian flows**Lifei Zhao<sup>1</sup>, Zhen Li<sup>2</sup>, Jie Ouyang<sup>1</sup>, Bruce Caswell<sup>3</sup>, and George E. Karniadakis<sup>2</sup><sup>1</sup>*Department of Applied Mathematics, Northwestern Polytechnical University, Xi'An, China;* <sup>2</sup>*Division of Applied Mathematics, Brown University, Providence, RI 02912, United States;* <sup>3</sup>*School of Engineering, Brown University, Providence, RI 02912, United States*

An active learning scheme is applied to the multiscale modeling of non-Newtonian flows. In particular, the continuum momentum simulator is constructed without the usual constitutive closure. The latter is learned 'on the fly' from mesoscopic dissipative particle dynamics (DPD) simulations of the dynamics of bead-spring chains subject to the deformation rates within each macro-element. In this work, the finite volume method is chosen as the continuum solver to provide transient flow fields which in turn initiate the local (DPD) simulations of the polymer fluid.

Thus the macroscopic rheology of the model polymer fluids needed for closure of the continuum solver is derived from the microscale dynamics of the model polymer chains. To minimize the need for expensive mesoscopic simulations of the entire flow field, DPD simulations are performed only as necessary by adaptively selecting them by with an active learning strategy based on Gaussian Process Regression (GPR). Results are presented from numerical experiments for flow past a cylinder between parallel plates for a fluid consisting of 25 bead-spring chains. At Reynolds number (Re) 10 only five DPD simulations were required to satisfy the continuum equations, and at Re 100 only one additional DPD simulation was needed. The computational cost of the proposed multiscale simulations using the GPR active learning scheme is significantly reduced when compared to other message-passing multiscale approaches.

Monday 10:40 Aspen

CR3

### **Probe rheology simulations for determining linear viscoelasticity of colloidal suspensions**

Dinesh Sundaravadivelu Devarajan, Pouria Nourian, and Rajesh Khare

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

Viscoelastic properties of colloidal suspensions are important for many industrial applications. In recent years, probe microrheology has emerged as an alternative experimental technique to traditional rheometry for the purpose of determining the viscoelastic properties of complex fluids. In previous work from our group, we have proposed a probe rheology simulation technique that uses molecular dynamics (MD) simulations along with continuum analysis involving the inertial generalized Stokes-Einstein relation (IGSER) to determine the linear viscoelastic moduli of polymer melts. Results from both passive and active probe rheology simulations were shown to be in good agreement with those obtained from the non-equilibrium molecular dynamics (NEMD) simulations and the Green-Kubo method. In this work, the applicability of the probe rheology simulation technique to colloidal suspensions is tested. Probe rheology results for colloidal suspensions with different volume fractions are compared with the results obtained using the NEMD technique. The results will be explained in the context of interplay of several length scales such as probe size, colloidal particle size, solvent bead size, and wavelength of the shear wave.

Monday 11:05 Aspen

CR4

### **Micro-structure and rheology of random patchy particles**

Gang Wang<sup>1</sup> and James W. Swan<sup>2</sup>

<sup>1</sup>MIT, Cambridge, MA, United States; <sup>2</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Colloidal particles with short-range, interactions are a staple of technology and biology. When interactions are treated as isotropic, such particles serve as a fundamental model for developing thermodynamic theories useful for interpreting experiments in colloid science. However, heterogeneities in the inter-particle interaction are common at the colloidal scale. Heterogeneous chemical functionalization, self-assembly, or phase separation during particle synthesis can lead to anisotropic inter-particle interactions. Such short-ranged, anisotropic interactions are common in biological systems as well in the form proteins. Therefore, understanding the assembly and transport of such particles can provide insight into a wide variety of relevant physical systems. In this computational study, we investigate dispersions of particles having surface patches with randomized functionality as a model for heterogeneous, anisotropic interactions. The characteristic of the surface functionalization are controlled with a Monte Carlo of an Ising model on the particle surface. The coupling between neighboring surface patches is adjusted freely, allowing us to study the structure, rheology, and dynamics of particles whose random surface patches interact of a length scale short relative to the particle radius. Particles with isotropic short ranged interactions are a fundamental model system in colloidal physics. We explore the differences between random patchy particles and isotropic particles having the same second virial coefficient and thus indistinguishable thermodynamically at low particle concentrations. Brownian Dynamics simulations with hydrodynamic interactions are utilized to simulate dispersions of these random patchy particles. We show that at modest particle concentrations significant deviations from the isotropic model are evident in thermodynamic quantities such as the pressure and microstructure as well and transport quantities such as the viscosity and mean squared displacement.

Monday 11:30 Aspen

CR5

### **Large-amplitude oscillatory shear (LAOS) of a dilute suspension of Brownian spheroids**

Toni M. Bechtel and Aditya S. Khair

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

The stress in a dilute suspension of monodisperse, rigid, Brownian spheroids is calculated under a large-amplitude oscillatory shear (LAOS) deformation. This is achieved by first numerically solving the Fokker-Planck equation for the orientational distribution function over a range of Weissenberg (Wi) and Deborah (De) numbers. Then, the stress tensor is determined from an orientational average of the stresslet exerted by the particles onto the suspending medium. Under a small-amplitude oscillatory shear (SAOS) deformation, where  $Wi \ll 1$ , the stress dynamics are relatively insensitive to the microstructure of the suspension, as parameterized by the aspect ratio ( $r$ ) of the particles. Specifically, the shear stress can simply be represented by a single Fourier mode (in the flow frequency) for aspect ratios ranging from rods ( $r \gg 1$ ), to near-spheres ( $r \sim 1$ ), to thin disks ( $r \ll 1$ ). However, under LAOS, where  $Wi \gg 1$  and  $Wi/De > 1$ , the stress dynamics are distinctly dependent upon the microstructure. The shear stress evolution of slender rods will exhibit quasi-steady behavior, which is periodically interrupted by sharp variations when the imposed flow momentarily vanishes. Conversely, the shear stress of a dilute suspension of nearly-spherical particles will mainly undergo rapid oscillations, followed by markedly slower oscillations when the imposed flow momentarily vanishes. Thus, our results indicate that LAOS is a useful tool to probe the dynamics of the microstructure in shear.

## Monday Afternoon

### Symposium EF Emulsions, Foams, and Interfacial Rheology

Organizers: Nicolas Alvarez and Vivek Sharma

Monday 1:30 Crystal A

EF6

#### **Does interfacial asphaltene aggregation actually stabilize crude oil/water emulsions through enhanced interfacial rheology?**

Minhazur Rahman<sup>1</sup>, Yu-Jiun Lin<sup>2</sup>, Sibani Lisa Biswal<sup>2</sup>, and Gordon F. Christopher<sup>1</sup>

<sup>1</sup>Mechanical Engineering, Texas Tech, Lubbock, TX 79409, United States; <sup>2</sup>Chemical Engineering, Rice University, Houston, TX 77005, United States

Surface active molecules play a key role for stabilizing water/crude oil emulsions. The stabilized emulsions create a range of flow assurance problems primarily in the transport and separation. The leading theory reinforced by numerous studies in the literature is that interfacial aggregation of Asphaltenes play a key role. Thus, it is important to understand how the interfacial rheological behavior of Asphaltenes at an oil/water interfaces is affected by relevant physical parameters.

In this work, we study 2 specific questions. First, what is the role of asphaltene surface concentration on interfacial rheology, and secondly how representative are model oils of in comparison to real crude systems. To study these questions, a Double Wall Ring (DWR) geometry with a modified base to allow visualization was used to characterize the interfacial viscosity, moduli and yield stress along with associated microstructure of the interface on a model oil (composed of toluene and dissolved asphaltenes at a range of weight concentrations) and crude oil at a water/hexane interface. As asphaltene concentration on the interface increases, the resulting interfacial film becomes more elastic with pronounced yield stresses, and denser larger structures are seen as well as visible fractures at high stresses. In comparison, lower concentration films are more viscous with pronounced shear thinning. Interestingly, when comparing crude oil to model oils with the same asphaltene content, crude oils behave very differently. Asphaltene concentrations in crude based on model oil results should create elastic, yielding films. However, crude films are viscous without any pronounced elasticity or yield. This indicates that other interfacial components in the crude are impacting film formation, and the multitude of work on model oils may be less applicable to actual crude emulsions.

Monday 1:55 Crystal A

EF7

#### **Effect of phase change on the rheology and stability of paraffin wax-in-water Pickering emulsions**

Purba Chatterjee and Patrick T. Underhill

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

Pickering emulsions are widely found in nature and industry including food, pharmaceuticals and oil industries. Often, Pickering emulsion studied have a Newtonian dispersed phase. However, the dispersed phase can be non-Newtonian such as one that can be subjected to a phase change under certain experimental conditions. This work examines how changing the physical state of dispersed phase alters the shear stability and bulk viscoelasticity of o/w emulsions. Model silica-stabilized, paraffin wax-in-water emulsions were synthesized and subjected to a phase change by changing the temperature between 15C and 80C. At lower temperatures (< 55C), the droplet deformability and particle mobility at the interface are significantly restricted while at higher temperatures (> 55C), the wax melts and expands, making the emulsion droplets deformable and the particles more relaxed. These directly affect bulk emulsion rheology both in steady shear and oscillatory shear. These properties are directly influenced by temperature, which alters the state of aggregation and network-structure of the emulsion droplets. The effect of emulsion concentration will also be described. Finally, we will show that the emulsions are sensitive to destabilization (gelation) under flow with the sensitivity directly varying with temperature and magnitude of shear fields (steady shear) applied. We believe that these observations will be instrumental in better understanding the stability and breakdown of such emulsion systems, and will help in their synthesis, transport and storage.

Monday 2:20 Crystal A

EF8

#### **Flow behavior of submicron emulsions in different concentration regimes**

Neda Sanatkaran and Reza Foudazi

*Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

Submicron emulsions are used in drug delivery systems, food products, and cosmetics. Therefore, it is essential to study the relationship between their rheology and structure for processing and application. In this work, we have studied the flow behavior of submicron oil-in-water emulsions (o/w) with different droplet sizes from dilute to highly concentrated regimes. First, we prepared a set of dilute o/w emulsions consisted of silicone oil dispersed in sodium dodecyl sulfate solution. Then, emulsions with different concentrations (10% to 80%) were obtained by centrifugation and dilution. The prepared emulsions show the viscoplastic behavior for all droplet sizes and volume fractions under investigation. Additionally, we examined different scaling models and fitting of experimental data. The scaling analyses show a strong dependence of the yield stress to volume

fraction in the concentrated emulsions, whereas it becomes almost independent of volume fraction below a critical concentration. As the droplet size decreases, the critical concentration is observed at lower volume fractions.

Monday 2:45 Crystal A

EF9

### **Shear-induced gelation and structural transitions in ultra-low interfacial tension microemulsions**

Katie Weigandt<sup>1</sup>, Javen Weston<sup>2</sup>, and Steven Hudson<sup>3</sup>

<sup>1</sup>*NIST Center for Neutron Research, Gaithersburg, MD 20899, United States;* <sup>2</sup>*NIST, Georgetown University, Gaithersburg, MD 20899, United States;* <sup>3</sup>*MSED, NIST, Gaithersburg, MD 20899, United States*

A rheological and microstructural characterization was conducted on a surfactant/brine/oil microemulsion that exhibits an interesting shear-induced gelation. The system consists of an industrially available extended surfactant (ethoxylated-propoxylated alkyl sulfate), sodium chloride brine, and a small amount of a refined alkane oil. At equilibrium, the mixture separates into two phases, a bicontinuous microemulsion phase and an excess brine phase. However, the fluid undergoes a phase transition when subjected to shaking or shear above a critical shear rate. After this transition, the sample behaves as a highly thixotropic gel; the viscosity of the solution greatly increases, a measurable amount of viscoelasticity develops, and the shear-induced structures require several days to fully relax. This sample has particular relevance to enhanced oil recovery techniques, where the shear-induced viscosity increase could have positive or negative effects on the oil production process depending on the application. Understanding the mechanism underlying this shear induced gel transition is necessary to realize the potential of this interesting phenomena. Small angle neutron scattering investigations of the gel using RheoSANS and 1-2 shear SANS devices have resulted in interesting scattering patterns at shear rates where gelation occurs. Additionally, at even higher shear rates, what appear to be large scale, monodisperse structures are observed, as evidenced by the appearance of distinct form factor peaks in SANS. Interpreting and understanding these scattering patterns in conjunction with the observed rheological behavior is the goal of this work.

Monday 3:45 Crystal A

EF10

### **Rheological and structural characterization of multiphase drops from its interfacial wave dynamics**

Rakhitha W. Udugama and Sukalyan Bhattacharya

*Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

This talk describes a novel mathematical theory to characterize the fluid properties and interior structures of a multi-component drop from its interfacial wave dynamics if recorded by an optical device like high-speed camera. For this purpose, the deformation due to natural pulsation at the surface of a suspended droplet has to be stored as a function of time and peripheral position. Then, the data has to be post-processed so that a dual Fourier transform in time and polar angle on the viewing plane can reveal the spectra of natural frequencies and decay constants associated with different modes of oscillation. The developed theory relates the measured spectra to desired system defining parameters like rheological coefficients as well as size, position and number of bubbles or particles embedded in the liquid domain. Accordingly, the talk mainly concentrates on three effects. Firstly, it shows how finer splits in frequencies akin to atomic energy levels appear in spectra if a bubble or a particle moves to an eccentric position inside the drop. Secondly, the results illustrate the effect of viscous dissipation on damped oscillation, where critical capillary numbers are calculated for specific modes dictating its transformation from under-damped vibration to over-damped one. Thirdly and finally, the analysis predicts how the frequencies and decay constants modify if the internal species are different. Comparisons are presented among three cases with 1) a gaseous bubble, 2) a solid particle and 3) a viscoelastic core residing inside the droplet. The comparative studies differentiate the spectral manifestations for each creating a possibility of their detection by reverse estimation even if the interior is opaque. Such capability can be potentially useful in scientific explorations of inaccessible domains as well as in quality control and performance enhancement of various combustive and manufacturing processes.

Monday 4:10 Crystal A

EF11

### **Transport of block copolymers to oil-water interfaces and impact on interfacial properties**

Michael L. Davidson<sup>1</sup>, Moshe Gottlieb<sup>2</sup>, and Lynn M. Walker<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States;* <sup>2</sup>*Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel*

Amphiphilic block copolymers are a broad class of materials that have been used to supplement or replace aliphatic surfactants. Although industrial use has been popular for several decades, determining structure/property relationships for wettability, detergency, and emulsification power is still an active area of research. We have characterized the adsorption behavior of two structures of block copolymer (diblocks of PEO-PDMS and triblocks of PEO-PDMS-PEO, where PEO is polyethylene oxide and PDMS is polydimethylsiloxane) at several fluid/fluid interfaces (water and a series of oils including isooctane, dodecane, silicone oil) using interfacial tensiometry and dilatational rheometry. The effects of interfacial curvature on interfacial tension and dilatational modulus will be discussed. Equilibrium interfacial layers have been characterized for irreversibility by solvent exchange, and these results will be compared with stress-relaxations performed by step changes in interfacial area. Ultra-low surface tensions have been observed at the silicone oil/water interface alongside the spontaneous formation of microbubbles. We explore this for several block copolymers and compare with bulk phase behavior and emulsion stability.

Monday 4:35 Crystal A

EF12

**Effect of salt valency and concentration on shear and extensional rheology of aqueous polyelectrolyte solutions**Anna V. Walter<sup>1</sup>, Leidy N. Jimenez<sup>2</sup>, Jelena Dinic<sup>2</sup>, Vivek Sharma<sup>2</sup>, and Kendra A. Erk<sup>1</sup><sup>1</sup>*School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States;* <sup>2</sup>*Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

The use of polyelectrolyte solutions is an effective method of Enhanced Oil Recovery (EOR); partially hydrolyzed polyacrylamide, HPAM, is the most commonly used polymer in EOR. In solution, HPAM interacts with monovalent and divalent cations that are present in oil basins. These interactions between HPAM and salt in solution can be studied using shear and extensional rheometry. The molecular weight (2 - 10 million g/mol) and concentration (0.005 - 0.3 wt%) of polymer was varied to include both dilute and semidilute regimes. Salt species (sodium chloride and calcium chloride) and salt concentrations ( $3.7 \times 10^{-4}$  - 1.5 M) were varied and chosen to model the concentration ranges found in oil basins. Both shear and extensional rheometry was performed on these solutions using a commercial torsional rheometer for measuring response to shear flow, and dripping-onto-substrate (DoS) rheometry for measurement of extensional viscosity and extensional relaxation time. The dripping-onto-substrate (DoS) rheometry protocols involve visualization and analysis of capillary-driven thinning and pinch-off dynamics of a columnar neck formed between a nozzle and a sessile drop. Increasing molecular weight and polymer concentration correlated with increased shear and extensional viscosity. It was found that all solutions were shear thinning but strain hardening in extension, regardless of salt species or concentration. While increasing monovalent salt concentration generally lowers shear viscosity and extensional relaxation times, the trend is non-monotonic. The trend with increasing divalent salt concentration is also non-monotonic; at higher divalent salt concentration, the extensional relaxation time is greater than that with any other salt concentration. This suggests divalent cations acting as temporary crosslinks when under extension. The combination of strain hardening and shear thinning may be especially beneficial for oil recovery, especially as these properties are maintained in the presence of salts.

Monday 5:00 Crystal A

EF13

**Drop breakup dynamics of dilute polymer solutions: Effect of molecular weight, concentration and solvent viscosity**Samrat Sur and Jonathan Rothstein*Mechanical Engineering, University of Massachusetts Amherst, Amherst, MA 01002, United States*

In a number of recent studies, the large extensional viscosity of dilute polymer solutions has been shown to dramatically delay the breakup of jets into drops. For the low shear viscosity solutions, the jet breakup is initially governed by a balance of inertial and capillary stresses before transitioning to a balance of viscoelastic and capillary stresses at later times. This transition occurs at a critical time when the radius decay dynamics shift from a  $2/3$  power law to an exponential decay as the increasing deformation rate imposed on the fluid filament results in large molecular deformations and rapid crossover into the elastocapillary regime. By experimental fits of the elasto-capillary thinning diameter data, relaxation time as low as 40 microseconds have been successfully measured. In this presentation, we will show that with better understand of the transition from the inertia-capillary to the elasto-capillary breakup regimes that relaxation times close to a single microsecond can be measured with the relaxation time resolution limited only by the frame rate and spatial resolution of the high speed camera. In this presentation, the dynamics of drop formation and pinch-off will be presented using Dripping onto Substrate Extensional Rheometry (DoS) for a series of dilute solutions Polyethylene Oxide in water and in a water and glycerin mixture. Four different molecular weights between 100k and 1M g/mol will be shown with varying solvent viscosities between 1mPa-s and 22mPa-s and at concentrations between 0.004 and 0.5c\*. We will show the dependence of the relaxation time and extensional viscosity on these varying parameters while searching for the lower limit in solution elasticity that can be detected. We will also show that this approach is a powerful technique for characterizing a notoriously difficult material, namely low-viscosity printing inks.

## Symposium SM

### Polymer Solutions and Melts

Organizers: Suraj Deshmukh and Reza Foudazi

Monday 1:30 Crystal B

SM6

**Relaxation dynamics of knotted polymers – knot swelling and end-to-end relaxation**Vivek Narsimhan, Alexander R. Klotz, and Patrick S. Doyle*Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

In recent years, there has been interest in understanding the dynamics of knotted DNA due to the fact that such molecules have been observed in nanotechnology applications such as single-molecule gene-mapping and sequencing. In this talk, we discuss our latest experiments and simulations to characterize the relaxation behavior of knotted chains from a highly extended initial state. We examine two behaviors: (a) the swelling of the knot, and (b) how this swelling process alters the overall relaxation of the chain. Our single-molecule experiments repeatedly stretch and relax knotted DNA in an extensional electric field, which allows us to obtain an ensemble of knot swelling profiles vs. time. These studies plus Brownian dynamics simulations observe: (1) knots swell at a time scale that is comparable to the end-to-end relaxation of the polymer chain, (2) the swelling dynamics appear insensitive to the chain topology, at least for the complex knots we sample. In the second part of the talk, we discuss how knots modify the overall end-to-end relaxation of polymer chains, and how this behavior depends on the overall chain length and topology. For short polymer chains, our Brownian dynamics simulations show that knots hasten the relaxation of stretched chains, greater than what naïve scaling

predictions would anticipate. We develop models to explain these trends and discuss what are the consequences of these effects on polymer rheology.

Monday 1:55 Crystal B

SM7

### Single polymer relaxation dynamics in entangled solutions

Yuecheng Zhou<sup>1</sup> and Charles M. Schroeder<sup>2</sup>

<sup>1</sup>*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Concentrated polymer solutions exhibit complex dynamic behavior due to an interplay between topological entanglements and non-equilibrium effects. The vast majority of prior work, however, has focused on bulk rheological characterization of concentrated polymer solutions. In this work, we directly observe the relaxation dynamics of single DNA molecules in semi-dilute entangled solutions using a combination of fluorescence microscopy and microfluidics. Fluorescently labeled tracer molecules are dissolved in a background of semi-dilute entangled  $\lambda$ -DNA solutions ( $c_e < c < c^{**}$ ), and the relaxation dynamics of entangled polymers are directly observed at the molecular level. Our results show that single polymer relaxation trajectories exhibit either a single-mode or double-mode exponential decay, which starkly contrasts relaxation behavior from ultra-dilute and semi-dilute unentangled solutions ( $c^* < c < c_e$ ). The fraction of molecules that exhibit single-mode exponential decay behavior decreases, while the fraction of double-mode exponential trajectories increases upon increasing polymer concentration from 3.6  $c^*$  to 19.1  $c^*$ , with nearly all relaxation modes showing a double exponential response at high concentrations. Furthermore, we explore the concentration-dependent scaling of the single-mode relaxation time  $t$ , fast double-mode relaxation time  $t_1$ , and slow double-mode relaxation time  $t_2$ . The slow double-mode relaxation time  $t_2$  scales with polymer concentration with a power-law coefficient of  $\sim 2.4$ , which is consistent with previous bulk rheology measurements on entangled  $\lambda$ -DNA solutions and scaling arguments from blob theory for semi-dilute entangled solutions in a good solvent. In addition, the faster double-mode relaxation time  $t_1$  and single-mode relaxation time  $t$  are found to have the same but weaker power law dependence on concentration. Finally, we provide physical interpretations of the relaxation behavior for these lightly entangled solutions.

Monday 2:20 Crystal B

SM8

### Linear and non-linear rheology of hyper-branched EAA-cb-PP comb block copolymers

Carlos R. López-Barrón, Patrick Brant, and Maxim E. Shivokhin

*ExxonMobil Chemical Company, Baytown, TX, United States*

A series of hyperbranched comb block (CB) copolymers with ethylene-acrylic acid (EAA; 4.5 mol% AA) backbone and polypropylene (PP) side chains were synthesized via a condensation reaction between the acrylic acid groups on the commercial long chain branched (LCB) EAA polymer and hydroxyl-functionalized (atactic or isotactic) polypropylene vinyl-terminated macromonomers. Small-angle X-ray scattering (SAXS) measurements, in the melt, reveal nano-segregation of the PP side chains from the EAA backbone, which results in great enhancement in the shear and extensional rheology. Both the elastic and viscous moduli in the terminal regime increase (up to three orders of magnitude) as a function of PP side chain length and weight fraction. A second (low frequency) elastic modulus plateau is observed in CBs with high PP side chains (>40 wt%), suggesting formation of a weak network made of EAA chains connecting PP segregated domains. This network formation has a strong effect on the non-linear response of the CBs, namely, a very large extensional strain-hardening is observed. The strain hardening strength (measured at Hencky strain of 2.5) increases from values of  $\sim 3$ , for the neat EAA polymer, to  $\sim 100$ , for some EAA-cb-PP compositions.

Monday 2:45 Crystal B

SM9

### Brittle fracture of polymer transient networks

Srishti Arora<sup>1</sup>, Aamir Shabbir<sup>2</sup>, Ole Hassager<sup>2</sup>, Christian Ligoure,<sup>1</sup> and Laurence Ramos<sup>3</sup>

<sup>1</sup>*Laboratoire Charles Coulomb, Université de Montpellier, Montpellier, France;* <sup>2</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kongens Lyngby, Denmark;* <sup>3</sup>*Laboratoire Charles Coulomb, CNRS, Montpellier, France*

We study the fracture of reversible double transient networks, constituted of a water suspension of entangled surfactant wormlike micelles reversibly linked by various amounts of telechelic polymers. We provide a state diagram that delineates the regime of fracture without necking of the filament from the regime where no fracture or break-up has been observed. We show that filaments fracture when stretched at a rate larger than the inverse of the slowest relaxation time of the networks. We quantitatively demonstrate that dissipation processes are not relevant in our experimental conditions and that, depending on the density of nodes in the networks, fracture occurs in the linear elastic regime or in a non-linear elastic regime. In addition, analysis of the crack opening profiles indicates deviations from a parabolic shape close to the crack tip for weakly connected networks. We demonstrate a direct correlation between the amplitude of the deviation from the parabolic shape and the amount of non-linear elasticity.

Monday 3:45 Crystal B

SM10

**Dynamics of Rouse chains undergoing head-to-head association and dissociation: Difference between dielectric and viscoelastic relaxation**Hiroshi Watanabe<sup>1</sup>, Yumi Matsumiya<sup>1</sup>, and Youngdon Kwon<sup>2</sup><sup>1</sup>*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan;* <sup>2</sup>*School of Chemical Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Republic of Korea*

Polymer chains having type-A dipoles parallel along the chain backbone exhibit slow dielectric relaxation reflecting their global motion. For mono-functionally head-associative Rouse chains having type-A dipoles, the Rouse equation of motion was combined with the association/dissociation kinetics to calculate the dielectric relaxation function,  $F_j(t)$  with  $j = 1$  and  $2$  for unimer and dimer.  $F_1(t)$  reflects orientation of the end-to-end vector of the unimer, whereas  $F_2(t)$  detects orientation of two end-to-center vectors of the dimer (having symmetrical dipole inversion), both in the direction of the applied electric field. The calculation was made by mapping the conformation of dissociating dimer onto the created unimer and vice versa with the aid of the Rouse eigenmode expansion of the bond vector of segments (Gaussian subchains). It turned out that  $F_j(t)$  is not influenced by the association/dissociation reaction. This result makes a striking contrast to the behavior of the viscoelastic relaxation function  $g_j(t)$ :  $g_j(t)$  is strongly affected by the motional coupling between the unimer and dimer due to the reaction (Watanabe et al., *Macromolecules* 48, 3014 (2015)). This difference emerged because the dielectric  $F_j(t)$  corresponds to the vectorial first-moment average of the segmental bond vector at time  $t$ ,  $\mathbf{u}(n,t)$  with  $n$  being the segment index, whereas the viscoelastic  $g_j(t)$ , to the tensorial second-moment average. Because of this difference in the averaging moment,  $F_j(t)$  is subjected to cancellation in the conformational mapping but  $g_j(t)$  is not, so that the reaction effect emerges only for  $g_j(t)$ . Experimental data of head-carboxylated high-cis polyisoprene (PI) chains (having the type-A dipoles), confirming this difference, are also presented.

Monday 4:10 Crystal B

SM11

**On the physics of the stress overshoot in entangled polymer liquids**Ken S. Schweizer and Shi-Jie Xie*Dept. Materials Science, University of Illinois at Urbana-Champaign, Urbana, IL, United States*

A universal scaling behavior in the overshoot region of the stress-strain response of entangled polymer liquids under fast nonlinear shear deformation (Rouse Weissenberg number  $WiR > 1$ ) has been experimentally established by SQ Wang and coworkers in both solutions and melts. The overshoot stress and strain scale as the one-third power of  $WiR$ , in disagreement with existing tube theories, but in accord with recent simulations and other experiments. The physical origin has been suggested to be a deformation-induced finite strength interchain grip force that is required to achieve polymer stretch and which results in a barrier to retraction. We construct a theory for the grip force using tension blob dynamic scaling ideas, and determine a mean critical ("yield") strain for force imbalance as when the grip force first becomes weaker than the intrachain retraction force. For  $WiR < 1$ , force imbalance occurs at strains (well) below  $\sim 2$ , suggesting the overshoot is due to the classic affine over-orientation mechanism of the Doi-Edwards model. However, for  $WiR > 1$  the grip force is much stronger and increases with deformation rate in such a way that the critical strain is predicted to grow as  $WiR^{1/3}$ . The dynamic scaling idea is combined with a simple model for chain stretch and retraction dynamics, with stress computed by ignoring orientational relaxation and convective constraint release. However, fluctuations of the local entanglement spacing induce a distribution of grip yield strains which is quantified using the Sussman-Schweizer theory of the anharmonic tube confinement field. The resultant model for the rate-dependent stress-strain response in the overshoot regime is in very good agreement with experiment, including the existence of a universal master curve. Its predictions for other mechanical and dynamic structural quantities will be presented. Comparison with tube theories that do not contain the grip force concept reveal qualitative differences.

Monday 4:35 Crystal B

SM12

**Dynamics of shape-persistent giant molecules: Zimm melt, elastic plateau, and cooperative glass**Gengxin Liu<sup>1</sup>, Xueyan Feng<sup>1</sup>, Kening Lang<sup>1</sup>, Ruimeng Zhang<sup>1</sup>, Dong Guo<sup>1</sup>, Shuguang Yang<sup>2</sup>, and Stephen Cheng<sup>1</sup><sup>1</sup>*Department of Polymer Science, University of Akron, Akron, OH 44325, United States;* <sup>2</sup>*Center for Advanced Low-Dimension Materials, Donghua University, Shanghai 201620, China*

Giant molecules are a new class of soft matter having 3-dimensional shapes and composed of chemically linked rigid molecular nanoparticles. Structurally, a 3D cluster of molecular nanoparticles can be one giant molecule or a few giant molecules associated together via specific interactions. The dynamics of clusters that is smaller than a critical diameter ( $\sim 5$  nm) obeys the Zimm model, a bead-spring model with dominant hydrodynamic interaction. Clusters that larger than this critical diameter often formed by the association of giant molecules, exhibit an elastic plateau due to caging of individual giant molecules. We hypothesize that if a giant molecule is larger than this critical diameter, the giant molecule as a whole cannot move even above its glass transition temperature. Thus it forms a "cooperative glass". A cluster of giant molecules can be abstracted as a cluster of unlinked but cooperatively rearranged beads. The latter cluster loses its mobility and reaches the glassy state when the diameter of the cluster is 6 times larger than the bead diameter, as derived in the random first order transition theory. The critical diameter on the dynamics of giant molecules is thus also 6 times the bead diameter, when we estimate the bead diameter by the glassy shear modulus of giant molecules.

## Symposium SC Suspensions, Colloids and Granular Systems

Organizers: Cari Dutcher and Lilian Hsiao

Monday 1:30 Crystal C

SC6

### Shear-induced structural rearrangement in jammed suspensions of soft particle glasses

Fardin Khabaz<sup>1</sup>, Tianfei Liu<sup>1</sup>, Michel Cloitre<sup>2</sup>, and Roger T. Bonnecaze<sup>1</sup>

<sup>1</sup>*McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States;* <sup>2</sup>*Laboratoire Matière Molle et Chimie, ESPCI ParisTech, Paris, Paris 75005, France*

The microstructure and shear rheology of highly concentrated, jammed suspensions of soft particles is shown to depend on polydispersity and shear rate from computational simulations. Rich behavior is observed depending on the degree of polydispersity and the shear rate. Glassy suspensions with a low degree of polydispersity evolve to face-centered cubic (FCC) and hexagonal close-packed (HCP) structures at low and high shear rates, respectively. The structural rearrangement occurs over several units of strain and reduces the shear stress and elastic energy. Suspensions with a higher degree of polydispersity exhibit a microstructural transition from a glass to a layered-like structure for sufficiently high shear rates. In this case the soft particles initially rearrange themselves in the flow-vorticity plane, and then layers parallel to the velocity-vorticity plane are formed. The rearrangement of particles in the flow-vorticity plane occurs after an induction strain (or time) for the layering. The induction strain decays exponentially with shear rate and shows a universal trend that depends only on polydispersity. A generic dynamical state diagram is found that depends on the polydispersity and the ratio of viscous to elastic forces due to shear.

Monday 1:55 Crystal C

SC7

### Effect of roughness on concentrated colloidal suspensions under flow

Alan R. Jacob and Lilian C. Hsiao

*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States*

Nearly hard sphere colloids are used as model systems in suspension rheology. Concentrated colloidal suspensions under flow have been investigated in detail using scattering, confocal microscopy, rheology, simulations and theory. Despite the presence of microscale roughness on nearly all types of colloidal particles, there is a lack of fundamental understanding of how particle roughness affects suspension rheology. Recently, our group developed rheological state diagram for particles with asperities that connects the steady state viscosity and first normal stresses to lubrication and friction-like interactions. Here, we further investigate the effects of asperities in concentrated colloidal suspensions on the microscopic dynamics and bulk flow properties. In this work, we follow shear stress, elastic and viscous moduli providing fundamental insights into yielding and relaxation of concentrated rough sphere suspensions and contrast with smooth sphere suspensions. Our goal is to use particle roughness as a means to control flow properties relevant to applications such as concentrated slurries, soft robots, and liquid body armor.

Monday 2:20 Crystal C

SC8

### Soft and hard particles as model systems to study the rheological behavior of concentrated colloidal dispersions

Xiaoguang Peng, Qi Li, Dongjie Chen, and Gregory B. McKenna

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

Colloidal dispersions have been considered as models that can provide insight into the phase and dynamic behaviors of molecular systems. In this study, we have synthesized and investigated two different colloidal dispersions, i.e., a soft thermo-sensitive PS-PNIPAM [Polystyrene-Poly(N-isopropylacrylamide)] latex with core-shell structure dispersed in water and a hard-sphere PMMA [Poly(methyl methacrylate)] dispersed in a mixture of octadecene and bromonaphthalene. The rheological behavior of these colloidal dispersions was characterized at equilibrium in the vicinity of the glass transition concentration using both dynamic and creep experiments. Master curve constructions show that the time-concentration superposition principle is not valid for these colloidal dispersions. The lack of validity of time-concentration superposition is also demonstrated using van Gurp-Palmen plots [1], i.e., phase angle  $d$  vs  $G^*$  or  $\tan d$  vs  $\omega$ . Other colloidal dispersions, i.e., micellar and silica-PEG, are also discussed. The shift factors and relaxation times follow super-Arrhenius behaviors as the glass transition concentration is approached. The BSW (Baumgaertel, Schausberger and Winter) model [2, 3] was used to fit the dynamic data for these colloidal dispersions and new findings are described and discussed.

[1] M. Van Gurp and J. Palmen, *Rheol. Bull.* 67, 5-8 (1998) [2] M. Baumgaertel, A. Schausberger, H. H. Winter, *Rheological Acta* 29:400-408 (1990) [3] H. H. Winter, M. Siebenburger, D. Hajnal, O. Henrich, M. Fuchs and M. Ballauff, *Rheological Acta* 48:747-753 (2009)

Monday 2:45 Crystal C

SC9

### Modeling the transient shear flow and predicting Large Amplitude Oscillatory Shear (LAOS) flow of a thermoreversible gel using a scalar structure parameter thixotropic model

Matthew J. Armstrong<sup>1</sup>, Antony N. Beris<sup>2</sup>, and Norman J. Wagner<sup>2</sup>

<sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemical and Biological Engineering, University of Delaware, Newark, DE, United States*

Recent work using small angle neutron scattering under flow has identified the existence of a microstructure that is dependent on flow conditions in soft colloidal systems. On the other hand, over the last twenty years or so, a large number of empirically based thixotropic rheological models has been developed that involve, albeit phenomenologically, a single scalar structural parameter,  $\lambda$ . These models involve the combination of a  $\lambda$ -dependent decomposition of the shear stress to an elastic and a viscous contribution with a relaxation-based evolution equation for  $\lambda$ . The rich behavior of the soft colloidal systems is primarily due to the interaction of the structure and the hydrodynamic force and this can be particularly enhanced applied through in transient flow, and/or large amplitude oscillatory shear flow. 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 a thermoreversible gel using a newly developed semi-empirical, thixotropic master-equation developed around a scalar internal structural parameter, and the best features of several published thixotropic constitutive equations. We examine a soft colloidal system, all involving collective phenomena of yield stress and thixotropy. The system is a thermo-reversible, adhesive hard sphere system, of 30 nm silica particles in n-tetradecane. The master equation uses the structure parameter with a constitutive equation to model the elastic and viscous components of rheological responses to shear rate. Both steady state and time-dependent shear experimental data are fit using a recently developed robust numerical method that stochastically and effectively searches for the global optimum of a suitably forced least squares residual in the allowed parameter space.

Monday 3:45 Crystal C

SC10

### Structure, elasticity, and non-equilibrium state diagram of depletion gels

Eric M. Furst<sup>1</sup>, Kathryn A. Whitaker<sup>1</sup>, Lilian C. Hsiao<sup>2</sup>, and Michael J. Solomon<sup>3</sup>

<sup>1</sup>*Dept. of Chemical & Biomolecular Engineering, Univ. of Delaware, Newark, MD, United States;* <sup>2</sup>*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States;* <sup>3</sup>*Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI 48105, United States*

We use a recent model depletion gel that enables the rheology, structure, and particle interactions to be measured in concert [1]. As the attractive strength between particles increases, the gel elastic modulus increases, but that this change cannot be accounted for by the immediate increase in bond stiffness between particles and clusters alone derived from the depletion interaction energy. The modulus is, however, consistent with an increasing number of cluster-cluster contacts. Based on the cluster model of gel rheology, two principal length scales emerge: at the particle level, the internal cluster structure becomes less dense with increasing attractive strength, and extends from the attractive glass line of colloids with short range attraction into the lower density gel region, similar to recent studies of protein gels [2], but in contrast to prior studies of suspensions that rely solely on imaging the microstructure [3]. However, the size of the clusters, the length scale over which stress is transmitted during elastic deformation, does not depend on the magnitude of the attractive strength; its origin remains an open question. These results confirm that there is an intimate connection between the gelation of colloids with short-range attraction and phase separation. Remarkably, the cluster gel model gives consistent results for depletion gels that span a range of length scales and chemistries, but otherwise capture the same relative range of attraction and interaction strengths [4].

[1] L. C. Hsiao, M. J. Solomon, K. A. Whitaker, and E. M. Furst, *J. Rheol.* 58, 1485-1504 (2014). [2] F. Cardinaux, T. Gibaud, A. Stradner, and P. Schurtenberger, *Phys. Rev. Lett.* 99, 118301 (2007). [3] P. J. Lu, E. Zaccarelli, F. Ciulla, A. B. Schofield, F. Sciortino, and D. A. Weitz, *Nature* 453, 499-504 (2008). [4] S. Ramakrishnan, Y.-L. Chen, K. S. Schweizer, and C. F. Zukoski, *Phys. Rev. E* 70, 040401(R) (2004).

Monday 4:10 Crystal C

SC11

### Large anisotropic density fluctuations in sheared attractive dispersions

James W. Swan and Zsigmond Varga

*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

The steady shear of weak colloidal gels results in vorticity aligned density fluctuations. These have been measured in neutron scattering and flow dichroism experiments and observed with microscopy coupled to rheometer tools of varying geometry. The origins of this instability remain a mystery, and discrete element simulations of colloidal gels have to date, failed to reproduce the phenomena. We use new Brownian Dynamics simulations to show that this instability is fluid mechanical in origin, and results from long-ranged hydrodynamic interactions among particles in the gel. Squeeze flows between vorticity aligned flocs prevent mutual collisions and realignment, thus promoting stability of large-scale anisotropic density fluctuations. The nonlinear rheology in sheared colloidal gels and measures of their structural anisotropy determined from simulations agree well with a wide variety of experiments. Finally, we demonstrate collapse of this data across different shear rates, strengths of interaction, and volume fractions using a single force scale -- the most probable rupture force for the inter-colloid bonds.

Monday 4:35 Crystal C

SC12

**High speed confocal imaging of sheared colloidal gels**Gabriele Colombo and Jan Vermant*Department of Materials, ETH Zürich, Zürich, Zürich 8093, Switzerland*

Colloidal gels are an important class of soft materials with a wide range of technological applications, exploiting the combination of solid-like rest structure and liquefaction under mechanical stress of these thixotropic materials. Even though such complex flow behavior is widespread in a number of consumer products and industrially relevant systems, the changes in microstructure underlying thixotropy remain poorly understood. Recent scaling arguments propose a dependence of the mechanical properties of gels under flow on subpopulations of rigid, isostatic clusters of closely packed particles. Such a scaling does not rely on fractal geometry or glassy dynamics, which only take into account ensemble averaged descriptors and are therefore insensitive to highly localized events, which may determine the rheological response. In this work, we intend to test these ideas of cluster rigidity and evaluate the microstructural basis of thixotropy, varying the packing behavior in model colloidal gels by changing the particle aspect ratio slightly. The experimental approach relies on the quantitative study of the gel microstructure using high-speed confocal microscopy. Microscopic studies under flow are performed using a stress controlled rheometer with a home-made shear cell for counter-rotation of the lower plate, allowing single particles to be located and tracked for long times at the stagnation plane. The stress is directly measured, so that the link between microscopic observations and nonlinear rheology can be established. We also intend to clarify the role of microstructural anisotropy under flow, resulting in the butterfly scattering patterns observed for colloidal gels. Recent simulation approaches also show the emergence of large structural elements in the vorticity direction of flow, whose relevance for the rheological properties of gels was recently shown by two-dimensional oscillatory measurements on a model thixotropic gel.

Monday 5:00 Crystal C

SC13

**A high frequency rheological study of partially aggregated colloidal dispersions**Bram Schroyen<sup>1</sup>, Peter Van Puyvelde<sup>1</sup>, and Jan Vermant<sup>2</sup>*<sup>1</sup>KU Leuven, Leuven, Belgium; <sup>2</sup>ETH Zurich, Zurich, Switzerland*

A critical parameter for the performance of nanomaterials is the degree to which the fillers are dispersed in the matrix. Due to their colloidal nature, dispersing nanoparticles is complex and there is a clear need for tools to assess the dispersion state. Rheology offers significant advantages for characterizing dispersions with respect to optical or scattering techniques since it can present a global view of the microstructure. In order to quantify the degree of dispersion of partially aggregated suspensions based on rheological measurements, a new approach is proposed. Information on the dispersion state is classically inferred from the low frequency elastic modulus as its behavior is mainly dictated by the particle contribution. However a more direct relationship between rheological properties and degree of dispersion can be derived from the loss modulus in the high frequency hydrodynamic limit. In this limit the loss modulus is not influenced by colloidal interactions but depends only on the hydrodynamic volume occupied by the particles or aggregates. As such, the individual building blocks of the dispersion can be probed even when being part of a global network. A homebuilt piezo shear rheometer with optimized alignment and measurement sensitivity is constructed to extend the accessible frequency range. Measurements on partially dispersed spherical silica particles prove the need for this extended range to enter in the hydrodynamic region. In this region, the relative loss modulus reaches a plateau. The asymptotic behavior towards this high frequency limit depends on the relative strength of the colloidal to the hydrodynamic interactions. A dispersion quality index is derived by quantifying the distance of the high frequency loss modulus to the hard sphere case for finely dispersed particles by means of a hydrodynamic viscosity model. This index can for instance be used to follow the evolution of the degree of dispersion as a function of mixing intensity and time.

## Symposium NF Non-Newtonian Fluid Mechanics

Organizers: Paulo Arratia and Chris Dimitriou

Monday 1:30 Crestone A

NF6

**Viscoelastic fluid-structure interactions between flexible circular cylinder and wormlike micelle solution: Role of structural natural frequency**Anita A. Dey, Yahya Modarres-Sadeghi, and Jonathan Rothstein*Mechanical Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

When a flexible cylinder is placed in a flow of a Newtonian fluid, the shedding vortices at high Reynolds number can drive the motion of the structure and couple with the structure's natural frequency to produce large amplitude motion. This phenomenon is known as Vortex-Induced Vibration (VIV). Unlike Newtonian fluids, the flow of viscoelastic fluids can become unstable even at infinitesimal Reynolds numbers due to a purely elastic flow instability that can occur at large Weissenberg numbers. We have recently shown that elastic flow instabilities can drive the motion of a number of different flexible structures including sheets and cylinders. The fluctuating fluid forces exerted on the structures from the elastic flow instabilities can grow large enough to result in significant motion of the flexible structure. This motion can in turn feed back into the fluid dynamics resulting in a coupling and enhancement of the flow instability at the resonance frequency of the structure. This phenomenon is known as lock in. In this talk, we will present an investigation into the influence of a varying natural frequency of a flexible circular cylinder on the form, frequency and amplitude of the viscoelastic fluid-structure interactions with the goal of understanding this lock-in behavior for viscoelastic fluid structure interactions. The static and dynamic responses of the flexible cylinder will be presented for a range of flow velocities

for a number of different wormlike micelle solutions with varying fluid viscosity and relaxation time. The time variation of the flow field and the state of stress in the fluid will be shown using particle image tracking and flow-induced birefringence images. Finally, the non-linear dynamics of the structural motion will be investigated to better understand an observed transition from a symmetric to an asymmetric structural deformation and oscillation behavior.

Monday 1:55 Crestone A

NF7

### **Flow of wormlike micelle solutions past a falling sphere: Role of boundary condition**

Hadi Mohammadigoushki<sup>1</sup> and Susan J. Muller<sup>2</sup>

<sup>1</sup>Florida State University, Tallahassee, FL 32310, United States; <sup>2</sup>UC Berkeley, Berkeley, CA 94710, United States

Flow of a wormlike micelle solution past a falling sphere with varying surface roughness is considered. A combination of particle tracking velocimetry, particle image velocimetry and microscopy is used to obtain detailed information on the flow of the wormlike micelle solution around the falling sphere. Particle tracking velocimetry measurements indicate that spheres with roughened surfaces fall faster than smooth spheres. In addition, in the direction perpendicular to the sphere motion, the wormlike micelle solution exhibit similar velocity profile for smooth and roughened spheres. However, in the axial direction and in the wake of the sphere, roughened spheres tend to generate a larger negative wake than the smooth spheres. More importantly and in contrast to the smooth spheres, we find that the surface of the roughened spheres is covered by numerous micro-bubbles. The presence of such micro-bubbles may potentially reduce the drag at the surface of roughened spheres and eventually lead to higher falling velocities.

Monday 2:20 Crestone A

NF8

### **Unsteady sedimentation of a sphere in wormlike micelle solutions**

Yiran Zhang and Susan J. Muller

Department of Chemical & Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States

Wormlike micellar (WLM) fluids have a wide range of applications in consumer products, oil recovery and drag-reduction. They also exhibit interesting rheological properties. Here we present an experimental study of the sedimentation of a sphere in a shear-thinning wormlike micellar fluid consisting of cetyltrimethylammonium p-toluenesulfonate (CTAT) and sodium chloride. By varying the size and density of the spheres, a wide range of Reynolds and Deborah number are investigated. The flow field around the falling sphere is characterized using particle imaging velocimetry. Beyond a critical condition, we found that a sphere does not settle with a constant terminal velocity, instead its velocity fluctuates over time. Furthermore, the fluctuation in sphere settling velocity is found to be periodic, and the frequency increases with increasing velocity. This is in contrast to the chaotic fluctuations reported in previous studies [Chen and Rothstein (2004), Mohammadigoushki and Muller (2016)], with shear-banding WLM solutions of cetyltrimethylammonium bromide (CTAB) and sodium salicylate. Potential causes of this difference, including differences in shear and/or extensional rheology, in microstructure of the WLM, and in local flow field, are discussed.

Monday 2:45 Crestone A

NF9

### **Measuring the effective viscosity of wormlike micelle solutions using complex geometries - does elimination of wall slip in complex geometries make the Cox-Merz rule useful for wormlike micelle solutions?**

William H. Hartt, Lori A. Bacca, and Emilio Tozzi

The Procter & Gable Co, West Chester, OH 45069, United States

This presentation summarizes recent efforts to evaluate and enhance the predictability of process flows involving wormlike micelle solutions from rheological properties. We examine flow in complex geometries. We explore the laminar flow of wormlike micelle solutions in static mixers of different size, which are complex geometries analogous to porous media. We utilize a model wormlike micelle system that is a mixture of commercially relevant surfactants. Our conclusion is that the linear viscoelastic complex viscosity is useful for predicting pressure drop in static mixer flows where shear banding is unlikely to occur. We show that an effective viscosity measured using this flow compares well to the complex viscosity obtained in small amplitude oscillatory flow. Analogies with the Cox-Merz rule are discussed.

Monday 3:45 Crestone A

NF10

### **Shear stress resonance caused by shear-banding in wormlike micellar solutions**

Tsutomu Takahashi and Masatoshi Ito

Department of Mechanical Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2145, Japan

The shear-banding generation is an important property in the flow of wormlike micellar solutions. During our investigation for examining the mechanical property of each band, we found interesting phenomena that the resonance in the shear stress occurs in both step-down flow and large amplitude oscillatory shear at the shear-banding state. Two samples are used as a wormlike micellar solution. Their molar concentration ratio of CTAB/NaSal is 2.0 and 7.7, respectively, and they have a very similar rheological property about viscosity and relaxation time. The solution of the concentration ratio 2.0 exhibits the regular and periodic shear stress oscillation at a certain shear rate. We have reported in the previous study that the state of the shear-induced structure in one of the band layers is synchronized with the stress oscillation. When the shear rate decreases to a certain value suddenly, the shear stress once decreases to zero, jumps up and achieves on a higher value compared with the original shear stress. When a large amplitude oscillatory shear is applied at the periodic shear stress condition, the shear stress at the same flow direction with the previous shear becomes large but the stress in the opposite direction becomes small, that is, the viscosity is changed by the rotation direction. This anomalous viscosity resonance keeps permanently at a certain condition. The solution with the molar concentration ratio 7.7 does not exhibit

these stress resonance phenomena. The shear-banding is generated in this solution but it becomes the fluctuated state quickly. The shear stress oscillation does not appear. Therefore, the shear-banding is strongly related to the shear stress oscillation and also related to both the resonance shear stress and the shear direction dependence on viscosity.

Monday 4:10 Crestone A

NF11

### **A device for simultaneous rheological and microstructural characterization of complex fluids at extreme shear rates**

Javen Weston<sup>1</sup>, Katie Weigandt<sup>2</sup>, and Steven Hudson<sup>3</sup>

<sup>1</sup>NIST, Georgetown University, Gaithersburg, MD 20899, United States; <sup>2</sup>NIST Center for Neutron Research, Gaithersburg, MD 20899, United States; <sup>3</sup>MSED, NIST, Gaithersburg, MD 20899, United States

We are working to develop slit rheometers that are compatible with simultaneous small angle neutron scattering (SANS) measurements to directly correlate structure and rheology over a broad range of conditions, with a focus on elevated shear rates above those available in most Couette geometries. Eventually, we hope to add the ability to measure fluid properties and microstructure under high hydrostatic pressure heads and elevated temperatures, as well. This sample environment builds upon an existing suite of Couette rheoSANS and flowSANS devices at the NIST Center for Neutron Research that are accessible to the scientific community through a peer reviewed proposal system. Industrial applications, such as lubrication, mixing, spraying and injection, involve the flow of complex fluids at high deformation rates. Clogging, fluid degradation, and other processing challenges can arise in these extreme contexts and are often driven by structural changes in the fluid. To date, we have developed a prototype slit rheometer capable of simultaneously measuring structure and rheology of relatively low viscosity or shear thinning fluids ( $\eta < 5$  mPa·s) up to moderate shear rates ( $O(100,000)$  s<sup>-1</sup>). Our initial investigations have focused on measuring the behavior of a rod-like micelle solution and comparing the results with Couette RheoSANS measurements. In this talk we will discuss the current state of device development in terms of experimental capabilities, results, and future improvements. Particularly, we will briefly describe our new robust  $\mu$ RheoSANS device, designed to withstand pressure drops or pressure heads up to 350 bar; allowing us to measure shear rates up to 106 in samples with  $\eta \sim 100$  mPa·s.

Monday 4:35 Crestone A

NF12

### **A new approach to characterising the conformation tensor in viscoelastic turbulence**

Ismail Hameduddin, Charles Meneveau, Tamer A. Zaki, and Dennice F. Gayme

*Department of Mechanical Engineering, The Johns Hopkins University, Baltimore, MD 21218, United States*

We address the problem of characterising fluctuating fields in viscoelastic turbulence where both the velocity and conformation tensor are important quantities. The conformation tensor is a second-order positive-definite quantity. Attempts to extract the fluctuation tensor using the Reynolds decomposition do not guarantee that the resulting tensor remains positive-definite. As a consequence, a physical interpretation of this tensor is not possible. Furthermore, defining scalar measures of the 'polymer turbulence intensity' requires precise notions of distances and paths between states of the polymer deformation. The Euclidean notions are inappropriate because the set of positive-definite tensors cannot be endowed with a Euclidean geometry. This work addresses these issues by proposing a multiplicative decomposition of the deformation gradient associated with the full conformation tensor. This procedure provides us with a fluctuating conformation tensor that is physically meaningful as a deformation to the mean configuration. We use the Riemannian geometry of the set of positive-definite tensors to define three scalar measures that characterize the turbulence intensity associated with the fluctuating conformation tensor: (i) logarithmic volume ratio, (ii) squared geodesic distance between the mean the fluctuation and (iii) the geodesic distance between the fluctuating conformation tensor and the nearest isotropic tensor. Our approach establishes a systematic method to study viscoelastic turbulence. We use direct numerical simulations of a turbulent channel flow at a friction Reynolds number of 180 to illustrate our framework. We find new insights that were not previously apparent such as the logarithmic increase of polymer fluctuating deformation up to  $\frac{1}{2}$  a channel half-height away from the wall.

Monday 5:00 Crestone A

NF13

### **Dynamics and structures of transitional viscoelastic turbulence in channel flow**

Ashwin Shekar, Sung-Ning Wang, and Michael D. Graham

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

Introducing a trace amount of polymer into turbulent flows can result in a substantial reduction of friction drag. This phenomenon has been widely used in fluid transport; However, the mechanism is not fully understood at high levels of drag reduction. In this work we perform direct numerical simulations (DNS) of viscoelastic channel flow turbulence using a high-resolution scheme that guarantees the positive-definiteness of polymer conformation tensor without artificial diffusion. We fix the bulk Reynolds number at 1000 and Weissenberg number at 100 and vary the viscosity ratio (ratio of the solvent viscosity and the total viscosity). MDR is observed with viscosity ratio  $< 0.99$ . As we decrease the viscosity ratio, i.e. increase polymer concentration, the mean velocity profile is almost invariant. However, this is accompanied by a decrease in velocity fluctuations but the flow stays turbulent. Turbulent kinetic energy budget analysis shows that, in this parameter regime, polymer becomes the major source of velocity fluctuations, replacing the energy transfer from the mean flow.

## Symposium IM Inverse Problems and Material Design

Organizers: Ron Larson and Florian Nettesheim

Monday 1:30 Crestone B

IM6

### Controlling fat digestion with a little help from interfacial rheology

Peter Fischer<sup>1</sup>, Nathalie Scheuble<sup>1</sup>, Thomas Geue<sup>2</sup>, and Andreas Steingoetter<sup>3</sup>

<sup>1</sup>IFNH, ETH Zurich, Zurich 8092, Switzerland; <sup>2</sup>SINQ, Paul Scherrer Institut, Villigen 5232, Switzerland; <sup>3</sup>Institute for Biomedical Engineering, ETH Zurich, Zurich 8092, Switzerland

The use of oil-in-water emulsions for controlled lipid release is of increasing relevance for poorly water-soluble drugs and gained major interest for treating obesity. In this conceptual study, we highlight the relevance of interfacial rheology combined with neutron reflectivity measurements in designing emulsion systems with stimuli-responsive biopolymers to generate specific lipid digestion kinetics. Stimuli-responsive biopolymers change their mechanical and emulsion stabilization properties at specific physicochemical conditions present in the human environment. We used whey protein isolate because of its sensitivity to pH, methylcellulose because of its sensitivity to temperature, and nanocrystalline cellulose because of its sensitivity to ionic strength [1]. The biopolymer-dependent effects on gastric lipolysis and gastric emulsion structuring, more precisely droplet size and viscosity, during digestion and resulting pancreatic lipolysis was investigated in-vitro. In order to establish a valid in-vitro/in-vivo correlation, emulsion structures formed during gastric digestion in-vitro were validated by in-vivo magnetic resonance imaging experiments visualizing emulsion structuring and stomach emptying [2]. In parallel, in-vivo lipid sensing and release patterns were investigated by repetitive measurements of measuring plasma triglycerides and cholecystocinin concentrations in healthy human volunteers. By taking all relevant physicochemical and mechanical processes of human digestion into account, we are thus able to propose design concepts for food and drug delivery systems [3].

[1] Scheuble N., Lussi M., Geue T., Carrière F., Fischer P.: *Biomacromolecules* 17 (2016) 3328-3337. [2] Steingoetter A., Buetikofer S., Curcic J., Menne D., Rehfeld J.F., Fried M., Schwizer W., Wooster T.J.: *J. Nutrit.*, 10.3945/jn.116.237800. [3] Scheuble N., Schaffner J., Schumacher M., Windhab E.J., Liu D., Parker H., Steingoetter A., Fischer P.: *J. Contr. Release*, submitted

Monday 1:55 Crestone B

IM7

### Characterizing and designing printable, spinnable and sprayable soft materials

Jelena Dinic, Leidy N. Jimenez, and Vivek Sharma

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

Designing soft materials with appropriate processability characteristics, often expressed in heuristic terms such as sprayability, spinnability, and printability, requires a systematic control over their response to both shear and extensional deformations. Liquid transfer and drop formation/deposition processes involve complex free-surface flows including the formation of columnar necks that undergo spontaneous capillary-driven instability, thinning and pinch-off. For simple (Newtonian and inelastic) fluids, a complex interplay of capillary, inertial and viscous stresses determines the nonlinear dynamics underlying finite-time singularity as well as self-similar capillary thinning and pinch-off dynamics. In rheologically complex fluids, extra elastic stresses as well as non-Newtonian shear and extensional viscosities dramatically alter the nonlinear dynamics. Stream-wise velocity gradients that arise within the thinning columnar neck create an extensional flow field, and many complex fluids exhibit a much larger resistance to elongational flows than Newtonian fluids with similar shear viscosity. Characterization of pinch-off dynamics and the response to extensional flows requires bespoke instrumentation not available, or easily replicated, in most laboratories. Here we show that dripping-onto-substrate (DoS) rheometry protocols that involve visualization and analysis of capillary-driven thinning and pinch-off dynamics of a columnar neck formed between a nozzle and a sessile drop can be used for measuring shear viscosity, power law index, extensional viscosity, relaxation time and the most relevant processing timescale for printing or spraying. We elucidate the critical influence of polymer concentration, flexibility, charge, hydrophobicity and extensibility determine on capillary-driven thinning and pinch-off dynamics, extensional rheology and consequently on spinnability and printability of a wide range of polymeric complex fluids.

Monday 2:20 Crestone B

IM8

### New polymer product development, reaction kinetics and computational rheology

Johannes M. Soulages

*Corporate Strategic Research, ExxonMobil Research and Engineering, Annandale, NJ 08801, United States*

Industrially produced polymers generally contain molecules with a wide range of architectures and sizes, which are responsible for their unique flow properties. For example, polyethylene (PE), despite its apparent chemical simplicity, is a complex mixture characterized by three distributions: (i) molecular weight, (ii) comonomer composition (e.g. butene or hexene), and (iii) branching.

When developing a new plastic, it is essential to understand how to relate these various distributions to its melt flow performance. Recent theoretical advances in reaction kinetics and computational rheology have enabled the prediction of polymer melt flow performance from molecular structure.

In this presentation, we describe a modeling platform which combines polymerization and computational rheology models in order to predict the flow of low density polyethylene. In particular, we show how the polymer branching distribution controls the ultimate resin flow performance

(e.g. extrudability and bubble stability for film blowing operations). This approach combines multiple characterization techniques such as gel permeation chromatography, shear, and extensional rheology, in order to establish a detailed inventory of branched species made in different reactors. Decoding the branching distribution is critical as rheology is highly sensitive to the molecular architecture and amount. In addition, there exists today no stand-alone experimental characterization tool capable of providing a complete quantitative polymer branching description. In this context, this framework opens up unique opportunities for the design of resins with targeted flow performance.

Monday 2:45 Crestone B

IM9

### **Tailoring rheological response via thickness and macromolecular architecture**

Dimitris Vlassopoulos, Salvatore Costanzo, Zhi-Chao Yan, and Daniele Parisi

*FORTH-IESL, HERAKLION, Greece*

Since entanglements represent the key feature of long polymers, altering their number and strength is a route to tailor rheology and processability. A known example is the constraint release effect in homopolymer mixtures. Here, we discuss two recent examples where the synergy of molecular rheology and polymer synthesis can possibly advance further the field: (i) Macromolecular thickness decreases the number of entanglements and makes polymers akin to supersoft elastomers, as demonstrated with bottlebrushes. Alternatively, dendronized polymers (DPs), comprising a backbone grafted with dendrons, exhibit orientational order, weak shear thinning and elasticity, which can vary by adjusting the degree of polymerization and dendron generation, allowing to span the gap from wormlike polymers to colloidal molecules. Selective introduction of strong associating groups into the first generation of the DPs leads to unusual linear and nonlinear viscoelastic properties, which can be completely damped by introducing additional branching that causes an effective molecular shielding for these groups. (ii) Entangled ring polymers are known to exhibit self-similar stress relaxation and a zero-shear viscosity much lower than that of their linear counterparts. Yet, their mixtures, with low fraction of rings (say 20%) exhibit higher viscosity. We present a systematic study of linear and nonlinear shear rheology with both symmetric and asymmetric mixtures, in order to elucidate the phenomenology of this and propose ways to selectively modify the viscosity of homopolymer melts via entropic mixing. These examples show the power of macromolecular engineering in manipulating the rheology of polymeric systems. Work in collaboration with A. D. Schlueter, T. Chang, J. Roovers, P. Lutz and M. Kalyva.

Monday 3:45 Crestone B

IM10

### **Fitting data is subjective: Structural inference from rheology and uncertainty quantification of single measurement data**

Piyush K. Singh<sup>1</sup>, Johannes M. Soulages<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup>

<sup>1</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Corporate Strategic Research, ExxonMobil Research and Engineering, Annandale, NJ 08801, United States*

Fitting data is subjective, which can undermine attempts to infer structure and molecular features from fitting rheology data. This is exemplified clearly by the fitting of small amplitude oscillatory shear (SAOS) data. The subjectivity arises from the non-uniqueness of SAOS data representation: in addition to  $G'$  and  $G''$ , it can be represented instead by torque-amplitude and phase:  $T_0$  and  $d$ , complex modulus  $G^*$  and  $\tan \delta$ , dynamic viscosities:  $\eta'$  and  $\eta''$ , dynamic compliances:  $J'$  and  $J''$ , or any other two-parameter pair that describes the resulting sinusoidal waveform. Additional subjectivity comes from the choice of weighting residuals in the fitting, i.e. how to penalize disagreement between data and the model. We argue based on statistical concepts, that an objectively chosen "best" fitting scheme is the one where data representation has Gaussian uncertainty and residuals are weighted by experimental data uncertainty. Although theoretically none of the commonly used SAOS data representations are Gaussian, some are more Gaussian than others under very reasonable assumptions. Interestingly though, the dominant factor in reducing subjectivity for fit parameters is to weight the residuals by the data uncertainty. When weighted by the data uncertainty, the fit parameters from various data representations are in close agreement within a small and acceptable variability. This finding further necessitates analytical estimation of data uncertainty for single measurements i.e. when replicate measurements are not available. To this end, we develop analytical expressions for estimating the uncertainty in single measurement SAOS data using error propagation from primary measurement variables:  $T_0$ ,  $\eta'$  and  $d$ . Interestingly,  $G'$  and  $G''$  do not show constant (and equal) relative uncertainties, an assumption inherently built into the most commonly used data weighted least squares fitting. Our findings establish best practices for SAOS data fitting in particular, and inverse problems of structural inference in general.

Monday 4:10 Crestone B

IM11

### **Selecting design-appropriate material descriptions for linear viscoelastic materials**

R. E. Corman<sup>1</sup>, Yong Hoon Lee<sup>1</sup>, James T. Allison<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup>

<sup>1</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Industrial and Enterprise Systems Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We describe a process to mathematically model and optimize design targets for linear viscoelastic systems. Our previous work [1] has shown that simple engineering design assumptions can be relaxed from a conventional spring-dashpot topology to a generalized linear viscoelastic relaxation kernel  $G(t)$  (though importantly, the viscoelastic moduli  $G'$  and  $G''$  are not independent design functions). With the relaxation kernel as the design variable, one can identify optimal viscoelastic properties agnostic to any specific material structure or spring-dashpot topology. We extend this work by evaluating different representations of linear viscoelasticity beyond the traditionally used Generalized Maxwell Model, such as simple parameterizations of continuous spectra including the log-normal continuous relaxation spectra. These parameterizations of relaxation spectra are known to be realistic descriptions of achievable materials. This approach provides the opportunity to reduce computational complexity (by

dramatically reducing the number of design parameters involved) while confining the designed systems to be realizable materials, aiding in the use of these early-stage design targets for either material-specific selection or later-stage material synthesis and design of materials.

[1] Corman, R.E., L. Rao, N.A. Bharadwaj, J.T. Allison, R.H. Ewoldt, "Setting material function design targets for linear viscoelastic materials and structures," *Journal of Mechanical Design*, 38 (5), 051402 (2016), <http://dx.doi.org/10.1115/1.4032698>

Monday 4:35 Crestone B

IM12

### **Application of a parallel tempering algorithm towards inverse modeling**

Matthew J. Armstrong<sup>1</sup>, Paul M. Mwasame<sup>2</sup>, Antony N. Beris<sup>3</sup>, and Norman J. Wagner<sup>4</sup>

<sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States;* <sup>3</sup>*Chemical and Biological Engineering, University of Delaware, Newark, DE, United States;* <sup>4</sup>*Chemical and Biological Engineering, University of Delaware, Newark, DE, United States*

Suspensions and dispersions are an important class of complex fluids and are prominent in many consumer-related products [1]. In many materials, the rheology is important in achieving the desired application performance e.g. paints and pastes. Further optimization of material performance through inverse modeling can be aided by models that connect the underlying microstructure to the observed rheological response. Our recent efforts in developing microstructural-based models [2,3] for thixotropic and polydisperse suspensions allow us to also elucidate important properties of a suspension that give rise to a desired rheological response. These models hold promise for inverse modeling since they incorporate microscopic information such as the stability ratio, particle size distribution and solids loading which are related to the suspension formulation. To harness the full potential of microstructure-based models, a robust optimization algorithm is required to establish (multiple) model parameters that correspond to a desired rheology. This is addressed through a novel parallel tempering algorithm [4] that is applicable to both static and dynamic rheological data. This algorithm also allows us to develop uncertainty intervals around model parameters allowing for sensitivity checking. Furthermore, many microstructure-based models are non-linear making the use of the parallel-tempering optimization algorithm appealing. Illustrative applications of the optimization scheme towards inverse engineering of practical suspensions and experimental design will be discussed.

[1] Mewis, J. and Wagner, N.J., 2012. *Colloidal suspension rheology*. Cambridge University Press. [2] Mwasame, P.M., Beris, A.N., Diemer, R.B. and Wagner, N.J., 2017. *AICHE Journal*. [3] Mwasame, P.M., Wagner, N.J. and Beris, A.N., 2016. *Physics of Fluids*. [4] Armstrong, M.J., Beris, A.N. and Wagner, N.J., 2016. *AICHE Journal*.

Monday 5:00 Crestone B

IM13

### **Direct and inverse shape problems in self-consistent field theory: Level set strategies**

Gaddiel Y. Ouaknin

*College of Engineering, Cornell University, Ithaca, NY 14850, United States*

We introduce level set methods to design new algorithms for self-consistent field theory (SCFT) in polymer physics. SCFT computes the structure and energy of inhomogeneous self-assembling polymers at thermodynamic equilibrium. Level set methods enable to represent the surface of an enclosing domain with an implicit function which in turn provides a powerful way to evolve a free surface. We introduce the concept of shape derivative into SCFT and rigorously derive expressions for the change of energy of a diblock copolymer melt with respect to its enclosing shape. The shape derivative is then used to embed SCFT into a variable shape simulation where the internal structure and the enclosing shape are coupled and evolve in tandem in order to reduce the energy. Finally an algorithm for the inverse geometric problem is presented. The algorithm finds a shape in order to obtain a desired internal structure of the confined polymeric material.

## **Symposium CR Computational Rheology**

Organizers: Jim Swan and Rekha Rao

Monday 1:30 Aspen

CR6

### **Three-dimensional Eulerian-Lagrangian solver for suspensions of solid spherical particles with a viscoelastic matrix fluid**

Salah Aldin Faroughi<sup>1</sup>, Agathe Robisson<sup>2</sup>, and Gareth H. McKinley<sup>1</sup>

<sup>1</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;*

<sup>2</sup>*Schlumberger-Doll Research Center, Boston, MA, United States*

Many industrial operations are involved with processing concentrated particle-laden complex fluids, in which the bulk rheological behavior of these fluids are of critical interest. When high volume fractions of particles are suspended in a viscoelastic matrix fluid (e.g. in polymer-based fracturing fluids that transport 'proppant'), simulating the dynamical response of the system becomes challenging not only due to non-linear interaction of the constituents, but also due to nonlinear rheology of the viscoelastic matrix fluid and the effects of elasticity on the extra stress arising from the particle. In this work, we present a 3D numerical model to analyze the transient dynamics of isothermal flow of viscoelastic-based-fluid suspensions based on the Eulerian-Lagrangian approach. The transport of an individual spherical particle is integrated using the

Discrete Element Model from the direct calculation of collision (using damped-linear-spring model) and hydrodynamic forces accounting for four-way coupling. For the viscoelastic fluid, which is treated as a continuum phase, the continuity, momentum and constitutive rheology equations (e.g. Oldroyd-B, Giesekus, PTT) are solved. A momentum-exchange model is required to close the formulation and couple the constituent phases. To provide this closure, we first studied the steady-state translation of a single particle and randomly positioned multiple particles to determine the effect of fluid elasticity on the drag and hindrance coefficients. We then adopted approximate models validated for inertia-less regimes to be integrated into our solver. The drag model, for example, captures the reduction in drag coefficient of a particle at low Deborah number, whereas at high  $De$  it is enhanced due to the large elastic extra stresses developing in the wake of the particle where the fluid undergoes a sudden change from shearing-dominant to extensional flow. The results obtained using the proposed solver are validated against settling experiments at low Reynolds numbers flow.

Monday 1:55 Aspen

CR7

### **Viscoelastic free surface flow: Blade coating of a Phan-Thien-Tanner fluid**

Richard M. Martin<sup>1</sup>, Rekha Rao<sup>2</sup>, and Kristianto Tjiptowidjojo<sup>1</sup>

<sup>1</sup>University of New Mexico, Albuquerque, NM, United States; <sup>2</sup>Sandia National Laboratories, Albuquerque, NM, United States

In this paper, we investigate the blade coating of a viscoelastic fluid. Blade coating is a self-metering process for coating a thin film of liquid onto a moving substrate. The factors that affect the coating process include the coating gap, blade length, angle, and curvature, as well as feed condition and effective shear rate and shearing time experienced by the fluid. Downstream of the blade, a free surface is created whose shape and height is not known a priori but must be solved as part of the problem. Here a finite element method is used for the viscoelastic flow coupled to a pseudo-solid mesh motion in order to track the free surface position. A multimode Phan-Thien-Tanner model is used to represent the complex rheology of the polymer solution. We investigate formulation changes to improve the convergence of the Galerkin finite element method as well as the maximum achievable Weissenberg number. The choice of inflow boundary conditions can also improve this critical Weissenberg number. An open-flow boundary condition coupled to residual-based stress inlet conditions, useful when the exact solution is unknown, increases the convergence at higher substrate velocities. In this work, we evaluate the rheological interactions with coating geometric parameters through blade length and coating gap variations. The effectiveness of applying the log-conformation tensor is also evaluated for this case and compared to classic methods such as DEVSS (Guenette, R. and Fortin, M., J. Non-Newtonian Fluid Mech. 60, 1995). Results from this study will be discussed for a 2-D model rigid blade coating problem with a rounded blade and a solid substrate.

Monday 2:20 Aspen

CR8

### **Applying computational tools of polymer field theory to out-of-equilibrium polymer solutions in flow**

Charles D. Young and Charles E. Sing

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

In polymer solutions, the relationship between hydrodynamic interactions (HI) and out-of-equilibrium polymer conformation has been an area of intense interest. This is an area of rheology that is fundamentally important for a wide array of polymer processing methods, especially those involving polymer solutions in flow; for example, fiber spinning, coating, and printing processes can lead to materials with properties that are sensitive to how molecular structure is controlled by fluid flow. This talk will focus on our efforts to expand the role of simulation in understanding the nature of the coupling between polymer conformation and hydrodynamics. First, we show that there are non-trivial connections between ring polymer architectures and HI, where the intramolecular HI effects can dominate conformation. This motivates the need for resolved simulations of polymer solutions. Inspired by simulation methods that have become standard in polymer field theory, we revisit early ideas in polymer dynamics and develop an iterative procedure for capturing HI. This method circumvents some standard computational bottlenecks in Brownian dynamics simulations, enabling large simulations of polymer solution dynamics. We demonstrate the advantages and limitations of this method, and show how we are beginning to apply these ideas to challenges at the forefront of molecular polymer rheology.

Monday 2:45 Aspen

CR9

### **Computational analysis of pinch-off dynamics and printability of simple and complex fluids**

Jelena Dinic and Vivek Sharma

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

Liquid transfer and drop formation/deposition processes underlying printing involve complex free-surface flows, including the formation of columnar necks that undergo spontaneous capillary-driven instability, thinning and pinch-off. For simple (Newtonian and inelastic) fluids, a complex interplay of capillary, inertial and viscous stresses determines the nonlinear dynamics underlying finite-time singularity, satellite drop formation as well as self-similar capillary thinning and pinch-off dynamics. In rheologically-complex fluids, extra elastic stresses as well as non-Newtonian shear and extensional viscosity dramatically alter the nonlinear dynamics. Stream-wise velocity gradients that arise within the thinning columnar neck create an extensional flow field, and complex fluids exhibit a much larger resistance to elongational flow than simple fluids with the same zero shear viscosity. Using FLOW-3D, we simulate flows within columnar necks or stretched liquid bridges formed by dripping, by applying step strain to fluid between two parallel plates, and by dripping-onto substrate. Using these three prototypical cases, we simulate free-surface flows realized in printing as well as in extensional rheometry devices used for studying pinch-off dynamics and the influence of microstructure and viscoelasticity. In contrast with often-used 1D or 2D models, FLOW-3D allows a robust evaluation of the magnitude of the underlying stresses and extensional flow field (both uniformity and magnitude). We find that the simulated radius evolution profiles match the scaling laws and pinch-off dynamics that are experimentally-observed and theoretically-predicted for Newtonian fluids. Finally, we describe our

experiments and Flow3D simulations to elucidate how viscoelasticity as well as non-Newtonian shear and extensional viscosity influence interfacial and nonlinear flows underlying pinch-off dynamics, extensional rheometry and printability of complex fluids.

## Symposium MM Microrheology and Microfluidics

Organizers: Travis Walker and Charles Schroeder

Monday 3:45 Aspen

MM1

### Multiple particle tracking microrheology of thermally gelling nanoemulsions

Li-Chiun Cheng<sup>1</sup>, Lilian C. Hsiao<sup>2</sup>, and Patrick S. Doyle<sup>1</sup>

<sup>1</sup>Massachusetts Institute of Technology, Cambridge, MA, United States; <sup>2</sup>Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

We perform multiple particle tracking (MPT) on a thermally-gelling oil-in-water nanoemulsion system developed by our group [1]. We investigate the role of the colloidal probe size and surface chemistry on MPT in the nanoemulsion systems. As temperature increases, hydrophobic groups of PEG-based gelators (PEGDA) partition into oil/water interfaces and bridge droplets. This inter-colloidal attraction generates a wide variety of microstructures consisting of droplet-rich and droplet-poor phases [2]. By tailoring the MPT colloidal probe surface chemistry, we can control the residence of probes in each domain, thus allowing us to independently probe each phase. Our results show stark differences in probe dynamics in each domain. For certain conditions, the mean squared displacement (MSD) can differ by nearly five orders of magnitude for the same probe size but different surface chemistry. Some probe surface chemistries result in "slippery" probes while others appear to tether the probe to the nanoemulsion gel. We also observe probe hopping between pores in the gel for "slippery" probes at certain conditions. Our approach allows for the unique ability to probe different regions of a colloidal gel and is useful for measuring local properties in these mesostructured hydrogels [3].

References: [1] Helgeson, M.E., Moran, S., An, H., and Doyle, P.S., "Mesoporous organohydrogels from thermogelling photocrosslinkable nanoemulsions", *Nat. Mater.*, 11, 344-352, 2012. [2] Hsiao, L.C. and Doyle, P.S., "Sequential phase transitions in thermoresponsive nanoemulsions," *Soft Matter*, 11, 8426-8431, 2015. [3] Hsiao, L.C., Badruddoza, A.Z.M., Cheng, L.-C., and Doyle, P.S. "3D Printing of Self-Assembling Thermoresponsive Nanoemulsions into Hierarchical Mesostructured Hydrogels," *Soft Matter*, 13, 921-929, 2017.

Monday 4:10 Aspen

MM2

### Characterization of consecutive phase transitions in a fibrous colloidal gel using $\mu^2$ rheology

Matthew D. Wehrman<sup>1</sup>, Melissa J. Milstrey<sup>1</sup>, Seth Lindberg<sup>2</sup>, and Kelly M. Schultz<sup>1</sup>

<sup>1</sup>Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; <sup>2</sup>Process and Engineering Development, Procter & Gamble, West Chester, OH 45069, United States

The gelation and degradation of colloidal particles is important in the design of materials used in commercial products, such as consumer and home care products. Of concern is whether the force that induces phase change can overcome processing history, particularly from shear stress. In this work, we characterize a hydrogenated castor oil (HCO) colloidal gel using  $\mu^2$ rheology, multiple particle tracking microrheology (MPT) in a microfluidic device. HCO is a colloidal fiber that gels and degrades in response to osmotic pressure gradients. Using  $\mu^2$ rheology, we determine the scaffold properties and structure during consecutive phase changes on a single sample. The microfluidic device design is a two-level device with two chambers: sample and suction chambers. Channels that deliver solvent from the second level into the sample chamber are spaced 60° around the chamber creating equal pressure around the HCO locking it in place during solvent exchange. MPT is used to characterize HCO during dynamic transitions. MPT measures the Brownian motion of particles embedded in the material and relates this movement to rheological properties using the Generalized Stokes-Einstein relation.  $\mu^2$ rheology measurements of consecutive phase changes of HCO start with a sheared solution of HCO (0.125 wt%) and an unsheared gel (4 wt%). Single samples are measured for 4 - 9 phase transitions. MPT measurements suggest the structure of the HCO is dependent on the starting materials shear history. When gelled, the sheared HCO solution cannot form a tightly associated, entangled network. During degradation, samples that begin as an HCO gel cannot completely degrade entanglements into single colloids. From these results, we conclude that the osmotic gradient is not a strong enough force to break or reform entanglements. Therefore, equilibrium structures depend on the shear history of the starting material, which can have important implications in end use products made with colloidal gel scaffolds.

Monday 4:35 Aspen

MM3

### Probe microrheology by differential dynamic microscopy

Alexandra V. Bayles, Todd M. Squires, and Matthew E. Helgeson

Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106, United States

Multiple particle tracking (MPT) has become a ubiquitous tool for probe microrheology, in which the mean squared displacement (MSD) of Brownian particles is used to extract viscoelastic information from complex fluids. However, MPT is limited to optically dilute suspensions, to probes with known intensity profiles, and by subjective user inputs that must be chosen in an ad hoc manner, resulting in significant information loss. We report an alternative method for extracting MSDs from passive probe video microscopy using differential dynamic microscopy (DDM), which analyzes the intensity fluctuations to extract the self-intermediate scattering function (SISF). DDM retains all information encoded in a probe experiment, and can be applied to systems that would otherwise be difficult to measure using traditional photocorrelation spectroscopy or MPT. We use a simple theoretical framework to show that the SISF obtained by DDM can be inverted to obtain the real-space MSD over length

and time scales comparable to MPT. As demonstrative examples, we apply DDM to videos of dilute probes in Newtonian fluids, viscoelastic wormlike micelles, and crosslinking polymer gels, exposing the relative strengths and weaknesses of DDM and MPT. Specifically, we find that when probes are optically dilute and undergo sufficiently large displacements, DDM accurately measures the MSD with fewer subjective inputs than MPT. Additionally, DDM successfully provides the MSD when probes are optically dense, enabling measurements in non-dilute suspensions. However, when optically dilute probes undergo small displacements relative to their intensity profile footprint, DDM is limited to larger displacements due to a convolution of pixel resolution and confined out-of-plane intensity fluctuations. In each example, the measured MSD compares well with bulk rheological data vis-à-vis the generalized Stokes-Einstein relation. Our results show that DDM can extend the range of probe microrheology experiments while circumventing many of the drawbacks of MPT.

Monday 5:00 Aspen

MM4

### **Differentiating effects of geometry and fluid rheology on particle dispersion in 2-D microfluidic porous media**

Jack D. Jacob, Ramanan Krishnamoorti, and Jacinta C. Conrad

*University of Houston, Houston, TX, United States*

Both fluid crowding and geometric confinement alter the transport of submicron particles through complex media. This scenario appears across a broad range of technological and environmental settings, e.g. when nanoparticles are used to enhance oil recovery from tight formations, to remove toxic compounds from wastewater, or to deliver therapeutic compounds to specific tissues within the human body. Because the efficacy of the particles depends in part on the ability to direct their transport, it is essential to understand how fluid properties and geometry affect the dispersion of submicron particles. Here, we show via pore-scale experiments how 2-D geometry and fluid viscoelasticity differently affect the dispersion of microscale particles in microfluidic porous media. Particles suspended in water/glycerol mixtures and in polymeric solutions of partially hydrolyzed polyacrylamide (HPAM) were flowed through micropost arrays of varying geometries and their trajectories over time obtained using imaging processing methods. Longitudinal dispersion was not affected by either post geometry or fluid nature. In sharp contrast, the transverse dispersion of particles flowed in the HPAM solution was increased in ordered post arrays but not in randomly distributed post arrays. At the pore scale, the enhanced transverse dispersion originated from the increased likelihood that particles switched between streamlines when flowed in the polymer solution, leading to a broadening of the velocity distributions and an increase in the velocity fluctuations.

## Tuesday Morning

### Symposium PL Plenary Lectures

#### *Bingham Lecture*

Tuesday 8:30 Cripple Creek Ballroom

PL2

#### **Flow, structure and function**

Julie A. Kornfield

*Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

Please join me for a celebration of rheology that includes diverse fluids that connect with the diverse rheologists who have influenced my trajectory in the field. Polymer melts are endlessly fascinating to me, starting with the effects of polydispersity and progressing through the way chemically distinct chains influence each other's motion, how segregation of distinct blocks opens pathways to flow-induced alignment and, currently, how flow dramatically transforms the morphology of crystallization from an entangled melt. Chance brought me into rheology of the eye-the cornea, vitreous and sclera-and the creation of materials for implanted lenses that can be deformed with high precision without touching them. Tragedy moved me to develop polymers that might someday make fuel safer and terrorist resistant. My career has been shaped by aesthetics, chance, event and, above all, people.

### Symposium AM Active, Motile, and Field Responsive Materials

Organizers: Patrick Underhill and Dan Klingenberg

Tuesday 9:50 Crystal A

AM1

#### **Programmable electrical conductivity of lignin- rubber composites for stress detection**

Ngoc A. Nguyen, Kelly M. Meek, Christopher C. Bowland, Sietske H. Barnes, and Amit K. Naskar

*Materials Sciences & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, United States*

In this work, we developed a method using silver nanoparticles coated shape memory composites to make programmable and switchable electrical conducting materials for human motion and stress history detection. Reactive lignins were melt-mixed with a rubber. The lignin-rubber composites demonstrated excellent strain fixity and recovery characteristics. A model for an ideally elastic neo-Hookean solid under uniaxial stretching was employed to quantify the elastic work density of the materials at different deformation and programming temperatures. Extensive improvement (several orders of magnitude) of the maximum and stored elastic work density was determined. The lignin- rubber composites revealed excellent shape- programming characteristics, in which heal-ability of electrical conducting layer was demonstrated.

Tuesday 10:15 Crystal A

AM2

#### **The dynamics of magnetic oblate spheroids under a rotating magnetic field**

Mingyang Tan and Travis W. Walker

*CBEE, Oregon State University, Corvallis, OR 97331, United States*

Anisotropic microstructures are commonly found in natural materials, endowing the materials with enhanced properties in certain orientations, including the prospect of self-shaping characteristics. Synthetic composites with anisotropic properties can be achieved by embedding aspherical particles inside a polymer matrix and by later using an external field (e.g., electric, magnetic, and optical field) to align the particles into a certain orientation. One- or two-dimensional anisotropy can be performed based on the geometry of the particles and the properties of the external field. In this study, aligning magnetic oblate spheroids via a rotating uniform magnetic field creates a two-dimensional anisotropic material. The particles undergo a rotational motion, induced by the external field, and a translational motion, induced by the dipole-dipole interaction between particles. We simulate the dynamics of the particles' motion in the Stokes flow region as a result of the trivial Reynolds number of this system. To obtain the realistic dynamics of this phenomenon, the hydrodynamic interactions are included by using Stokesian dynamics. While short-range interactions between two oblate spheroids are intractable to obtain, we use a pseudo-disk model, where spheres are packed into a disk shape, to simulate the spheroid-spheroid hydrodynamic interaction. At equilibrium, a hexagonal grid of particles form aligned sheets that are separated along the direction perpendicular to the sheets. The separating distance depends on the volume fraction of the particles.

Tuesday 10:40 Crystal A

AM3

**Surpassing the theoretical sensitivity of magneto-rheological elastomers**Gaurav Chaudhary<sup>1</sup>, Ken S. Schweizer<sup>2</sup>, Paul V. Braun<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup><sup>1</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Dept. of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

A magnetically responsive composite consisting of a semiflexible network of fibrin and iron particles is fabricated and the effects of magnetic field on the viscoelasticity are investigated. We report drastic stiffening, exceeding what is possible with typical magneto-elastomers in terms of both total stiffness change and the power-law sensitivity to magnetic field. This occurs even at a very modest iron particle concentration (1% v/v). We hypothesize that magnetic interaction between the iron particles induces the strain stiffening response of the semiflexible polymer mesh. This stiffening, together with the particle-particle interaction, leads to this huge increase in the elastic shear modulus of the composite. We examine the response as a function of the particle-to-mesh size ratio. Particles larger than the mesh size are arrested and produce a composite with dramatic dependence of shear modulus on magnetic field strength ( $G \sim B^4$ , approximately). Particles much smaller than the polymer mesh size are able to move through the network and rearrange to form chains, leading to a typical response found in magneto-elastomers ( $G \sim B^2$ ). We explain our observations through a particle interaction-based model that includes the strain stiffening effects of a polymer matrix.

Tuesday 11:05 Crystal A

AM4

**Deformation dynamics of magnetically actuated colloidal clusters**Sibani Lisa Biswal*Chemical Engineering, Rice University, Houston, TX 77005, United States*

Colloidal particles have proven to be a useful for creating microscale models of macromolecular systems. The system utilizes a magnetic field to direct and control the spacing between particles and DNA as the spring that chemically connects the particles together, as a mimic to fundamental bead-spring models. This letter elucidates the rotational dynamics of these colloidal chains, and demonstrate our understanding of the results both computationally and analytically. While some rotational modes are in line with other well-studied systems in the literature, we access and classify new modes, such as coiling, as a function of magnetic field frequency and chain length.

Tuesday 11:30 Crystal A

AM5

**Application of nonuniform magnetic fields in a Brownian dynamics model of ferrofluids with an iterative nonstraint scheme to fulfill Maxwell's equations**Lewis E. Wedgewood and Sean H. Dubina*Department of 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. In magnetic separation operations, nonuniform magnetic fields elicit a phenomenon known as magnetophoresis so that the ferroparticles will undergo migration toward areas of higher magnetism. To comprehend this behavior, the authors developed a Brownian dynamics simulation of particles in ferromagnetic clusters under the influences of a simple shear flow and an applied magnetic field gradient. An iterative constraint mechanism was implemented to satisfy Maxwell's Equations throughout the dense colloidal suspension, ensuring that essential laws of magnetostatics are rigorously fulfilled at all times over small, finite sub-volumes of the system. Because of the presence of nonuniform magnetic fields, magnetophoresis and magnetic separation behavior were analyzed to assess the effectiveness of the model. Results showed that, when compared to "unconstrained" models, separation caused by magnetic field gradients occurred at a decreased rate under the constraint scheme due to relatively weaker non-Newtonian aggregation property trends. Through application of a dimensionless number analysis to observe varied levels of particle-particle interaction, thermal fluctuation, and viscous shearing, it was confirmed that the aggregation and magnetic separation modeling of ferrofluid colloidal suspensions without acceptable adherence to Maxwell's equations produces an unreliable representation of current ferrofluids.

## Symposium SM Polymer Solutions and Melts

Organizers: Suraj Deshmukh and Reza Foudazi

Tuesday 9:50 Crystal B

SM14

**Entanglement density equilibration after cessation of steady shear flow**Pradipto K. Bhattacharjee<sup>1</sup>, Duc A. Nguyen<sup>1</sup>, Gareth H. McKinley<sup>2</sup>, and Tam Sridhar<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia;* <sup>2</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

The tube model proposed by Doi-Edwards forms the backbone of the present understanding of the dynamics of entangled polymeric liquids. A key concept in the original model was that the entanglement density remains constant during flow. However, this idea has been challenged by recent theoretical analysis that suggests that the entanglement density can decrease during flow and recover to its equilibrium state when the flow is stopped. In this work shear flow experiments on tailored, well-characterised polystyrene solutions are used to demonstrate that the modulus,

which depends on the entanglement density, is indeed depressed during flow and recovers to the equilibrium value once the flow is stopped. We also compare the predictions of a single mode tube model that include entanglement dynamics to the experimental data.

Tuesday 10:15 Crystal B

SM15

### **On the dynamics of semiflexible polymers solutions in the tightly-entangled regime: The fall of a theoretical framework**

Manlio Tassieri

*Division of Biomedical Engineering, University of Glasgow, Glasgow G12 8LT, United Kingdom*

In this article, I corroborate an important experimental evidence reported by [Schuldt *et al.*, PRL, 2016, **117**, 197801] revealing the incapability of the current theoretical framework to fully describe the dynamics of semiflexible polymers solutions in the *tightly-entangled* regime. These results have been endorsed here by means of previously published data by [Tassieri *et al.*, PRL, 2008, **101**, 198301; Tassieri *et al.*, Biophysical J., 2008, **94**, 2170]. The ensemble of information provides a strong evidence that the scaling law of the plateau modulus as function of polymer's concentration and persistence length, i.e.  $G^0 \propto c^\alpha L_p^\beta$ , should have both the exponents positive; in contrast with all the existing predictions converging on similar values of  $\alpha > 0$  and  $\beta < 0$ . In particular, the collected data provide a strong evidence that  $\beta$  is actually a positive number ranging between 1 and 5 *circa*, depending on *yet unknown* factors; but certainly different from the expected negative values. On the other hand,  $\alpha$  remains undetermined on whether it is 7/5 or 4/3 in the *tightly-entangled* concentration regime, and it spans between  $\approx 1.4$  and  $\approx 2$  in the *loosely-entangled* regime. To conclude, the ensemble of independent experimental data presented in this paper must serve as a springboard for theoreticians to revise current models and to develop new comprehensive theories able to better interpret the contribution of the polymer bending rigidity to the viscoelastic properties of the polymer network.

Tuesday 10:40 Crystal B

SM16

### **Characterization of polymer architecture: Modeling and experiment**

Nestor E. Valadez-Perez<sup>1</sup>, Konstantin Taletskiy<sup>1</sup>, Maksim E. Shivokhin<sup>2</sup>, and Jay D. Schieber<sup>1</sup>

<sup>1</sup>*Center for Molecular Study of Soft Condensed Matter, Illinois Institute of Technology, Chicago, IL 60616, United States;*

<sup>2</sup>*ExxonMobil Chemical Company, Baytown, TX 77520, United States*

We use a coarse-grained slip-link model to investigate the rheology of polydisperse linear and star-shaped polymer melts. Our slip-link model is a well-defined mathematical object that can describe the equilibrium dynamics and non-linear rheology of flexible polymer melts with arbitrary polydispersity and architecture with a minimum of inputs: the molecular weight of a Kuhn step, the entanglement activity and the Kuhn step shuffling time. The model takes into account the explicit creation and destruction of entanglements along polymer backbones in a stochastic way derived from a master equation. The computational implementation of this model is accelerated with the help of graphics processing units, which allow us to simulate in parallel large ensembles made of up to 50000 chains with variable number of entanglements. We report the storage and loss moduli for polymer melts with different molecular weight and polydispersity. Also we compare our predictions with experimental results obtained from small amplitude oscillatory shear, for polybutadiene, polypropylene and polyethylene melts. We show that our simulation can predict the dynamic moduli for highly entangled polymer melts over nine decades.

Tuesday 11:05 Crystal B

SM17

### **Role of topological friction in polymer stretching dynamics**

Ahmad K. Omar and Zhen-Gang Wang

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

The dynamics of polymer chains in the presence of topological constraints (such as chains diffusing in an entangled polymer melt or gel) has been an area of significant research for nearly a half century. The current physical picture is that the motion of a chain is constrained to a path defined by the surrounding topology - with diffusion along this one-dimensional path proceeding via Rouse dynamics. Despite the success of models inspired by this picture, controlled experiments/simulations that directly explore the effects of the topological interactions remain scarce. In this talk, we return to an early model system for topologically constrained polymers - a two dimensional chain in the presence of point-like obstacles. By exactly controlling the topology (the obstacle spatial distribution and primitive paths can be defined exactly) and single-chain statistics (the Rouse time is defined exactly) of our chains, we are able to perform controlled dynamical computer experiments wherein all relevant time/length scales are exactly known. In this talk, we present results quantifying relaxation times and forces on the chain in the longitudinal direction of the topological path as (1) the chain relaxes from extension or is (2) pulled at a constant force. The observed deviations from simple Rouse relaxation suggests that in addition to defining the path for chain motion, the topological constraints can also influence the longitudinal motion along the path - the origin of which will be discussed in this talk.

Tuesday 11:30 Crystal B

SM18

### **The hierarchical multi-mode MSF model for extensional and shear flows of linear and LCB polymer melts**

Manfred H. Wagner and Esmaeil Narimissa

*Polymer Engineering and Physics, Berlin Institute of Technology - TU Berlin, Berlin D-10623, Germany*

The Hierarchical Multi-mode Molecular Stress Function (HMMSF) model for linear and long-chain branched (LCB) polymer melts implements the ideas of hierarchical relaxation, dynamic dilution and interchain tube pressure. It is based on the assumption that stretch and orientation are coupled, and stretch is implemented through a tube diameter which decreases with increasing deformation. Therefore, stretch and orientation of

tube segments have the same dynamics as characterized by the linear-viscoelastic relaxation spectrum. The HMMSF model, with one non-linear parameter, the dilution modulus, is able to model the extensional viscosity data of linear and LCB polymer melts in uniaxial, equibiaxial and planar deformation modes (J. Rheol. 60 (2016) 625; Polymer 104 (2016) 204). However, this model in its original version is not capable of providing a satisfactory prediction of the shear flow behaviour of polymer melts at higher shear rates. Therefore, a convective constraint release (CCR) mechanism is implemented into the model, which reduces chain stretch at larger shear deformations and shear rates. We argue that CCR is only important in the case of shear flows. CCR is implemented in the evolution equation of the molecular stress function by use of a specific combination of the second order Rivlin-Ericksen tensors in such way that CCR is only active in shear flows. The modified HMMSF model, with only two non-linear material parameters, the dilution modulus and a constraint release parameter, is capable of modelling the shear data of broadly distributed linear and LCB polymer melts at all shear rates investigated, without compromising the excellent agreement of the HMMSF model with the respective extensional viscosity data.

## Symposium EF Emulsions, Foams, and Interfacial Rheology

Organizers: Nicolas Alvarez and Vivek Sharma

Tuesday 9:50 Crystal C

EF14

### Physical stability of structured fluids containing air bubbles

Shadi Mirzaagha<sup>1</sup>, Rossana Pasquino<sup>1</sup>, Nino Grizzuti<sup>1</sup>, Vincenzo Guida<sup>2</sup>, and Fabio Zonfrilli<sup>3</sup>

<sup>1</sup>Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Naples, Italy; <sup>2</sup>Brussels Innovation Center, Procter&Gamble, Brussels, Belgium; <sup>3</sup>Procter & Gamble, Brussels, Belgium

Home-care products are detergent systems that differ for applications and formulation. From a physical point of view, detergents are usually suspensions where a surfactant-based, worm-like micellar solution represents the continuous phase and colloidal fibers are added in order to provide the matrices of specific properties. In spite of the many advantages assured by the presence of the fibers in terms of shelf life, the resulting system can be mechanically unstable. The main responsible for this instability is the load applied by air bubbles, which are found into the final product, due to the process itself. Academic and product-oriented researchers are interested in understanding the failure dynamics and, ultimately, in obtaining predictions on the physical stability of structured fluids over ageing. The aim of this work is to analyze the physical stability of a structured detergent in presence of air bubbles. We studied various samples, which differ from each other for aeration level and fiber concentration. The rheological behavior and the microstructure of these fluids has been characterized. In parallel, a time lapse photography technique has been used to monitor the time evolution of the bubbles trapped in the fluids. The motion of single bubbles as well as the cooperative motion of bubble ensembles have been analyzed to verify the possibility of microstructure collapse. We found that fiber concentration, which dictates the yield stress of the fluid, aeration level and temperature can influence the stability of the final product. Under given conditions, bubbles can apply a remarkable load on the fiber network during their buoyancy-driven rise, thus inducing the collapse of the structure. The result is a clear phase separation, with the matrix without fibers standing on the bottom of the fluid volume, while a more concentrated system is moving towards the free surface. Data have been critically analyzed and compared with theoretical predictions and simulation model made by Comsol Multiphysics software.

Tuesday 10:15 Crystal C

EF15

### Cocontinuous ternary polymer nanocomposites with interfacial graphene nanoplatelets

Lian Bai, Radhika Sharma, Christopher W. Macosko, and Xiang Cheng

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

Interfacial localization of graphene at the interfaces in cocontinuous polymer blends is shown to be effective in stabilizing the cocontinuous morphology and increasing conductivity with a low electrical percolation threshold. In this study, we created ternary polymer nanocomposites composed of cocontinuous polylactic acid (PLA) and polystyrene (PS) blends intercalated with interfacial graphene nanoplatelets. The resulting conductive nanocomposites show dramatically improved conductivity at low filler loadings and an ultralow percolation threshold. By exploring different melt compounding times and sequences, we showed that the graphene nanoplatelets can be transferred from premixed in the PLA phase to the interface during melt compounding and form a spanning 3D network during annealing. The coverage of graphene platelets on the interface effectively suppresses the coarsening of the cocontinuous structure during annealing and dramatically improves the storage modulus and electrical conductivity of the composite. Thanks to the correlation of rheological, electrical and morphological properties in the composites with different melt compounding times, the kinetics of graphene nanoplatelets transfer between PLA/PS blend phases during melt compounding were quantitatively studied.

Tuesday 10:40 Crystal C

EF16

### Global strain-field mapping of a carbon nanotube-laden interface using digital image correlation

Sahil Vora, Huseini Patanwala, Brice Bognet, Shing-Yun Chang, Michelle Si Wan Li, and Anson Ma

University of Connecticut, Storrs, CT, United States

Identifying the correct stress-strain relationship experimentally is important to understanding the mechanical response of an interface and provides the basis for the theoretical development and experimental validation of any constitutive models. Langmuir-Pockels (LP) trough is one of the most

commonly used tools for studying an interface. In a typical LP trough experiment, as the interface is compressed by a pair of barriers, a Wilhelmy microbalance is used to measure the corresponding "surface pressure". Despite the relatively simple experimental setup, a mixed deformation field is created, further complicating the interpretation of the experimental results. Most, if not all, existing studies assume a 1D uniaxial compression during a LP-trough compression experiment. To examine this assumption, we custom-built a glass-bottomed LP trough equipped with a camera to capture a series of optical images as an interface is compressed. Carbon nanotubes (CNTs) were chosen as the model system as they formed a "speckle pattern" when spread onto an air-water interface. Based on the change in this speckle pattern, the displacement and strain fields were calculated using digital image correlation (DIC) analysis. Our experimental findings clearly show, for the first time, the development of a non-uniform and complex 2D strain field during compression. Although the compressive strain averaged over the whole trough area closely resembles the 1D uniaxial compression strain, the 1D compression assumption underestimates the local strain at the center of the trough by about 36% (for a compression area of 25 cm<sup>2</sup>). This DIC-based method may be applicable to other systems with similar optical texture, allowing the correct identification of stress-strain relationship of an interface.

This work is supported by NSF CAREER (#1253613), GE fellowship, and Anton Paar fellowship.

Tuesday 11:05 Crystal C

EF17

### **Visualization of interfacial particle contact angle distributions**

Md. Anisul Islam, Gordon F. Christopher, and [Craig Snoeyink](#)

*Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The properties of Pickering Emulsions or particle stabilized droplets are highly dependent upon the three-phase contact angle of the particles. In addition it has recently become clear that the contact angle is not a monolithic value for the population of interfacial particles an instead takes on a rather large distribution of values. To improve our understanding of the physical behavior of these interfaces will require a better understanding of how this distribution varies in response to surface coverage, particle-particle interactions, and even particle shape. We will present a new method for measuring the three-phase contact angles of statistically robust populations of interfacial particles. This method uses Bessel Beam Microscopy to localize fluorescent particles in three dimensions and is capable of observing even very dense surface coverages and determining both the mean contact angle and orientation of ellipsoidal interfacial particles.

Tuesday 11:30 Crystal C

EF18

### **Stokesian dynamics simulations of interfacial colloidal aggregation under shear flow**

[Nader Laal-Dehghani](#) and Gordon F. Christopher

*Mechanical Engineering, Texas Tech, Lubbock, TX 79409, United States*

Controlling the formation of colloidal aggregates at fluid interfaces is important due to the prevalence of Pickering emulsions and particle laden interfaces in commercial applications and industrial processes. As a result, recent experimental studies have focused on microstructure formation of particle laden interfaces undergoing surface flow. However, there is a wide phase space of parameters that affect these systems, making it difficult to generalize experimental results. Computational approaches are well suited to address this problem through use of non-dimensional control parameters and allow explicit characterization of the effect of underlying physical mechanisms.

In this study, colloidal aggregation at an air-water interface under shear flow is explored by means of 2D Stokesian dynamics simulations. Monodisperse, spherical, charged particles are modeled on an interface with dominant attractive inter-particle interactions balanced by solvent-mediated interactions, including hydrodynamic and Brownian forces. Two initial configurations of particles, crystal packed and randomly placed, are subjected to a surface Couette flow and aggregation kinetics are monitored. Particles form anisotropic aggregates extended by the subjected shear flow for both initial configurations. However, initial positioning of the particles changes kinetics and structural properties of these aggregates. In particular, randomly positioned particles aggregate faster, forming denser less open structures. Furthermore, fractal dimension of aggregates depends primarily on shear rate and secondarily on surface coverage. The simulation results indicate that controlling surface microstructure of such systems through flow is a viable strategy in manipulating properties of interface.

## **Symposium CR Computational Rheology**

Organizers: Jim Swan and Rekha Rao

Tuesday 9:50 Crestone A

CR10

### **Evaluation of reptation-based modelling of entangled polymeric fluids including chain rotation via NEMD simulation**

[Mohammad H. Nafar Sefiddashti](#), Brian J. Edwards, and Bamin Khomami

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

Recent simulation results of a moderately entangled linear polyethylene C<sub>700</sub>H<sub>1402</sub> liquid have confirmed prior simulation and experimental evidence that individual polymer molecules experience periodic rotation and retraction cycles under steady shear flow at high Weissenberg number. With this new insight, theoreticians have begun to grapple with this additional complicating physical phenomenon that needs to be incorporated into rheological models to help explain the new data under conditions of high shear. In this work, we examine these recent efforts by using NEMD simulations to provide insight into the requisite theoretical variables, and their assigned evolution equations, to evaluate the capability

of these new tube-based models to predict accurately the simulated data sets. This analysis has revealed that the primary variables used in tube models to impart a conceptual basis to the theory, namely, the tube orientation tensor and the tube stretch, remain fundamental system properties even far away from equilibrium; however, the theory describing their evolution under flow is not well-suited to quantitative prediction. Furthermore, it is demonstrated that key system properties, such as the entanglement number and disengagement time, should play a more significant role in model development since these quantities can change dramatically under flow, particularly at high Weissenberg number where the chain rotation and retraction cycles dominate the system physics.

Tuesday 10:15 Crestone A

CR11

### **How to extract medium-amplitude nonlinearities from large-amplitude oscillatory shear (LAOS)?**

Luca Martinetti<sup>1</sup>, Piyush K. Singh<sup>1</sup>, Johannes M. Soulages<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup>

<sup>1</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Corporate Strategic Research, ExxonMobil Research and Engineering, Annandale, NJ 08801, United States*

We describe best practices and an automated algorithm for extracting the leading-order nonlinearities from large-amplitude oscillatory shear (LAOS) strain sweeps, which are completely described by four frequency-dependent material functions, e.g. represented by  $[e1](\omega)$ ,  $[e3](\omega)$ ,  $[v1](\omega)$ , and  $[v3](\omega)$  (Bharadwaj and Ewoldt, *Rheol. Acta* (2013)). These weakly nonlinear measures describe a regime known as medium-amplitude oscillatory shear (MAOS), which is the systematic step beyond small-amplitude oscillatory shear (SAOS), e.g. as represented by  $G'(\omega)$  and  $G''(\omega)$ . Although four material functions exist in the MAOS shear stress response, many researchers only report a single metric, such as the intrinsic third-harmonic intensity known as  $Q_0$  (Hyun and Wilhelm, *Macromol.* (2009)). Our objective is to make extraction of all four measures fast, reliable, and with quantified uncertainty. We consider the various mathematical approaches for direct calculation and indirect fitting of experimental data, and describe best practices. Our algorithm, implemented in MATLAB<sup>®</sup>, takes in strain-sweep data of harmonic coefficients (Fourier or Chebyshev) and outputs the four MAOS material functions. It considers instrument resolution at small strains and adopts Bayesian principles of model selection (Ewoldt and Freund, *J. Rheol.* (2015)) to identify power law scaling and strains that are beyond the medium-amplitude regime. The algorithm quantifies uncertainties in all four MAOS measures, which is essential for inferring molecular information from these bulk rheological measurements. Probing this MAOS regime is a powerful characterization technique that enables structure-rheology insight and constitutive model selection while avoiding experimental artifacts associated with very large deformations. Our algorithm provides a fast and reliable method, with quantified uncertainty, for easily computing these rigorously defined material functions from strain sweep data.

Tuesday 10:40 Crestone A

CR12

### **Non-equilibrium conformational dynamics of a coarse-grained polymer model with internal friction and hydrodynamic interactions**

Ramalingam Kailasham<sup>1</sup>, Rajarshi Chakrabarti<sup>2</sup>, and J. Ravi Prakash<sup>3</sup>

<sup>1</sup>*Department of Chemistry, IITB-Monash Research Academy, IIT Bombay, Mumbai, Maharashtra 400076, India;* <sup>2</sup>*Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai, India;* <sup>3</sup>*Department of Chemical Engineering, Monash University, Melbourne, Australia*

The influence of internal friction on the rheological response of polymer solutions has been studied from the inception of the development of coarse-grained kinetic theory models for polymer dynamics. The inclusion of a resistive force proportional to the rate of change of the connector vector between beads leads to a shear-rate dependent viscosity, a finite limiting value for the infinite frequency limit of the dynamic viscosity, and to instantaneous stress jumps at the inception of steady shear flow. More recently, experimental, and theoretical studies have shown that the presence of internal friction modulates conformational changes in a number of different biological contexts. These include slowing down the process of protein folding, influencing stretching transitions in single biomolecule force spectroscopy, and affecting the dynamics of intermolecular interactions in intrinsically disordered proteins. In all these situations, internal friction arises from configurational rearrangements of biomolecules on an underlying 'rough' energy landscape. In parallel, recent advances in modelling polymer solution rheology have revealed the crucial influence of fluctuating hydrodynamic interactions (HI) on polymer dynamics. Models that include both internal friction and HI are rare, with the majority including HI in a pre-averaged manner. In this work, a coarse-grained model incorporating finite chain extensibility, internal friction and fluctuating HI is used to study the relative roles played by internal friction and HI in determining macromolecular dynamics. Brownian dynamics simulations are used to evaluate a number of dynamic properties such as polymer diffusivity, relaxation times from stretch-relaxation simulations, and non-equilibrium properties in shear and extensional flow. The results enable a careful differentiation of the influence of solvent-mediated friction on conformational dynamics, from the influence of a dissipative mechanism that is independent of solvent viscosity.

Tuesday 11:05 Crestone A

CR13

### **The dominant role of rheology in flow-induced, multi-phase, multi-morphological crystallization kinetics of isotactic polypropylene**

Gerrit W. Peters, Enrico M. Troisi, and Giovanna Grosso

*Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5600MB, The Netherlands*

Understanding the complex crystallization behavior of isotactic polypropylene (iPP) in conditions comparable to, e.g. injection molding, where the polymer melt experiences a combination of high shear rates and elevated pressures, is key for modeling and, therefore, predicting the final structure and properties of iPP products. In this work, we show the importance of a quantitative description of the complex rheological behavior of the material, i.e. the influence of the rheology on crystallization kinetics and, vice versa, the coupling between the evolving crystalline structures

and the rheology. Coupling a unique experimental setup, capable to apply wall shear rates similar to the ones experienced during processing and carefully control the pressure before and after flow is imposed, with in-situ X-ray scattering and diffraction techniques (SAXS and WAXD) at fast acquisition rates (up to 30 Hz), a well-defined series of short-term flow experiments are carried out using 16 different combinations of wall shear rates (110 to 440 1/s) and pressures (100-400 bar) [1]. The overall apparent crystallinity evolution, amounts of different phases ( $\alpha$ ,  $\beta$  and  $\gamma$ ), and morphologies developing in the shear layer (parent and daughter lamellae both in  $\alpha$  and  $\gamma$  phase) are fully quantified from the analysis of WAXD data. Both, flow rate and pressure were found to have a significant influence on both the nucleation and the growth process of oriented and isotropic structures. Flow affects both shish formation and the growth of  $\alpha$ -parents, pressure acts both on relaxation times, enhancing the effect of flow, and (mainly) on the growth rate of  $\gamma$ -phase [2]. All the observations were tested with the flow induced crystallization model framework developed in our group [3], and used for model validation.

[1] *Macromolecules*, accepted (2017). [2] *Macromolecular Theory and Simulations*, 22(5), 307-318 (2013) [2] *Polymer*, 89, 69-80 (2016).

Tuesday 11:30 Crestone A

CR14

### **Encapsulation and porous imbibition models of curing epoxy**

Kristianto Tjiptowidjojo<sup>1</sup>, Rekha Rao<sup>2</sup>, Christine C. Roberts<sup>2</sup>, and Amy K. Kaczmarowski<sup>2</sup>

<sup>1</sup>*University of New Mexico, Albuquerque, NM, United States*; <sup>2</sup>*Sandia National Laboratories, Albuquerque, NM, United States*

We are developing engineering models to help design encapsulation processes for electronic parts. The encapsulant is a two-part epoxy embedded with glass microbubbles. The high voltage assemblies rely on the encapsulant to ensure standoff between sensitive components. Processing of these assemblies is quite rigorous as even small voids, cracks, or delamination in the polymer materials can lead to component failure. Since we do not currently have a non-destructive test that can distinguish between filled-epoxy and void, we are using numerical models to help understand regions of under-filling or gas trapping. In high voltage applications, thorough infiltration of epoxy dielectric materials through the transformer windings is key to ensuring good performance. However, epoxies change viscosity as they react making infiltration particularly time dependent. Often transformers potted by new technicians or towards the end of the epoxy pot life can suffer from voids that enhance their breakdown and lead to component failure. We have developed a series of numerical models to help elucidate the effect of processing on encapsulation of an idealized transformer geometry building on our previous work with modeling curing epoxies and mold filling. A coupled curing epoxy-level set method to look at the current process where encapsulant is poured from the top, flowing via gravity. The webbing and transformer are modelled using a porous Brinkman equation, which will allow the permeability to decrease as the epoxy cures. For this model, the particles will be included only as an isotropic increase in viscosity. We will also use this model to investigate infiltration using a different encapsulation technique where pressure is used to flow the epoxy into the domain from a side fill. Results from the two models are used to suggest process improvements.

## **Symposium GS Gels and Self-Assembled Systems**

Organizers: Kendra Erk and Simon Rogers

Tuesday 9:50 Crestone B

GS1

### **Mechanistic constitutive model for wormlike micelle solutions with flow-induced structure formation**

Sarit Dutta and Michael D. Graham

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

We present a tensor constitutive model for predicting stress and flow-induced structure formation in dilute wormlike micellar solutions. The micellar solution is treated as a dilute suspension of rigid Brownian rods whose length varies dynamically. Consistent with the mechanism presented by Turner and Cates [*J. Phys.:Condens. Matter* 4, 3719 (1992)], flow-induced alignment of the rods is assumed to promote increase of rod length that corresponds to the formation of flow-induced structures observed in experiments. At very high deformation rate, hydrodynamic stresses causes the rod length to decrease. These mechanisms are implemented in a phenomenological equation governing the evolution of rod length, with the number density of rods appropriately modified to ensure conservation of surfactant mass. The model leads first to an increase in both shear and extensional viscosity as deformation rate increases and then to a decrease at higher rates. If the rate constant for flow-induced rod growth is sufficiently large, the model predicts a multivalued relation between stress and deformation rate in both shear and uniaxial extension. Predictions for shear and extensional flow at steady state are in reasonable agreement with experimental results. The model is simple enough to serve as a tractable constitutive relation for computational fluid dynamics studies.

Tuesday 10:15 Crestone B

GS2

### **Rheology of wormlike micellar solutions in pressure-driven and simple shear flow**

Carla Caiazza<sup>1</sup>, Denis O'Sullivan<sup>2</sup>, Vincenzo Guida<sup>2</sup>, Abel Jerez<sup>2</sup>, Valentina Preziosi<sup>1</sup>, Giovanna Tomaiuolo<sup>1</sup>, and Stefano Guido<sup>1</sup>

<sup>1</sup>*DICMaPI, Università degli Studi di Napoli, Federico II, Naples, Italy*; <sup>2</sup>*Brussels Innovation Center, Procter&Gamble, Brussels, Belgium*

Thanks to their unique and tunable viscoelastic properties, wormlike micelles are extensively used in a wide range of industrial applications, such as enhanced oil recovery, drag reduction, and consumer goods. Production and processing of wormlike micellar solutions, as well as their industrial and daily applications, involve a broad variety of operations, in some of which the system experiences high shear rates, such as in pumps, dispensers, tank and static mixers, and injectors nozzles.

Modeling and predicting the flow behavior of a wormlike micellar solution in such processes requires rheological data covering a wide range of shear rates, up to around  $100\,000\text{ s}^{-1}$ , well beyond the instrumental limits of classical rotational rheometry. As it is well known, due to problems such as shear-induced fracturing or sample ejection, a rotational rheometer can hardly reach shear rates as high as  $1000\text{ s}^{-1}$ . On the other hand, other rheological techniques are better suited to investigate high shear rate ranges, but provide a worse performance at low shear rates.

In this scenario, matching several measurement techniques can play a key role in filling the gap between classical rotational rheometry and high-shear rate data. Indeed, by coupling techniques with different characteristic shear rates, one can cover the whole operating range of the most common industrial operation units involved in wormlike micellar solutions processing.

Here, we measure the flow curve of a widely used wormlike micellar solution in an extended range of shear rates by using classical mechanical rheology tests, such as creep and stress relaxation, together with microrheology, diffusing wave spectroscopy, and pressure drop measurements in pipes. Finally, we will discuss steady state build up, slip velocity and shear banding effects of the selected model system.

Tuesday 10:40 Crestone B

GS3

### **Linear wormlike micelles behave similarly to entangled linear polymers in fast shear flows**

Danila Gaudino, Rossana Pasquino, Giovanni Ianniruberto, and Nino Grizzuti

*Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Naples, Italy*

The rheology of wormlike micellar solutions is very sensitive to the concentration of binding salts. At relatively low salt concentration, worms have a linear architecture, while branches form at higher concentrations. We here examine the linear and nonlinear rheological behaviour of two low-salt linear wormlike micellar systems (with a different salt chemistry), highlighting analogies with the rheological behaviour of ordinary entangled linear polymers. The two solutions, both containing Cetylpyridinium Chloride (CPyCl), are prepared by adding Sodium Salicylate (NaSal) and Diclofenac Sodium (Diclo), respectively. Rheological experiments are conducted through the strain-controlled rheometer ARES (TA Instrument), by using 50mm-0.017rad cone-plate geometry. The nonlinear rheological behaviour is explored by performing shear start-up tests, and by measuring both the viscosity and the first normal stress difference. In order to emphasize the rheological similarities with ordinary polymers, data are compared with the predictions of a model recently used to successfully describe the nonlinear rheological behaviour of entangled polymeric solutions and melts. In particular, it is here confirmed that in order to quantitatively describe the rheology in fast shear flows molecular tumbling must be accounted for. It is also confirmed that the shear viscosity is more sensitive to tumbling than the first normal stress difference.

Tuesday 11:05 Crestone B

GS4

### **Multiple energy dissipation processes determined in the linear viscoelasticity of worm-like micelles via measurements of recoverable strain**

Simon A. Rogers, Johnny Lee, and Jun Dong Park

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

The linear viscoelastic response of multiple worm-like micellar solutions and polymer suspensions is mapped in terms of the recoverable and unrecoverable strains in stress- and strain-controlled experiments. It is shown that a successful description of the responses requires a minimum of three parameters, rather than the traditionally-used two. Within this framework, one modulus and two viscosities are shown to account for relaxation and retardation processes that are clearly decoupled. All dynamics within these systems are accounted for by the movement of the equilibrium position. Notably, we measure a constant modulus (the plateau modulus) and a constant viscosity (the zero-shear viscosity) in the micelle solutions in the fast-breaking limit. Such measurements are obtained over a wide range of frequencies in small-amplitude oscillatory shearing (SAOS). Having identified and measured the recoverable strain, modulus, and viscosities, we are able to calculate the instantaneous energy stored and dissipated. We show that at higher frequencies the energy dissipation from retardation processes is significant, while at lower frequencies energy is dissipated mostly by relaxation processes. The averages of our measured stored and dissipated energies scale with the dynamic moduli, as expected. We show that the micellar rheology can be described by a single equation that accounts for responses to step strains, step rates, step stresses, and oscillatory stresses and strains. The successful description of the micellar and polymeric rheology suggests that detailed transient measurements of the recoverable strain and a moving equilibrium have significant utility in understanding other nonlinear protocols, notably large amplitude oscillatory shear (LAOS).

Tuesday 11:30 Crestone B

GS5

### **Dielectric properties of shear-aligned micelles studied by simultaneous impedance spectroscopy and rheoSANS**

John K. Riley<sup>1</sup>, Jeffrey J. Richards<sup>1</sup>, Paul D. Butler<sup>1</sup>, and Norman J. Wagner<sup>2</sup>

<sup>1</sup>*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States;*

<sup>2</sup>*Chemical and Biological Engineering, University of Delaware, Newark, DE, United States*

Colloidal dispersions display dielectric relaxations arising from interfacial polarization, most commonly described by Maxwell-Wagner theory. The strength and characteristic time scale of the interfacial polarization depends on the dielectric properties, i.e. permittivity and conductivity of the medium and particles as well as the volume fraction and shape of the dispersed particles. In an applied external electric field, this interfacial polarization can be used to drive assembly of colloids into ordered structures, providing a mechanism for dielectrophoretic particle assembly and the design of responsive electro-rheological fluids. Further, anisotropic particles such as rods or ellipsoids display dielectric properties dependent on the particle orientation relative to the applied electric field. Methods to measure dielectric properties of colloidal dispersions in the quiescent state fails to capture these directional properties because Brownian motion drives the particles to orient randomly. This talk will discuss our efforts to resolve shape and orientation contributions to the interfacial polarization in colloidal suspensions using simultaneous impedance spectroscopy

and rheo-small angle neutron scattering (Dielectric rheoSANS). Non-ionic PEO-PPO-PEO triblock copolymer (Pluronic P85) micelles in H<sub>2</sub>O and D<sub>2</sub>O are used as a model colloids whose shape can be controlled in-situ via spherical to rod-like to lamellar microstructural transitions with increasing temperature. Emphasis will be placed on rod-like micellar solutions which display viscoelasticity and undergo strong alignment when sheared. We evaluate the micelle microstructure in the quiescent state and under flow and evaluate the extent of alignment directly using SANS, while performing simultaneous impedance spectroscopy to evaluate the permittivity and conductivity of the micellar solutions. These Dielectric RheoSANS are used to directly determine the reduced dielectric strength as a function of average particle orientation angle.

## Symposium MM Microrheology and Microfluidics

Organizers: Travis Walker and Charles Schroeder

Tuesday 9:50 Aspen

MM5

### **Effect of capillary-driven snap-off on fluid displacement in microfluidic porous media with different surface wettability**

Jorge A. Avendaño<sup>1</sup>, Nicolle M. Lima<sup>1</sup>, Jose A. Quevedo<sup>2</sup>, and Marcio S. Carvalho<sup>1</sup>

<sup>1</sup>*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Brazil;* <sup>2</sup>*Autonomous University of Queretaro, Queretaro, Mexico*

Wettability plays a major role in many natural and industrial processes, such as oil recovery, CO<sub>2</sub> sequestration, mineral processing, soil mechanics, coating, printing and many others. The pore level physics of one liquid being displaced by another is a strong function of the wettability characteristics of the channel. However, the quantification of this effect is still not clear. In the particular case of two-phase flow in oil reservoirs, conflicting data have shown that in some oil displacement experiments in rocks, the volume of trapped oil falls as the porous media becomes less water-wet while in some microfluidic experiments the volume of residual oil is higher in oil-wet media. The reasons for this discrepancy, details of the pore-scale physics and their consequence on macroscopic behavior are not fully understood. Here we analyze oil displacement by water injection in two microfluidic porous media with different wettability characteristics over a range of Capillary number. The microfluidic device models a complex structure comprised of channels which have a near circular cross section (100µm x 110µm) along with constrictions, or pore-throats, of 63 µm and 85 µm which are randomly distributed. This configuration promotes capillary-driven snap-off of the displacing phase in addition to the expected capillary and viscous fingering. The resulting residual oil ganglia size distribution is quantified by image processing. The results show that the oil-wet porous media has a smaller volume of residual oil with a larger number of small oil ganglia and a much smaller number of large oil ganglia. This size distribution is a strong evidence that in the conditions explored, snap-off was critical to reduce the water phase mobility, leading to a more efficient oil displacement.

Tuesday 10:15 Aspen

MM6

### **Microfluidic-based particle and cell manipulation in strongly shear-thinning fluids**

Francesco Del Giudice<sup>1</sup>, Sathish Shivani<sup>1</sup>, Gaetano D'Avino<sup>2</sup>, and Amy Q. Shen<sup>1</sup>

<sup>1</sup>*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan;* <sup>2</sup>*Dipartimento di Ingegneria Chimica, dei Materiali e della P, Università degli Studi di Napoli Federico II, Napoli, Italy*

In the last decades, microfluidic platforms have been widely used for the manipulation of particles and cells in channels with micrometer-size scale. The unpredictable intrinsic nature of any cell population makes cell manipulation challenging. Indeed, cells with different sizes and with different deformabilities are found within the same population. Hence most microfluidic devices have been tested mainly on rigid particles because of their well-defined properties. Very recently, particle and cell manipulation were successfully achieved in simple straight channels, by simply using dilute aqueous polymer solutions as the suspending fluid. Particles and cells tend to align along the channel centerline when the suspending liquid is elastic with a near constant viscosity. For strongly shear-thinning fluids, very few work was reported. In this work, we study the transversal migration of particles and cells suspended in a strongly shear thinning liquid flowing in a straight square-shaped microchannel with channel height  $H=100\ \mu\text{m}$ . We used particles with four different diameters ( $d=6, 10, 15, 20\ \mu\text{m}$ ), and two type of cells, namely Jurkat cells ( $d=15\pm 2\ \mu\text{m}$ ) and Fibroblasts NIH 3T3 ( $d=19\pm 2\ \mu\text{m}$ ). The suspending liquid is an aqueous solution of hyaluronic acid 0.8 wt% with a power index  $n=0.35$ . We found that rigid particles of  $d=6, 10, 15\ \mu\text{m}$  migrate towards both the center and the corners of the microchannel at low flow rates, while particles detach from the corner at higher flow rates. Rigid particles of  $d=20\ \mu\text{m}$  migrate towards the channel centerline regardless of the flow rate. Meanwhile, Jurkat and Fibroblast cells migrate towards the channel centerline regardless of the flow rate. We infer that Jurkat cells behave differently from rigid particles of the same size because of their high deformability. Our results lay the foundation for further experimental investigations of manipulating the spacing of viscoelastic particles/cells in straight channels, which has only been explored theoretically.

Tuesday 10:40 Aspen

MM7

### Investigating the dynamics of droplet-breakup in a microfluidic cross-slot device for characterizing the extensional properties of weakly viscoelastic fluids

Kristin A. Marshall, Shelley R. Haug, and [Travis W. Walker](#)  
*CBEE, Oregon State University, Corvallis, OR 97331, United States*

Dilute and semi-dilute polymer solutions are used in a wide range of applications. In these processes, small amounts of macromolecule are added to enhance the performance of the working fluid, and regardless of being a desired outcome or not, the presence of elasticity may significantly impact the fluid response to a disturbance, particularly in extension. The present research was conducted in an effort to make improvements to and to provide an in-depth assessment of the techniques available for characterizing low-viscosity elasticity. A microfluidic device is presented that uses a cross-slot geometry to observe a two-phase droplet breakup event. For viscoelastic fluids, we report that a cylindrical filament forms between droplet segments which appears to decay exponentially in time. In optically tracking this decay, both transient extensional viscosity and relaxation times can be evaluated. For validating and optimizing the device, a range of poly(ethylene oxide) (PEO) and Newtonian solutions were tested. Comparisons of the evolution profiles as a result of the presence of elasticity are made, and these results are compared with the results from other emerging extensional techniques.

Tuesday 11:05 Aspen

MM8

### Passive non-linear microrheology for determining extensional viscosity

Kaiwen Hsiao<sup>1</sup>, Jelena Dinic<sup>2</sup>, Vivek Sharma<sup>2</sup>, and [Charles M. Schroeder](#)<sup>1</sup>

<sup>1</sup>*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

In this talk, we present a new microrheological method for determining extensional viscosity by directly observing particle migration in non-equilibrium flows. Particles are confined in two-dimensions in a planar extensional flow using a Stokes trap. During this experiment, particles are observed to migrate in the direction transverse to flow in non-Newtonian fluids such as viscoelastic polymer solutions due to normal stresses in the microdevice. Particle migration in the transverse direction is monitored and tracked in real-time using a piezo-nano stage, and the experiment is performed using several different polymer solutions (DNA and PEO) across a range of flow strengths. Particle trajectories obtained from experiments are analyzed using a second-order fluid model, which enables determination of the extensional viscosity for the suspending polymer solution. Extensional viscosities determined from particle migration experiments are found to be in good agreement with bulk rheological measurements of extensional viscosity based on the dripping onto substrate (DoS) method. Overall, this work demonstrates that non-equilibrium materials properties can be determined by passive yet non-linear microrheology for complex fluids.

Tuesday 11:30 Aspen

MM9

### Steady extensional viscosity measured by a differential pressure extensional rheometer (DPER) on a chip

Seo Gyun Kim<sup>1</sup>, Susan J. Muller<sup>2</sup>, and [Heon Sang Lee](#)<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Dong-A University, Busan 604-714, Republic of Korea;* <sup>2</sup>*UC Berkeley, Berkeley, CA 94710, United States*

We will present a method to construct a fully developed elongational flow at nearly constant extension rate in a converging microchannel. For a Giesekus-Leonov fluid, we show that under appropriate conditions, the first normal stress difference in a fluid element flowing along the channel centerline reaches its steady-state value early in the converging region, so that the time-averaged normal stress difference is approximately equal to the spatially-averaged normal stress along the converging section. We demonstrate that the averaged normal stress in the converging region (with contraction ratios of 4.9 or 10.343) maintains greater than 90% of the steady value up to an extension rate of 100 s<sup>-1</sup>. At higher extension rates, the averaged normal stress becomes significantly smaller than the steady value. A differential pressure elongational rheometer (DPER) is proposed where the pressure difference between the converging channel and a reference channel can be monitored. The reference channel is a straight channel geometry in which the viscous contribution to the pressure drop equals that in the converging channel. We will also present the steady extensional viscosities of various low viscosity fluids measured by DPER.

## Tuesday Afternoon

### Symposium AM Active, Motile, and Field Responsive Materials

Organizers: Patrick Underhill and Dan Klingenberg

Tuesday 1:30 Crystal A

AM6

#### **An active particle in a complex fluid**

Gwynn Elfring and Charu Datt

*University of British Columbia, Vancouver, Canada*

Active particles are self-driven objects, biological or otherwise, which convert stored or ambient energy into systematic motion. The motion of small active particles in Newtonian fluids has received considerable attention, with interest ranging from phoretic propulsion to biological locomotion, whereas studies on active bodies immersed in complex fluids are comparatively scarce. A simple model for an active particle considers a sphere with an axisymmetric distribution of slip-velocities on its surface, known as the squirmer model. This model has been helpful in developing insights into the dynamics of both biological swimmers, like *Volvox* and *Opalina*, and synthetic self-propelling colloids. In this talk we present a theory for an active squirmer-type particle in a complex fluid, and then discuss the effects of viscoelasticity and shear-thinning rheology in the context of biological locomotion and the propulsion of colloidal Janus particles.

Tuesday 1:55 Crystal A

AM7

#### **Not so fast: Single-particle motion in active suspensions**

Eric W. Burkholder and John F. Brady

*Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

The mechanics of active matter — materials in which the constituents are able to self-propel — are characterized by a mechanical swim stress exerted by the active particles. This stress gives rise to fascinating behaviors such as phase-separation and "superfluidity" under shear. On the microscale, the effect of the swim force (the self propulsive force of the active particles) on the suspension rheology has not been well-studied. To this end, we determine the force required for a Brownian probe of size  $R$  to translate at velocity  $U$  through a bath of active Brownian particles (ABPs) of size  $a$ , characteristic swim velocity  $U_0$ , and reorientation time  $\tau_R$ . In a Newtonian solvent this force is given by Stokes drag law, and in passive suspensions the bath particles exert an additional resistive drag force on the probe; this competition between the probe's advective disturbance and the thermodynamic restoring force in the bath is governed by a Péclet number  $Pe$ . In an active suspension, when the probe moves quickly,  $Pe \gg 1$ , the swimmers hinder probe motion and the applied force must be greater than the Stokes drag. However, when the probe moves slowly ( $Pe \ll 1$ ) through a bath of highly active particles, the force required to move the probe may become zero — or even negative! — as a result of hydrodynamic interactions: one may need to apply an external force opposite to  $U$  to prevent the swimmers from carrying the probe along at an even greater velocity.

Tuesday 2:20 Crystal A

AM8

#### **Symmetric shear banding in bacterial "superfluids"**

Shuo Guo<sup>1</sup>, Devranjan Samanta<sup>1</sup>, Yi Peng<sup>1</sup>, Xinliang Xu<sup>2</sup>, and Xiang Cheng<sup>1</sup>

<sup>1</sup>*Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States;* <sup>2</sup>*Beijing Computational Science Research Center, Beijing 100193, China*

Bacterial suspensions—a premier example of active fluids—show an unusual response to shear stresses. Instead of increasing the viscosity of the suspending fluid, the emergent collective motions of swimming bacteria can turn a suspension into a "superfluid" with zero apparent viscosity. Although the existence of active superfluids has been demonstrated in bulk rheological measurements, the microscopic origin and dynamics of such an exotic phase have not been experimentally probed. Here, using high-speed confocal rheometry, we study the dynamics of concentrated bacterial suspensions under simple planar shear. We find that bacterial superfluids under shear exhibit unusual symmetric shear bands, defying the conventional wisdom on shear-banding of complex fluids, where the formation of steady shear bands necessarily breaks the symmetry of unsheared samples. We show quantitatively that active superfluids arise from the detailed stress balance and preserve the symmetry via sampling all allowed nonequilibrium shear configurations. This remarkable ability of active fluids is reminiscent of ergodicity generally considered as a defining feature of equilibrium systems.

Tuesday 2:45 Crystal A

AM9

**Collective motion of microorganisms in complex fluids**Arezoo M. Ardekani and Gaojin Li*Purdue University, West Lafayette, IN, United States*

We study the active turbulence induced by a suspension of rodlike microswimmers in a two-dimensional film of viscoelastic fluids. We find that the fluid elasticity has a small effect on a suspension of pullers, while it significantly affects the pushers. The attraction and orientational ordering of the pushers are enhanced in viscoelastic fluids. The induced polymer stresses break down the large-scale flow structures and suppress velocity fluctuations. In addition, the energy spectra and induced mixing in the suspension of pushers are greatly modified by fluid elasticity.

## Symposium SG Solids, Glasses, and Composites

Organizers: Xiaolong Yin and Jonathan Stickel

Tuesday 3:45 Crystal A

SG1

**Surface detection error in nanoindentation of polymers**Zhiyuan Qian<sup>1</sup>, Jared Risan<sup>2</sup>, Benjamin Stadnick<sup>2</sup>, and Gregory B. McKenna<sup>1</sup><sup>1</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>2</sup>*Nanomechanics Research Laboratory, Bruker Nano Surfaces, Minneapolis, MN 55344, United States*

Nanoindentation is a widely-used technique to characterize the mechanical properties of polymeric materials at the nano scale. Extreme surface stiffening has been reported for soft polymers such as poly(dimethylsiloxane) (PDMS) rubber. Our recent work [J. Polym. Sci. Pol. Phys., 2017, 55, 30-38] provided a quantitative model which demonstrates such extreme stiffening can be associated with experimental artifacts, i.e., false surface detection. In the present work, we have further investigated the effect of surface detection error on the determination of mechanical properties by varying the sample modulus, surface detection criterion, as well as probe geometry. We have examined materials having moduli from approximately 2 MPa (PDMS) to 3 GPa (Polystyrene). The results show that surface detection error leads to apparent large stiffening. The errors are lower for the stiffer materials, but still be significant if care is not taken to establish the range of the surface detection error. We have also examined the effect of pressure beneath the probe on modulus of Polystyrene.

Tuesday 4:10 Crystal A

SG2

**Creep responses of amorphous Teflon films deep in the glassy regime**Heedong Yoon, Yung P. Koh, Sindee L. Simon, and Gregory B. McKenna*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Over the past decade, the physical vapor deposition technique has been used to produce stable glasses with low enthalpy, high density, and high kinetic stability. [1] Prior works for stable glasses were made using low molecular weight materials, and there are no reports of ultra-stable polymeric glasses. Recently, we have succeeded in producing high molecular weight ultra-stable amorphous Teflon films by vapor pyrolysis deposition method. [2] The films produced here exhibited 57 K fictive temperature ( $T_f$ ) reduction when the substrate temperature is between to 0.75 to 0.97 times the glass transition temperature ( $T_g$ ). This large  $T_f$  reduction gives an opportunity to study the dynamic behavior deep in the glassy regime. In the current work, we use this ultra-stable glass to study the relaxation behavior of the polymer in the temperature range between  $T_f$  and  $T_g$  where the glass has lower enthalpy and specific volume than the equilibrium system. The relaxation behavior of stable Teflon films was measured using the TTU nano bubble inflation technique [3] and following Struik's protocol [4]. The results show that the relaxation time decreases with increasing aging time, implying that devitrification is occurring in this regime. The results will be compared with previous work suggesting that such high density glasses [5] evidence a strong deviation away from Vogel-Fulcher-Tammann (VFT) dynamics determined above  $T_g$ .

[1] Swallen, S. F.; Kearns, K. L.; Mapes, M. K.; Kim, Y. S.; McMahon, R. J., Ediger, M. D.; Wu, T.; Yu, L.; Satija, S. *Science* 2007, 315, 353-356. [2] Yoon, H.; Koh, Y. P.; Simon, S. L.; McKenna, G. B. *Macromolecules* 2017, Under Review. [3] O'Connell, P. A.; McKenna, G. B. *Rev. Sci. Instrum.* 2007, 78, 013901-1-013901-12. [4] Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978. [5] Zhao, J.; Simon, S. L.; McKenna, G. B. *Nat. Commun.* 2013, 4, 1783.

Tuesday 4:35 Crystal A

SG3

**From simple to complex glass-forming liquids: broadening of the glass transition as studied by shear rheology**Olli-Ville Laukkanen<sup>1</sup>, H. Henning Winter<sup>1</sup>, Hilde Soenen<sup>2</sup>, and Jukka Seppälä<sup>3</sup><sup>1</sup>*Dept. of Chem. Eng. & Dept. of Polymer Sci. and Eng., University of Massachusetts Amherst, Amherst, MA 01003, United States;* <sup>2</sup>*Nynas NV, Antwerpen 2000, Belgium;* <sup>3</sup>*Department of Chemical and Metallurgical Engineering, Aalto University, Espoo 02150, Finland*

In the current literature, there seems to be a complete lack of research on the rheological properties of complex glass-forming liquids, i.e. molecular glass-forming liquids that are composed of a variety of molecular species and exhibit different types of molecular interactions. This study focuses on the rheological characterization of complex glass-forming liquids (CGFL) in shear and compares their rheological behavior with that of selected

simple glass-forming liquids (SGFL). Petroleum fluids exhibit various degrees of chemical and structural complexity depending upon their boiling point ranges, and therefore they serve as ideal model materials for CGFLs. In this study, the low-temperature rheological properties of the petroleum CGFLs are measured by small-diameter parallel plate rheometry [1]. A systematic broadening of the viscoelastic glass transition in CGFLs is demonstrated. In particular, this broadening effect is apparent in the shape of the calculated relaxation time spectra; the linear viscoelasticity of SGFLs is described by a power-law spectrum with a sudden cut-off at the longest relaxation time [2], whereas the power-law spectrum of CGFLs has a broad cut-off. The relaxation time spectra of CGFLs are fitted with the broadened power-law spectrum model in which the stretching exponent  $\beta$  describes the broadness of the relaxation time spectrum at long times [3,4].  $\beta$  is observed to decrease systematically with the increasing complexity of a glass-forming liquid. Finally, it is shown that a power-law correlation exists between  $\beta$  and the width of the glass transition region as measured by differential scanning calorimetry (DSC).

[1] O.V. Laukkanen, *Rheol. Acta*, Accepted for publication. [2] H.H. Winter, *Macromolecules*, 46, 2425 (2013). [3] O.V. Laukkanen, H.H. Winter, H. Soenen & J. Seppälä, *Annu. Trans. Nord. Rheol. Soc.*, 24, 17-21 (2016). [4] O.V. Laukkanen, H.H. Winter, H. Soenen & J. Seppälä, *Rheol. Acta*, Submitted.

Tuesday 5:00 Crystal A

SG4

### **A fundamental approach to structural relaxation and aging of thermally-driven glass formers**

Patricia Mendoza-Méndez<sup>1</sup>, Martín Chávez-Paez<sup>2</sup>, Pedro E. Ramírez-González<sup>2</sup>, Magdaleno Medina-Noyola<sup>2</sup>, and Gregory B. McKenna<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>2</sup>*Instituto de Física, Universidad Autónoma de San Luis Potosí, SAN LUIS POTOSÍ, SLP 78290, Mexico*

A fundamental description of the non-equilibrium behavior of thermally-driven glass-forming liquids is presented in this work. The relaxation of the structural and dynamical properties are studied by means of the recently developed non-equilibrium self-consistent generalized Langevin equation (NE-SCGLE) theory, using the temperature as control parameter in the context of soft-sphere interactions. We observe a similar scenario than the observed in density-driven glass formers when the system is approaching to the dynamic arrest suggesting that cooling and compressing lead to equivalent scenarios regarding the glass transition. The theoretical predictions are contrasted with the corresponding non-equilibrium Brownian simulation results obtaining a very good comparison.

## **Symposium SM Polymer Solutions and Melts**

Organizers: Suraj Deshmukh and Reza Foudazi

Tuesday 1:30 Crystal B

SM19

### **Extensional viscosity of unentangled polymer melts**

Yumi Matsumiya and Hiroshi Watanabe

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

Uniaxial extensional behavior was examined for unentangled Polystyrene (PS;  $M = 27k$ ) and Poly (*tert*-butyl styrene) (PtBS;  $M = 53k$ ) with a commercially available filament stretching rheometer, VADER 1000. At sufficiently high stretching rates, strain hardening was observed in viscosity growth function of both PS and PtBS, in particular for PtBS. Stress relaxation just after stretch to Hencky strain of 2.5 was also examined. Relaxation time was insensitive to stretching rate when the Weissenberg number  $Wi$  defined with respect to the terminal relaxation rate in the linear regime is smaller than unity, whereas the initial relaxation (just after cessation of stretching) was considerably accelerated when  $Wi > 1$ . This result is consistent with previously reported results for entangled PS chains, where the initial Rouse relaxation was accelerated under fast stretch. Thus, the reduction of monomeric friction under stretching at high  $Wi$  plays a significant role in uniaxial extensional behavior of the polymer irrespective of entanglement.

Tuesday 1:55 Crystal B

SM20

### **The mechanism of fracture for entangled polymer liquids in extensional flow**

Qian Huang, Liyun Yu, Sara L. Wingstrand, Anne L. Skov, and Ole Hassager

*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby 2800, Denmark*

In extensional flow of entangled polymer liquids, fracture may happen when the stretch rate is fast enough. High-speed imaging shows that the local shear rates near the crack tip can be 3 orders of magnitude higher than the stretch rate imposed. Such high shear rates correspond to the frequencies close to the third crossover point (in the glassy region) in linear viscoelastic (LVE) measurements [1]. This observation suggests that fracture happens in a much shorter length scale than entanglement strands, and thus the number of entanglements per chain ( $Z$ ) may be an unimportant parameter in fracture.

In this work we investigate two groups of entangled polymer liquids. In Group I we compare polystyrene (PS) melts with poly(methyl methacrylate) (PMMA) solutions. The samples have the same number of Kuhn segments ( $N_e$ ) per entanglement strand. We also compare PS solutions at a same concentration (so that  $N_e$  is the same) but with different solvents in this group. In Group II we compare PS solutions at different concentrations but with the same  $Z$ .

We first perform LVE measurements up to the frequency at the third crossover point. It has been experimentally confirmed that the distance between the first and second crossover points is related to  $Z$  for both melts and solutions [2]. We here show that the distance between the second and third crossover points is related to  $N_e$  for the entangled systems. We then stretch the samples in uniaxial extensional flow. We show that the critical strain at fracture decreases with increasing stretch rate, and reaches a constant value at faster rates. The value of the constant critical strain seems to be related to the maximum stretch ratio of the polymer chain (determined by  $N_e$ ), while it is independent of  $Z$ . The results are also compared with the critical strain of chemically crosslinked polymer networks.

[1] Huang et al., PRL 117, 087801 (2016). [2] Huang et al., Macromolecules 46, 5026-5035 (2013)

Tuesday 2:20 Crystal B

SM21

### **Extensional rheology and flow-induced crystallization of polyethylene above $T_m$**

Sara L. Wingstrand<sup>1</sup>, Kell Mortensen<sup>2</sup>, Qian Huang<sup>1</sup>, Bo Shen<sup>3</sup>, Julie A. Kornfield<sup>3</sup>, Luna Imperialy<sup>4</sup>, Roman Stepanyan<sup>4</sup>, and Ole Hassager<sup>1</sup>

<sup>1</sup>Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kongens Lyngby, Denmark; <sup>2</sup>Niels Bohr Institute, University of Copenhagen, Copenhagen 2100 Kbh O, Denmark; <sup>3</sup>Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States; <sup>4</sup>Royal DSM, Geleen, Netherlands Antilles

The morphology of polymeric products is highly dependent on the deformation history during processing. In processes like fiber spinning, blow moulding etc. the material undergoes extensional deformation. Due to instrumental limitations the number of studies investigating the influence of extensional flows on crystallization is very limited compared to the number of studies on shear induced crystallization. In this study we investigate the coupling between extensional flow dynamics and crystallinity of various linear polymeric systems containing some degree of ultrahigh molecular weight polyethylene (UHMwPE). It is known from shear induced crystallization studies, that the obtained morphology changes dramatically even when a very small fraction of a high molar mass component is added to the system. The fraction is so small that it is undetectable in the shear rheology [1]. The interesting aspect of investigating such systems in extension is that, inherently extensional rheology is highly sensitive to the presence of a high molar mass fraction, that also seems to govern the crystallinity. Indeed we find that the extensional response of the systems is directly correlated with the onset of crystallization as well as the final morphology.

[1] Seki et al. Macromolecules. 35 (7) , 2583 (2002).

Tuesday 2:45 Crystal B

SM22

### **Pinch-off dynamics and extensional rheology of polyelectrolyte solutions**

Leidy N. Jimenez, Jelena Dinic, Nikhila Parsi, and Vivek Sharma

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

Biological macromolecules like proteins, DNA and polysaccharides, and many industrial polymers, are classified together as polyelectrolytes for in solution, the repeat units in their backbone are decorated with disassociated, charge-bearing ionic groups, surrounded by counter-ions. In diverse applications like inkjet printing, sprayable cosmetics and insecticides, paints and coatings that involve formation of fluid columns or sheets that undergo progressive thinning and pinch-off into drops, the dominant flow within the necking filament is extensional in nature. The extensional rheology response of the charged macromolecular solutions is not as well understood as that of their uncharged counterparts. Here focus on the characterization of capillary thinning and pinch-off dynamics, extensional rheology and printability of two model systems: sodium (polystyrene sulfonate) and poly(acrylic acid) by using dripping-onto-substrate (DoS) rheometry technique. Both the measured extensional relaxation times and the extensional viscosity values show salt- and polymer concentration-dependent behavior that is not expected or anticipated from the typical shear rheology response.

Tuesday 3:45 Crystal B

SM23

### **Rheology and fused deposition modeling**

Michael E. Mackay<sup>1</sup>, Zachary Swain<sup>1</sup>, and David Phan<sup>2</sup>

<sup>1</sup>Materials Science & Engineering, University of Delaware, Newark, DE 19716, United States; <sup>2</sup>Chemical & Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

There are many additive manufacturing technologies, however, fused deposition modeling (FDM) has unique advantages over all others. The first advantage is that different polymeric materials can be simultaneously used to make heterogeneous structures on a ca. 100  $\mu\text{m}$  length scale, a scale that is not practical with subtractive manufacture. Another advantage is that internal constructs can be created within these heterogeneous structures, a fabrication technique that is impossible with the other AM techniques. The final advantage is that FDM has the potential to generate orientation within fabricated parts, this is considered here. Flow in the FDM extruder die and when laying down tracks will be analyzed and the potential to promote orientation considered.

Tuesday 4:10 Crystal B

SM24

**Molecular weight dependence of weld formation in material extrusion additive manufacturing**Jonathan E. Seppala<sup>1</sup>, Claire McIlory<sup>2</sup>, Peter D. Olmsted<sup>2</sup>, and Kalman Migler<sup>1</sup><sup>1</sup>Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8542, United States; <sup>2</sup>Dept. of Physics and Institute for Soft Matter Synthesis, Georgetown University, Washington, DC 20057, United States

Material extrusion (MatEx) additive manufacturing (AM), after several decades of development, is now an established production method for small volume or highly complicated parts. While MatEx has transitioned from prototyping to end use production, little is known about the mechanisms that dominate strength development between layers. Previously, in separate works, we reported on 1) a framework for determining weld time and weld strength of MatEx processed welds, comparing those results to traditional polymer-polymer weld formation and 2) non-isothermal constitutive (Rolie-Poly) modeling of polymer deformation during the MatEx process, which includes flow-induced changes in the polymer entanglement fraction. This model predicts that the structure of the weld region between printed layers is slightly anisotropic and partially disentangled for typical printing conditions. Here we extend that work by systematically varying the weight average molecular weight ( $M_w$ ) of entangled bisphenol-A-polycarbonate (PC) MatEx filaments and measuring weld time and weld strength. The resulting weld formation will be discussed in the context of traditional polymer-polymer welding, with the model providing insight to the evolution of the entanglement network and weld thickness (inter-penetration depth) during the unique shear and thermal history produced by the MatEx process.

Tuesday 4:35 Crystal B

SM25

**In situ measurements of polycaprolactone crystallization in additive manufacturing processes**Anthony P. Kotula, Lily A. Northcutt, and Kalman Migler*Materials Science and Engineering, NIST, Gaithersburg, MD 20899, United States*

Polycaprolactone is a semicrystalline polyester often used in additive manufacturing processes for biomaterials. Filament-based additive manufacturing processes often force molten polymer through a printer nozzle at high ( $> 100$  s<sup>-1</sup>) shear rates prior to cooling and crystallization. Although the phenomenon of flow-induced crystallization is well-known, the effect of flow on the crystallization and hardening kinetics of polymers are unknown for additive manufacturing. A significant barrier to understanding this process is the lack of in situ measurement techniques to quantify crystallinity after polymer filament extrusion. To address this issue we use a fiber optic probe to measure the Raman spectrum of extruded polycaprolactone during additive manufacturing. We quantify crystallinity as a function of time for the nozzle temperatures and filament feed rates accessible to the apparatus. We also perform simultaneous rheology and Raman spectroscopy measurements on polycaprolactones to determine the effect of shear (1 s<sup>-1</sup>) in the melt state on the relationship between crystallinity and the shear modulus during the crystallization process. Applying shear at low temperatures and long times in the melt state are shown to enhance crystallization kinetics and the crystallinity-modulus relationship, and we discuss the applicability of the specific work concept to our experimental results.

Tuesday 5:00 Crystal B

SM26

**Electrodeposition of metals in entangled polymer electrolytes**Shuya Wei<sup>1</sup>, Snehashis Choudhury<sup>1</sup>, Mukul D. Tikekar<sup>2</sup>, and Lynden A. Archer<sup>1</sup><sup>1</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States; <sup>2</sup>School of Mechanical & Aerospace Engineering, Cornell University, Ithaca, NY 14853, United States

Electrodeposition is used in various manufacturing processes for creating coatings on conductive substrates. The process also plays an important role in electrochemical energy storage in batteries, where it must be carefully managed to facilitate stable operations at low operating temperatures and at high deposition rates. A successful process requires fast transport of charged species (e.g. ions, particles, polymers) in an electrolyte and stable transport at the electrolyte/electrode interface. Low-viscosity, high-dielectric constant liquids are therefore the most common electrolyte media used for the process. In all currently used electrolytes, deposition is subject to a variety of hydrodynamic and morphological instabilities that lead to complex transport phenomena in the electrolyte and unstable deposition, including formation of ramified structures known as dendrites on the substrate/electrode. This talk considers the effects of polymer stresses and viscoelasticity on the stability of electrodeposition at planar interfaces. We show by means of direct visualization measurements and stability analysis that semidilute, entangled solutions of ultra high molecular weight neutral polymers stabilize electrodeposition by multiple processes. First, at low solution concentrations polymer entanglements produce large increases in viscosity without compromising ionic conductivity of liquid electrolytes, which leaves the base state ion transport at electrodes unchanged, but suppresses field-induced electroconvective instabilities at all wavenumbers. Second, at intermediate concentrations, entangled polymers produce a Brinkman-like screening of electroconvection, which stabilizes deposition at intermediate wave numbers. Finally, at high solution concentrations, time-dependent secondary fluid flow induced by polymer elasticity triggers turbulence-like states, which promote unsteadiness and mixing, stabilizing electrodeposition.

## Symposium SC Suspensions, Colloids and Granular Systems

Organizers: Cari Dutcher and Lilian Hsiao

Tuesday 1:30 Crystal C

SC14

### Non uniform flows in soft glasses of associative colloids

Maddalena Mattiello<sup>1</sup> and Michel Cloitre<sup>2</sup>

<sup>1</sup>*Soft Matter and Chemistry, ESPCI Paris, Paris 75005, France;* <sup>2</sup>*Laboratoire Matière Molle et Chimie, ESPCI ParisTech, Paris, Paris 75005, France*

Soft glasses form a broad family of yield stress materials made of deformable particles, jammed at volume fractions above close-packing. These materials, which can be as diverse as microgels suspensions, emulsion, star polymers and copolymer micellar solutions, are used in countless applications for their unique rheological properties. Soft glasses can exhibit inhomogeneous flow profiles consisting of two or several bands with distinct shear rates. The occurrence of shear banding is often explained in terms of a constitutive instability due to strong shear thinning properties. However, the connection with the microstructure and the interparticle interactions is still poorly understood.

Here we address this question using submicron microgels functionalized with alkyl groups responsible for short range attractions. We tune the strength of the interactions by varying the length and the architecture of the hydrophobic groups. In contrast with purely repulsive or weakly attractive suspensions, associative microgels exhibit remarkable flow heterogeneities - a combination of wall slip and shear-banding with a stress plateau- which depends on the strength of the attractive interactions. To understand these results we propose a two-state model which involves two characteristic timescales associated to the relaxation of in-cage associations and to cage opening, respectively. Shear banding occurs when the shear rate exceeds the relaxation frequency of in-cage associations which is measured by linear rheology and is directly related to the characteristics of the hydrophobic groups. These results establish a link between the existence of strength of short-range attractions and macroscopic flow instabilities.

Tuesday 1:55 Crystal C

SC15

### The role of multivalent ion – polyelectrolyte interactions in microgel rheology

Christopher S. O'Bryan<sup>1</sup>, Christopher P. Kabb<sup>2</sup>, Sangwoo Park<sup>2</sup>, Brent S. Sumerlin<sup>2</sup>, and Thomas E. Angelini<sup>1</sup>

<sup>1</sup>*Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611, United States;*

<sup>2</sup>*Department of Chemistry, University of Florida, Gainesville, FL 32611, United States*

Highly swollen crosslinked polymeric particles, commonly referred to as microgels, are used across multiple industrial and academic fields. In their diverse applications, microgels are used as rheological modifiers, drug delivery vehicles, and support materials for soft matter 3D printing. The most effective and widely employed microgels rely on highly charged polyanion backbones to drive their swelling at low polymer concentrations. However, multivalent cations condense onto the highly charged cationic backbones, driving deswelling and possibly resulting in microgel precipitation. These interactions between multivalent ions and polyelectrolytes have a substantial impact on the rheological properties of the microgel systems and limit their application. For example, the use of microgels as support for 3D cell culturing and bioprinting is limited by the presence of the multivalent ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in cell culture media. To investigate the interactions between anionic microgels and cations, we create polyacrylamide-methacrylic acid co-polymer microgels with varying charge density, crosslinking species, and crosslinking concentrations. We measure changes in rheological properties, swelling behavior, and ion sequestration, identifying compositions that maintain desirable rheological properties in the presence of multivalent cations.

Tuesday 2:20 Crystal C

SC16

### Effect of particle-size dynamics on flow properties of dense spongy-particle systems

Patrick Anderson, Markus Hutter, and Monica Zakhari

*Eindhoven University of Technology, Eindhoven, The Netherlands*

Suspensions of soft, open-porous particles are indispensable for applications where tailored overall properties is a necessity. The single-particle elastic network gives rise to their elastic behavior, while the flow of the viscous solvent through the particle structure establishes their rate-dependent behavior when subjected to deformation. In this work, we study the coupling between single-particle properties, in particular, their elastic modulus and permeability, and the overall properties of spongy-particle suspensions subjected to shear deformation. For this purpose, the dynamic two-scale model developed by Hutter et al. [Faraday Discuss., 158, 407- 424 (2012)] is used. Suspensions of spongy-particles as well as impermeable particles undergo a transition from a glassy state to a shear-induced ordered state. The particle permeability is found to affect the rate at which the ordered state is reached. At a fixed elastic modulus, the particle-permeability prolongs the time scale at which shear-induced ordering occurs and extends the range of shear rates where these systems exist in a disordered state. On the other hand, the long-time stress values of the ordered state is dominated by the elastic properties of the individual particle. The stress response is found to depend sub-linearly on the particle elastic modulus. In addition, spongy particles with lower elastic modulus sustain large volume changes which implicitly alters the dynamics of the system. The implicit effect of the particle elastic modulus on their size- and position-dynamics effectively separates the time scales and the shear rates, for spongy- and impermeable-particle systems, at which shear-induced ordering occurs.

Tuesday 2:45 Crystal C

SC17

**Long-term aging behaviors in a model soft colloidal system**Qi Li, Xiaoguang Peng, and Gregory B. McKenna*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79415, United States*

In the vicinity of glass transition, colloidal and molecular systems share similar behaviors. Inspired by temperature jump aging experiments in molecular systems, volume fraction up-jump experiments (induced by temperature down-jumps) were used to study both aging responses and equilibrium dynamics for a thermo-responsive PS-PNIPAM/AA soft colloidal system using light scattering (diffusing wave spectroscopy, DWS). Long-term aging responses were investigated under both equilibrium and non-equilibrium conditions. In the equilibrium state, liquid-to-glass transitions were observed as effective volume fraction increases. For the equilibrium  $\alpha$ -relaxation processes, the  $\alpha$ -relaxation time of the samples aged into equilibrium deviate from the Vogel-Fulcher-Tammann (VFT)-type expectations and the super-Arrhenius signature disappears below the glass transition volume fractions. The non-equilibrium aging responses of the samples show decoupling of the  $\alpha$ -relaxation time and the time for the structural evolution into equilibrium. As a microrheological method, DWS was found to probe the dynamics of the investigated colloidal systems differently from macroscopic rheology when in non-equilibrium regimes. Origins of these differences will be discussed.

Tuesday 3:45 Crystal C

SC18

**Wall slip of soft-jammed systems: A simple lubrication process**Philippe Coussot<sup>1</sup>, Xiao Zhang<sup>1</sup>, Elise Lorenceau<sup>2</sup>, and Tarik Bourouina<sup>3</sup><sup>1</sup>Laboratoire Navier, University Paris-Est, Champs sur Marne 77420, France; <sup>2</sup>LIPHY, Univ. Grenoble-Alpes, Grenoble, France;<sup>3</sup>ESIEE, Université Paris-Est, Champs sur Marne, France

Various materials, such as foams, emulsions, concentrated suspensions and colloids, are yield stress fluids which may also glide along smooth solid surfaces, i.e. the bulk material apparently moves as a rigid block for a stress lower than the yield stress. The fundamental approaches consisted to fit a model to the apparent flow curve in the slip regime, or directly measure the slip velocity, and possibly discuss the physical origin of the parameters, for the different material classes (concentrated suspensions, soft particle suspensions, emulsions, foams). Generally power-law dependencies for the stress vs slip velocity variations were obtained, with an exponent ranging from  $\frac{1}{2}$  to 1. Here we show that sufficiently long creep tests at different stress levels allow to have a clear view of the effective behavior of the system in the slip regime. In particular they make it possible to determine precisely the value of the residual yield stress in the slip regime. Further experiments with different geometries show that the residual yield stress is a priori due to edge effects, more precisely the attachment of the material along the line of contact of the material onto the solid surface. By removing this edge effect we can determine the stress solely associated with steady state wall slip below the material yield stress (i.e. in the pure slip regime). This stress is found to vary linearly with the slip velocity for a wide range of materials whatever the structure, the interaction types between the elements and with the wall, and the concentration. This suggests that wall slip in general results from the laminar flow of some given free liquid volume remaining between the (rough) jammed structure formed by the elements, and the smooth wall. At a macroscopic scale this phenomenon may nevertheless be described by the simple shear flow in a Newtonian liquid layer of uniform thickness. For various systems (emulsions, foams, gels, thixotropic colloids) this equivalent thickness varies in a rather narrow range (20-60 nm).

Tuesday 4:10 Crystal C

SC19

**How measurements of the recoverable strain lead to an enhanced understanding of the linear rheological behavior of a colloidal glass**Jun Dong Park and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

The linear rheology and dynamics of a hard-sphere colloidal glass under small amplitude oscillatory shear (SAOS) are explored with respect to the recoverable strain with Brownian dynamics simulation. Most rheological studies present linear viscoelastic data in terms of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) under the implicit assumption of the Kelvin-Voigt model. In this work, a series of oscillatory deformation and recovery tests shows a discrepancy between total applied deformation and recoverable strain in the linear regime (SAOS). The discrepancy implies that the established analysis of linear rheological behavior based on  $G'$  and  $G''$  is oversimplified. As an alternative, the linear viscoelastic response of the colloidal glass is quantitatively interpreted in terms of an elastic strain and the movement of the equilibrium position. This novel approach provides a more detailed probe of linear rheological behavior of colloidal glasses by distinguishing multiple energy dissipation processes that are typically accounted for by a single parameter. A consistent interpretation emerges from the bulk rheology and the particle-scale nonaffine deformations: At low frequencies, viscous energy dissipation is dominated by relaxation through movement of the equilibrium position, while at high frequencies where particles lack enough time to be relaxed, energy is predominantly dissipated through retardation processes those are proportional to the elastic strain rate. While this approach has been confined to the linear regime in the current study, it poses significant potential to assist understanding of nonlinear processes.

Tuesday 4:35 Crystal C

SC20

**Is volume jump isochoric aging the answer to structural recovery in colloidal glasses?**Sourya Banik and Gregory B. McKenna*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Colloidal systems are often touted as model glass forming systems [1]. McKenna and coworkers [2,3] had put this belief to test by performing the Kovacs' physical aging experiments on thermo-sensitive colloidal particles undergoing volume fraction jumps. Model simulations using the TNM-

KAHR model are performed on isobaric and isochoric conditions to explore the experimental results and identify whether molecular glass undergoing isochoric temperature jumps behave like colloidal systems undergoing volume fraction jumps or not. Such a study would help identify if structural recovery in colloidal glasses is mechanistically different from structural recovery in molecular glasses or are we just looking at the same behavior differently. Here we assume a molecular glass undergoing a simultaneous volume and temperature jump followed by isochoric aging replicates the behavior of a colloidal glass undergoing volume fraction jumps. The model predictions show both agreement and contradiction with the experimental results. The time to reach equilibrium in intrinsic isotherms was found to be relatively independent of the jump magnitude as observed in colloidal systems. Model predictions for asymmetry of approach showed more asymmetry than observed for colloidal systems. A significant memory effect was also observed from the model predictions unlike the colloids. The conflicting results remain crucial to ascertain the similarities and differences in structural recovery in colloids and provide newer ways to visualize structural recovery in conventional glasses.

[1] Weeks, Eric R. "Introduction to the Colloidal Glass Transition." (2016): 27-34. [2] Di, X., Win, K. Z., McKenna, G. B., Narita, T., Lequeux, F., Pullela, S. R., & Cheng, Z. (2011). "Signatures of structural recovery in colloidal glasses. " *Physical review letters*, 106(9), 095701. [3] Peng, Xiaoguang, and Gregory B. McKenna. "Physical aging and structural recovery in a colloidal glass subjected to volume-fraction jump conditions." *Physical Review E* 93.4 (2016): 042603

Tuesday 5:00 Crystal C

SC21

### Testing the paradigms of the colloidal glass transition

Jialun Wang<sup>1</sup>, Xiaoguang Peng<sup>2</sup>, Qi Li<sup>2</sup>, Gregory B. McKenna<sup>2</sup>, and [Roseanna N. Zia](#)<sup>3</sup>

<sup>1</sup>*Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, United States;* <sup>2</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>3</sup>*Chemical Engineering, Stanford University, Stanford, CA 94305-4125, United States*

We study the colloidal glass transition from a micromechanical perspective via large-scale dynamic simulation. Many molecular liquids solidify without crystallization upon sufficiently rapid cooling; the amorphous structure is retained but the dynamics become extremely slow. The new "state" is path dependent, i.e. is not an equilibrium phase: material properties such as enthalpy continue to evolve in time toward an "intransient" state, as measured by the Kovacs signature experiments, i.e. the intrinsic isotherms, the asymmetry of approach and the memory effect. The reasons for this path- and time-dependence are not fully understood in molecular glass-formers, owing partly to molecular relaxation that is so fast that the transition is conflated with the subsequent aging process, making it difficult to capture structural changes during the transition. Colloidal glass-formers provide a natural way to model such behavior, owing to the disparity in colloidal versus solvent time scales that allows tracking of particle dynamics and structure, and how these evolve with liquid-to-glassy macroscopic behavior. To shed light on the ambiguity of the glass transition and the glassy state, we study via large-scale dynamic simulation the aging of a hard-sphere colloidal glass following a range of quenches into the glass via volume-fraction jumps. We focus on post-jump structural relaxation and particle dynamics, where we implement the protocols of the McKenna-Kovacs signature experiments. During and following each jump, the positions, velocities, and particle-phase stress are tracked and utilized to characterize relaxation time scales. The impact of both quench depth and quench rate on arrested dynamics and "state" variables is explored. In addition, we expand our view to various structural signatures, and a rearrangement mechanism is proposed. The results provide insight into not only the existence of an "ideal" glass transition, but also the role of structure in such a dense amorphous system.

## Symposium NF Non-Newtonian Fluid Mechanics

Organizers: Paulo Arratia and Chris Dimitriou

Tuesday 1:30 Crestone A

NF14

### Elastic turbulence in channel flows at low Reynolds number

[Boyang Qin](#) and Paulo E. Arratia

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

In this talk, the flow of a viscoelastic fluid is experimentally investigated using particle velocimetry methods in a microfluidic device. The device is a long and straight microchannel that is 100-  $\mu\text{m}$  wide and deep; the channel has a short 3-mm region that contains a linear array of cylinders (perturbation region) followed by a 3-cm long and straight region (parallel shear region). We find that, both in the wake of the cylinders and far downstream in the parallel shear region, the flow is excited over a broad range of frequencies and wavelengths. These velocity fluctuations are consistent with the main features that characterize elastic turbulence at low Re. In the wake of the cylinder, we find that the decay in velocity temporal and spatial spectra is approximately -2.7 and -3.0, respectively. However, the decay of the initial elastic turbulence around the cylinders is followed by a growth downstream in the straight region. The emergence of distinct flow characteristics both in time and space suggests a new type of elastic turbulence, markedly different from that near the curved cylinders.

Tuesday 1:55 Crestone A

NF15

**Viscoelastic shear flow through wavy-wall microchannels**Simon J. Haward and Amy Q. Shen*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

We examine the flow of Newtonian fluids and viscoelastic polymer solutions through rectangular microchannels with one wavy wall. The channels have high depth:width ( $d:w$ ) ratios, small wave amplitudes  $A \ll w$  and various dimensionless widths  $0.6 < a = 2pw/\lambda < 10$ , where  $\lambda$  is the wavelength of the surface. Dilute polymer solutions are formulated by dissolving high molecular weight polyethylene oxide (PEO) into aqueous solvents viscosified using low molecular weight polyethylene glycol (PEG). This provides fluids with a wide range of rheological properties, specifically elasticity numbers in the range  $0.001 < El = (1-\beta)Wi/Re < 44$ , where  $\beta$  is the viscosity ratio,  $Wi$  is the Weissenberg number and  $Re$  is the Reynolds number. We employ micro-particle image velocimetry ( $\mu$ -PIV) to measure the flow fields for the various fluids within the microchannels as we increment  $0 < Wi < 50$  and  $0 < Re < 500$ . In all cases we observe vortical perturbations being generated at the wavy surface, with positive vorticity rolls located above peaks and negative vorticity rolls above troughs. However, there is a subtle interplay between the rheological properties of the fluids, the magnitude of  $a$ , and the imposed flow conditions, that together affect the shape of the vortical rolls and the distance from the wavy wall to which the vorticity penetrates (defined as the penetration depth,  $P$ ). Our experiments support recent theoretical predictions of a 'critical layer' within the channel, the depth of which depends on  $El$  [1]. If conditions are such that the depth of the critical layer is  $< P$ , significant vorticity amplification can occur within the layer, thus influencing  $P$ . In parallel with predictions for viscoelastic plane Couette flow over a wavy surface [1], we observe the existence of three broad flow regimes, which can be classified as "shallow-elastic", "deep-elastic" and "transcritical", that can be summarized in a phase diagram in an appropriately defined dimensionless parameter space.

[1] J Page &amp; TA Zaki (2016) J. Fluid Mech. 801: 392

Tuesday 2:20 Crestone A

NF16

**Towards a mechanism for instability in channel flow of highly shear-thinning viscoelastic fluids**Hugo A. Castillo and Helen J. Wilson*Mathematics, University College London, LONDON, United Kingdom*

In recent experimental work, Bodiguel and coworkers (PRL, 114, 2015) discovered a supercritical instability in channel flow of a viscoelastic shear-thinning fluid (a high molecular weight polymer solution). The steady rheometry of their fluid suggested that both the shear viscosity and the relaxation time of the fluid could be modelled with a power-law dependence on shear-rate. This scenario was modelled theoretically by Wilson & Loridan (JNNFM, 223, 2015) using linear stability theory and a modified UCM model whose physical parameters (relaxation time and shear modulus) were allowed to depend instantaneously on the local shear rate. They had some success in reproducing the experimental observations, but no real insight into the mechanism of the instability. It is clear that the instability is neither inertial (since it exists at zero Reynolds number) nor the well-known curved-streamline instability, since the streamlines are straight. A natural question to ask is whether the mechanism of this instability is truly elastic or principally a result of strong shear-thinning. To address this, we augmented the fluid model of Wilson and Loridan in the simplest way possible, and studied the effect of reducing elasticity while maintaining the shear-thinning velocity profile. We considered the linear stability of channel flow of a shear-thinning viscoelastic fluid, replicating an instability recently discovered in experimental (Bodiguel et. al) and theoretical work (Wilson and Loridan). We have extended the fluid model to allow for an inelastic shear-thinning stress component by introducing a non-Newtonian solvent (which shear-thins at the same rate than the elastic-polymer). We found that this additional contribution always has a stabilising influence on the instability. We concluded that, while shear-thinning is critical to the instability, the mechanism is primarily elastic.

Tuesday 2:45 Crestone A

NF17

**The Einstein viscosity with fluid elasticity**Jonas Einarsson, Mengfei Yang, and Eric S. Shaqfeh*Stanford University, Stanford, CA 94305, United States*

We give the first correction to the suspension viscosity due to fluid elasticity for a dilute suspension of spheres in a viscoelastic medium. Our perturbation theory is valid to  $O(Wi^2)$  in the Weissenberg number  $Wi = \gamma \lambda$ , where  $\gamma$  is the typical magnitude of the suspension velocity gradient, and  $\lambda$  is the relaxation time of the viscoelastic fluid. For shear flow we find that the suspension shear-thickens due to elastic stretching in strain 'hot spots' near the particle, despite the fact that the stress inside the particles decreases relative to the Newtonian case. We thus argue that it is crucial to correctly model the extensional rheology of the suspending medium to predict the shear rheology of the suspension. For uniaxial extensional flow we correct existing results at  $O(Wi)$ , and find dramatic strain-thickening at  $O(Wi^2)$ . We validate our theory with fully resolved numerical simulations.

Tuesday 3:45 Crestone A

NF18

**Stress modeling in colloidal dispersions undergoing heterogeneous flows**Benjamin E. Dolata and Roseanna N. Zia*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

We present a theoretical study of the stress in a colloidal dispersion undergoing non-viscometric flow. In such flows, the traditional volume averaging approach employed to compute the stress tensor in a statistically homogenous suspension is no longer generally valid; to circumvent this issue, we utilize a point-wise formulation for the stress. The non-homogeneous suspension stress thence depends on not only the local average

total stresslet—the sum of symmetric first moments of both the hydrodynamic surface traction and the interparticle force—but also on the average quadrupole, octupole, and higher-order moments. To compute the average moments, we formulate a six-dimensional Smoluchowski equation governing the microstructural evolution of a suspension in an arbitrary inhomogeneous fluid velocity field. Under the conditions of rheologically slow flow, where the Brownian relaxation of the particles is much faster than the spatiotemporal evolution of the flow, the Smoluchowski equation can be solved asymptotically to reveal a suspension stress that follows a second-order fluid constitutive model. We obtain a reciprocal theorem from a generalization of Green's second identity and utilize it to show that all weakly non-linear constitutive parameters of the second-order fluid model may be obtained from two simpler linear-response problems: a suspension undergoing simple shear and a suspension undergoing isotropic expansion. The consequences of relaxing the assumption of rheologically slow flow, including the appearance of memory and microcontinuum behaviors, are discussed.

Tuesday 4:10 Crestone A

NF19

### **Vorticity banding in Taylor-Couette flow of graphene-oxide dispersions**

Cameron C. Hopkins<sup>1</sup>, Francesco Del Giudice<sup>2</sup>, John R. de Bruyn<sup>1</sup>, and Amy Q. Shen<sup>2</sup>

<sup>1</sup>*Department of Physics and Astronomy, The University of Western Ontario, London, Ontario N6A3K7, Canada;* <sup>2</sup>*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

Since the pioneering work of Taylor and Couette, the Taylor-Couette geometry has been a staple for studying flow instability for nearly a century. The onset of instability strongly depends on the properties of the fluid confined between the two rotating cylinders. Newtonian fluids show instability above a critical value of the Reynolds number, depending on the ratio between the inner and outer cylinder radii. For non-Newtonian fluids, numerical studies show that the occurrence of instability is also affected by shear-thinning power index, yield-stress, and thixotropy. Graphene Oxide (G-O) dispersions in water are aqueous suspensions containing chemically modified graphene sheets. G-O dispersions have exhibited the non-Newtonian properties described above, serving as a good model system to test the numerical predictions. Here we present an experimental investigation of the Taylor-Couette instability for G-O dispersions of varying volume concentrations in a Couette cell with a stationary outer glass cylinder and a rotating inner cylinder. At fixed concentration, we observe the occurrence of different flow instabilities depending on the rotational speed. The onset of the first detected instability and the influence of rotational speed on the vortices were studied for different concentrations in the range  $0.04 < c < 1$  wt%, using high-speed imaging. The observed critical Reynolds numbers for the onset of instability are significantly lower than those predicted by any model available in the literature for purely inertial instabilities. We infer that the instability we observe in G-O dispersions in Taylor-Couette flow is a so-called vorticity banding instability, which has also been shown to occur for rod-like anisotropic virus dispersions.

Tuesday 4:35 Crestone A

NF20

### **The temperature dependent non-Newtonian rheological characteristics of oil-based metal oxide nanofluids**

John Shelton and Nanda Saini

*Northern Illinois University, DeKalb, IL, United States*

The rheological properties of nanofluids play an important role in determining heat transfer capacity and pumping power of a fluid as they have the potential to improve heat transfer capacity and pumping power over a base fluid. In this presentation, a clear understanding of how particle concentration and type of nanoparticle affect the viscosity of a nanofluid at elevated temperatures of up to 80 degC, which is the main parameter that influences the rheological properties of a fluid based on range of shear rates for various concentrations. Nanoparticles used for the experimentation are Al<sub>2</sub>O<sub>3</sub> (5nm) and TiO<sub>2</sub> (5nm) with paraffin oil (white, CAS No: 8020-83-5) as the base fluid. Nanofluids containing nanoparticles at 0.2 - 1.5 % volumetric concentrations are prepared using two step method with a sonication time of 12 hours and viscosity is measured using Brookfield Dv2T rotational viscometer with a cone (cp-40Z) and plate apparatus. Results show that Newtonian behavior of the basefluid changes to non-Newtonian (shear thinning) on addition of nanoparticles and the viscosity increases upon increasing the particle concentration despite elevated temperatures of up to 80 degC.

Tuesday 5:00 Crestone A

NF21

### **Nonlinear rheology of nematic liquid crystals in oscillatory shear in a magnetic field**

Eric P. Choate<sup>1</sup> and Jacob Britton<sup>2</sup>

<sup>1</sup>*Department of Mathematics and Statistics, Radford University, Radford, VA 24142, United States;* <sup>2</sup>*Department of Mathematics and Statistics, Radford University, Radford, VA 24142, United States*

We model the effects of applying an oscillatory shear flow to a nematic liquid crystal in the presence of a magnetic field. If the liquid crystal anchoring conditions and the magnetic field are both aligned parallel or orthogonal to the plates, there is no qualitative difference from the linear rheological response without the magnetic field. However, applying a magnetic field in the shearing plane that is neither parallel nor orthogonal to the plates generates a nonlinear rheological response even for oscillatory shear that would normally be considered small amplitude. Furthermore, the liquid crystal alignment with the oblique magnetic field creates an asymmetry in the shear stress with respect to the forward and backward motion of the plates so that even harmonics are present in the shear stress beyond start up.

## Symposium GS Gels and Self-Assembled Systems

Organizers: Kendra Erk and Simon Rogers

Tuesday 1:30 Crestone B

GS6

### **Modeling a hydrodynamic instability in freely settling colloidal gels**

Zsigmond Varga, Jennifer L. Hofmann, and James W. Swan

*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

Attractive colloidal dispersions, suspensions of fine particles which aggregate and frequently form a space spanning elastic gel are ubiquitous materials used as thermal insulators, catalytic electrodes, and in consumer care and food products. The colloidal networks in these materials can exist in a mode of free settling when the network weight exceeds its compressive yield stress. An equivalent state occurs when the network is held fixed in place and used as a filter through which the suspending fluid is pumped. In either scenario, hydrodynamic instabilities leading to loss of network integrity occur. Recent observations using ghost particle velocimetry have shown that loss of integrity is associated with the formation of eroded channels (streamers) through which the fluid flows rapidly. In this talk, we use Brownian dynamics simulations of sedimenting and hydrodynamically interacting colloids in dilute gels to examine the initiation and propagation of this instability. We measure the evolution of the network settling rate and identify a critical point in time beyond which the velocity grows rapidly. The rapid increase of the streamer volume in the network is shown to coincide with increasing settling rate. A phenomenological model is developed that describes the radial growth of a streamer due to erosion of the network by rapid fluid back flow. The model exhibits a finite-time blow-up - the onset of catastrophic failure in the gel - due to activated breaking of the inter-colloid bonds, controlled by the relevant dimensionless groups describing the network: the ratio of buoyant forces to network strength, the particle volume fraction, and the strength of bonds relative to the thermal forces. The model dynamics show good agreement with simulation results and experimental measurements of streamer growth in different gelling systems. We summarize our findings in a stability-state diagram that provides insight into engineering strategies for avoiding settling instabilities in networks meant to have long shelf-lives.

Tuesday 1:55 Crestone B

GS7

### **Evaporation-driven convective assembly for continuous fabrication of colloidal crystals**

Kedar Joshi and James F. Gilchrist

*Lehigh University, Bethlehem, PA, United States*

Convective deposition is a scalable method for directing colloidal self-assembly. Ordered layers of deposited particles have numerous applications as advanced materials for optical devices and membranes. Over the past 20 years, a simple mass balance derived by Dimitrov and Nagayama has been widely used for relating film thickness to deposition velocity, suspension concentration and evaporation rate and particle size. This balance works well for a small range of deposition velocities, but it fails to predict the coating thickness over a broader range. Specifically, in this balance the length scale related to drying is not well-posed and the drying length generally thought to be roughly constant. This work derives an analytical expression for the drying length in convective deposition for a more general set of conditions by considering the resistance to flow through the deposited particles. This analysis allows prediction of coating thickness over a wider range of velocities from low density coatings to multilayer particle assemblies. Other aspects related to drying length, such as film cracking and effect of solvent concentration gradients will also be highlighted.

Tuesday 2:20 Crestone B

GS8

### **Permeabilities and fractal dimensions of colloidal networks**

Lev Gelb<sup>1</sup>, Alex Mertz<sup>2</sup>, Peter Koenig<sup>3</sup>, and Alan Graham<sup>2</sup>

<sup>1</sup>*University of Texas - Dallas, Dallas, TX, United States;* <sup>2</sup>*University of Colorado - Denver, Denver, CO, United States;* <sup>3</sup>*Procter and Gamble, Cincinnati, OH, United States*

In unstable colloidal gels, the viscous flow through the non-neutrally buoyant colloidal network determines the initial rate of collapse. 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 (DLCA) networks of spheres and other particle are generated along with ordered lattices that span the containing structure or periodic cells. These networks will be characterized using the fractal dimension by measuring the length of the network strands with different sized measurement scales. The permeability is then determined using finite element solutions of Stokes equations for pressure-driven flow of Newtonian fluids through the networks. With this method, we calculate the permeability's dependence on volume fraction, particle size and shape, and fractal dimension. The fractal dimensions of our DLCA networks is in good agreement with the experimental data. However, the calculated permeability of these DLCA networks is almost a factor of 50 lower than the available experimental data which implies a much larger pore size in the experimental systems.

Tuesday 2:45 Crestone B

GS9

**Microstructure, rheology and heterogeneity in colloidal gels**Safa Jamali<sup>1</sup>, Gareth H. McKinley<sup>2</sup>, and Robert C. Armstrong<sup>3</sup><sup>1</sup>*Mechanical Engineering, Northeastern University, Cambridge, MA, United States;* <sup>2</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;* <sup>3</sup>*Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

A wide range of complex and structured fluids including colloidal gels can be identified as Thixotropic ElastoViscoPlastic (TEVP) materials. TEVPs, show a rich and complex set of rheological responses to imposed deformations in different regimes: before yielding, the network formed by individual particles remains intact and resists large deformations and the material acts as a viscoelastic solid. Above the yielding point, the material starts to flow and undergoes plastic deformation and microstructural rearrangement over a wide range of length scales. Plastic flow results in a viscous-like response; however, due to constant formation and breakage of interparticle bonds that form the network, thixotropic behavior begins to emerge. These time/rate dependent responses lead to other secondary effects including micro-phase separation, vorticity-aligned structure formation, etc. We employ a mesoscale numerical simulation method that captures attractive colloids at a sufficiently coarse-grained level that we can reproduce characteristic rheological features of a TEVP fluid under flow, and identify the sequence of microstructural changes that give rise to these macroscopic features. In order to correlate the microstructural changes of a TEVP fluid to its rheological response, we define a fabric tensor,  $Z$ , formed by an ensemble average of the spatial configuration of particle-particle bonds. In this work we will show that the fabric tensor provides a quantitative microstructural measure of the system and correlates to the macroscopic stress response in a TEVP fluid in both steady and transient states. The evolution in the components of  $Z$  with strain provides quantitative insight on the flow instabilities and secondary structures that develop in the sheared microstructure.

Tuesday 3:45 Crestone B

GS10

**Optimal Fourier transform for probing oscillatory rheology of networks: Introduction and application to thermoreversible gels**Michela Geri<sup>1</sup>, Bavand Keshavarz<sup>1</sup>, Thibaut Divoux<sup>2</sup>, Christian Clasen<sup>3</sup>, Daniel J. Curtis<sup>4</sup>, and Gareth H. McKinley<sup>1</sup><sup>1</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;* <sup>2</sup>*MIT-CNRS, Cambridge, MA 02139, United States;* <sup>3</sup>*KU Leuven, Heverlee, Belgium;* <sup>4</sup>*Swansea University, Swansea, United Kingdom*

Measuring linear viscoelastic spectra of time-varying networks requires signals that can provide both time- and frequency-resolution. Several methods have been proposed for developing new and improved protocols, including multi-wave techniques, random/white noise sequences, short-time Fourier transformations and step-strain pulses. In this work, we focus on an alternative technique that has been effectively used in radar and audio signal processing, based on a chirp, an input signal with constant amplitude and continuously modulated frequency. Exponential chirps have been proposed in the past to determine the linear viscoelastic properties of gels and have been claimed to be an optimal Fourier rheometry technique. However, analyses using a model entangled polymeric fluid reveal that spectral leakage in the chirp power spectrum can compromise the precision of the measurements, especially when the signal length is decreased to improve time-resolution. Inspired by the echolocation signals of bats and dolphins, we modulate the amplitude of the chirp with a specific envelope and show that this dramatically reduces the error due to spectral leakage. By using the same semi-dilute polymer solution we optimize the envelope modulation and show that the resulting Optimally Windowed Chirp (OWCh) waveform can be used to extract linear viscoelastic moduli with both improved time- and frequency-resolution and minimum error. The versatility of the OWCh input sequence is demonstrated by studying the gelation of a model thermoreversible gel composed of mineral oil and paraffin wax. Using a series of OWCh signals, we study the evolution of the gel properties under different thermal and shear histories and elucidate the complex nature of the thermogelation process in this material. This new signal processing protocol can be applied to resolve details of gelation dynamics for a wide range of mutating systems.

Tuesday 4:10 Crestone B

GS11

**Measuring the viscoelastic properties of gelling systems using optimal Fourier transform techniques**Bavand Keshavarz<sup>1</sup>, Michela Geri<sup>1</sup>, Thibaut Divoux<sup>2</sup>, and Gareth H. McKinley<sup>1</sup><sup>1</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;* <sup>2</sup>*MIT-CNRS, Cambridge, MA 02139, United States*

We analyze both the advantages and the limitations of a newly proposed amplitude- and frequency-modulated rheological test sequence, that uses exponential chirps. Using this new technique, we study the linear viscoelastic response of a slowly mutating acid-induced protein gel and show that by combining the exponential chirp with a modulated amplitude envelope for the input strain signal we can considerably increase the accuracy of the measured frequency response. This optimally-windowed-chirp (OWCh) signal enables us to rapidly measure the transient evolution of the elastic and loss moduli of the casein acid-induced gels over a broad range of frequencies. The linear viscoelastic response of these gels over two decades of frequency ( $0.3 = \omega = 30$  rad/s) can be accurately measured using a test signal of just 15 seconds in length. We study, the gelation process for casein gels at different mutation numbers and compare the performance of the OWCh signal to other signal processing techniques such as multi-wave and step strain measurements. A simple numerical model of the gelation process shows how the fidelity of the viscoelastic measurements depends on the time-frequency bandwidth of the input waveform and a dimensionless mutation number that characterizes the speed of the gelation process. Finally, we discuss the sources of error in the measurements performed with windowed chirp signals and provide theoretical scalings for the error magnitude as a function of a single dimensionless window length parameter.

Tuesday 4:35 Crestone B

GS12

**Connecting gel architecture to linear and non-linear rheology**Mehdi Bouzid and Emanuela Del Gado*Georgetown University, Washington, DC, United States*

Soft elastic networks like gels can form in extremely dilute particle suspensions. They feature a heterogeneous microstructure characterized by a variety of lengthscales. As a consequence, the relaxation processes depend on the nature of the parameter that controls the gel formation (Temperature, shear deformation, compression...), on the connectivity and on the internal stresses frozen-in upon solidification. Understanding the dynamical mechanisms controlling the mechanical response remains a challenge. Here we use molecular dynamics simulations of a model system to investigate the linear viscoelastic response. The frequency dependence of the elastic and the loss modulus is investigated through a new technique (Optimal Fourier Rheometry) recently introduced in experiments [Ghiringhelli et al., *Rheol Acta* 51, 413 (2012)] that consists in performing a continuous frequency sweep over time via imposing a pseudo-harmonic function for the strain. We show how such a method is extremely efficient and allows us to obtain the whole spectrum in one simulation and use a simple fractional Kelvin-Voigt model with a single Scott-Blair (or springpot) element to capture the power law frequency spectrum, reminiscent of various experimental observations in polysaccharide and protein gels. In addition, during the shear start up protocol, the system exhibits strong localization of tensile stresses that may be released through the breaking and formation of new bonds. We show how the non-linear response can be controlled by tuning the gel architecture.

Tuesday 5:00 Crestone B

GS13

**Non-integer power law scaling of asymptotically nonlinear viscoelasticity of capillary suspensions**Irene Natalia<sup>1</sup>, Randy H. Ewoldt<sup>2</sup>, and Erin Koos<sup>3</sup><sup>1</sup>*Institute of Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany;*<sup>2</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>3</sup>*Soft Matter, Rheology and Technology, KU Leuven, Leuven 3001, Belgium*

The asymptotically nonlinear response of a material to medium-amplitude oscillatory shear (MAOS) is only a function of frequency and not amplitude. Typically, constitutive models report that the leading order of nonlinearities occur at a scaling  $\sigma \sim O(\gamma_0^3)$ , as explained by a multiple integral expansion of the Boltzmann superposition [1]. Here we report atypical non-integer MAOS power law scaling for capillary suspensions, that is, particle suspensions in a two-fluid system that creates capillary interactions.

The addition of small amounts of an immiscible secondary fluid to a suspension can dramatically change the rheological behavior of the suspension behavior from a fluid-like to gel-like state by inducing gelation or reinforcing a weak network into a strong network [2]. This transition is caused by strong attractive capillary force between the particles and two fluids, producing a sample-spanning network. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles, and a capillary state when the bulk fluid is preferentially wetting.

A theory of Blackwell and Ewoldt predicts non-integer scaling based on a thixotropic-viscoelastic constitutive model; they also observed non-integer scaling experimentally with a Carbopol system [3]. For the capillary suspension studied here, the capillary bridges rupture under shear and then rebuild the network upon cessation, and such thixotropic behavior might be the origin of the observed non-integer scaling. Such a scaling might also occur because of the fractal microstructure in the percolated sample-spanning network. These theories are compared to direct observations of the network structure using confocal microscopy. The influence of the relative secondary fluid volume will also be discussed for both capillary and pendular states.

[1] Davis, Macosko, *Journal of Rheology*, 1978. [2] Koos, Willenbacher, *Science*, 2011. [3] Blackwell, Ewoldt, *JNFM*, 2016

## Symposium MM Microrheology and Microfluidics

Organizers: Travis Walker and Charles Schroeder

Tuesday 1:30 Aspen

MM10

**Microfluidics measurements of interfacial tension and viscosity of complex emulsions**Shweta Narayan and Cari Dutcher*Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States*

The stability of complex emulsions, which depends on both liquid-liquid interfacial tension and viscosity, is relevant to a variety of technological applications that deal with these systems, ranging from oil recovery to food and cosmetics. Conventional measurement techniques include Wilhelmy plates and pendant drop tensiometry for interfacial tension and rheometers for viscosity measurements. However, these are macro-scale measurement techniques which require at least a few milliliters of sample volume and have characteristic length scales on the order of a few millimeters. In contrast, microfluidic techniques offer a viable alternative for probing properties of emulsions at much smaller length scales. Here, we employ biphasic microfluidics to study complex emulsions, using contraction-expansion geometries as well as hydrodynamic traps. Monodisperse droplets of a dispersed phase deform as they enter or exit a contraction in a microfluidic device under the influence of an elongational flow field. High-speed videos of these deforming droplets are analyzed to extract the deformation of the droplets in complex emulsions, and used to calculate the interfacial tension between the two phases and viscosity of the inner or outer phase using existing theory. Microfluidic interfacial

tensiometry using is particularly effective in measuring dynamic interfacial tension, since the length and time-scales involved in microfluidic measurements are more representative of real systems. Additionally, hydrodynamic traps are used in this work to confine and perturb single droplets generated on a microfluidic chip. Perturbed droplets with low viscosities undergo periodic oscillations before returning to a spherical shape, whereas high viscosity droplets will relax back to a spherical shape in an aperiodic manner. High-speed videos of such trapped droplet shape oscillations can also be used to extract fluid properties.

Tuesday 1:55 Aspen

MM11

### **Design and fabrication of elastically tunable monodisperse microcapsules**

Debora F. do Nascimento, Jorge A. Avendaño, Ana Mehl, Maria J. Moura, Wynter J. Duncanson, and Marcio S. Carvalho  
*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Brazil*

We design and fabricate elastically tunable monodisperse microcapsules using microfluidics and cross-linkable polydimethylsiloxane (PDMS). The overall stiffness of the microcapsules is governed by both the thickness and cross-link ratio of the polymer shell. Flowing suspensions of microcapsules through constricted spaces leads to transient blockage of fluid flow, thus altering the flow behavior. The ability to tune microcapsule mechanical properties enables the design of elastic microcapsules that can be tailored for desired flow behavior in a broad range of applications such as oil recovery, reactor feeding, red-blood-cell flow and chemical targeted delivery.

Tuesday 2:20 Aspen

MM12

### **Structural and rheological relaxation upon flow cessation in colloidal dispersions: Transient, nonlinear microrheology**

Ritesh P. Mohanty and Roseanna N. Zia

*Chemical Engineering, Stanford University, Stanford, CA 94305-4125, United States*

We present a theoretical study of the impact of particle roughness, Brownian motion, and hydrodynamic interactions on relaxation of colloidal dispersions upon cessation of active microrheological flow. We focus on the disparity in timescales over which microscopic forces - hydrodynamic, Brownian and interparticle - influence structural and rheological relaxation. In our recent work, we studied the formation of structure and rheology during flow startup, and found that the steady-state balance between entropic and hydrodynamic forces is not present at all timescales; its evolution over time leads to time-dependent rheology such as viscosity overshoots, even at low volume fraction. However, open questions remain involving the influence of microscopic forces on material relaxation after the external flow shutoff. In particular, how the strengths of external flow and hydrodynamic interactions affect structural relaxation and probe motion upon flow cessation. To study this, we formulate a time-dependent Smoluchowski equation governing the spatiotemporal evolution of the suspension around a probe driven by arbitrarily strong force; the initial and boundary conditions are set by deformed, steady-state structure just prior to flow cessation. The strength of hydrodynamic and entropic forces is varied and their influence studied systematically. Upon flow cessation, the non-Newtonian rheology arising directly from hydrodynamic forces dissipates instantaneously, as expected, while the entropic contributions decay over longer times. The two mechanisms by which these entropic stresses relax are discussed, and connected to the relaxation timescales of Brownian and interparticle forces. We find that while increasing the pre-cessation flow strength enhances both the structural and rheological relaxation rates, hydrodynamic interactions slow down both relaxation rates as the relative motion between particles slows. The dissipation of stored entropic energy is discussed.

Tuesday 2:45 Aspen

MM13

### **Flow of wormlike micellar solutions around confined microfluidic cylinders**

Amy Q. Shen and Simon J. Haward

*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

Wormlike micellar (WLM) solutions are frequently used as fracture and proppant-carrying fluids in enhanced oil and gas recovery applications in porous rock beds where complex microscopic geometries result in mixed flow kinematics with strong shear and extensional components. To gain understanding of WLM fluids flowing through porous media, we examine the flow around a single micro-scale cylinder aligned on the flow axis. We study flow behavior of an aqueous WLM solution consisting of cationic surfactant cetyltrimethylammonium bromide (CTAB) and a stable hydrotrope 3-hydroxy naphthalene-2-carboxylate (SHNC) in microfluidic devices with three different cylinder blockage ratios,  $\beta$ . The WLM solution is strongly viscoelastic and exhibit shear banding behaviour. Flow of WLM solutions around confined cylinders results in the onset of a sequence of low Re flow instabilities, which depend on both  $Wi$  (as high as 105) and  $\beta$ . Interestingly the flow instabilities first emerged upstream of the cylinder, which are associated with high stresses in fluid that accelerates into the narrow gap between the cylinder and the channel wall, while upstream vortex growth is reminiscent of that seen in microfluidic contraction geometries. Instabilities downstream of the cylinder are associated with stresses generated at the trailing stagnation point and the resulting flow modification in the wake, coupled with the onset of time-dependent flow upstream and the asymmetric division of flow around the cylinder. The strong shear thinning and shear banding nature of the WLM solution also contributes to the observed instabilities.

Tuesday 3:45 Aspen

MM14

### Complex flow structuring and velocity profile evolution in wormlike micellar solutions flowing in a glass microcapillary

Carla Caiazza<sup>1</sup>, Valentina Preziosi<sup>1</sup>, Giovanna Tomaiuolo<sup>1</sup>, Denis O'Sullivan<sup>2</sup>, Vincenzo Guida<sup>2</sup>, and Stefano Guido<sup>1</sup>

<sup>1</sup>DICMaPI, Università degli Studi di Napoli, Federico II, Naples, Italy; <sup>2</sup>Brussels Innovation Center, Procter&Gamble, Brussels, Belgium

In the last decades, applied research has devoted a growing attention to wormlike micellar solutions. Indeed, their remarkable viscoelastic properties underlie an extensive use in tuning the rheological response of many everyday products, such as detergents and shampoos. On the other side, basic research is devoting a great effort in elucidating the unique rheological and flow behavior of these systems, which is characterized by the occurrence of flow instabilities [1] at high shear rates (such as shear banding [2]), with the possibility of the appearance of flow induced structures.

In this scenario, microfluidics is a powerful tool to get a deeper insight into the flow behavior of a wormlike micellar solution. Indeed, as flow instabilities are surface forces driven phenomena, their onset is facilitated in a highly confined geometry, as a microfluidic device. Furthermore, the small dimensions of these devices provides the opportunity of easily coupling microfluidics with optical microscopy, thus allowing a direct visualization of flow structuring phenomena.

Here, we flow a widely used wormlike micellar solution through a glass microcapillary. By coupling the microfluidic device with particle tracking techniques, we relate the detected complex flow structuring to the evolution of velocity profiles and to the rheological properties of the system investigated.

[1] E. K. Wheeler et al., *J. Non-Newtonian Fluid Mech.* 75 (1998). [2] T. Dioux et al., *Annu. Rev. Fluid Mech.* 48 (2016)

Tuesday 4:10 Aspen

MM15

### DWS microrheology of wormlike micelles as a tool for monitoring drug release

Danila Gaudino<sup>1</sup>, Mathias Reufer<sup>1</sup>, Chi Zhang<sup>2</sup>, and Frank Scheffold<sup>2</sup>

<sup>1</sup>LS Instruments AG, Fribourg 1700, Switzerland; <sup>2</sup>Department of Physics, University of Fribourg, Fribourg 1700, Switzerland

Micelles are aggregates made of amphiphilic molecules that, in aqueous solution, self-assemble in a way to reduce the contact between their hydrophobic part and water. These systems are commonly employed in a wide range of applications thanks to the possibility to tune their rheological properties by changing their microstructure [1]. Recently, surfactant micellar systems have also been used as carriers for non-steroidal anti-inflammatory drugs (NSAIDs), due to their low cost and the ability to regulate the drug release in this manner [2]. In this work, we present a study on the release of the commercial medicine Aspirin in a surfactant system based on Cetylpyridinium Chloride. The drug release is monitored by following the evolution of the viscoelastic response of the sample during time. Experiments based on micro- and macro-rheological measurements, using Diffusing Wave Spectroscopy (DWS) and a stress-controlled rheometer respectively, show a transition from a pure Newtonian behavior to a viscoelastic Maxwell-like response as the Aspirin dissolves. The non-monotonic trend of both, the relaxation time and the Newtonian viscosity plateau, as functions of the time and, thus, of the amount of the drug released follows the behaviors already observed for a similar surfactant system as a function of the Sodium Salicylate content [3,4]. This analogy must be related to the similar molecular structure of Aspirin and its sodic salt, confirming the crucial role of binding molecules in the determination of the morphology and dynamics of surfactant micelles [3]. Our results illustrate the potential of DWS based microrheology for the study of delivery and release of drug molecules.

[1] R. Zana and E. W. Kaler, eds. *Giant micelles: properties and applications*. Vol. 140. CRC Press, 2007. [2] R. Pasquino et al., *Colloids Surf., B*, 146, 2016, 938. [3] D. Gaudino et al., *PCCP*, 19, 2017, 782. [4] S. Rogers et al., *Curr. Opin. Colloid Interface Sci.*, 19, 2014, 530.

Tuesday 4:35 Aspen

MM16

### High-pressure linear viscoelasticity measurements of polymer solutions and gels

Kimberly A. Dennis<sup>1</sup>, Yan Gao<sup>2</sup>, Alhad Phatak<sup>2</sup>, and Eric M. Furst<sup>1</sup>

<sup>1</sup>University of Delaware, Newark, DE 19716, United States; <sup>2</sup>Schlumberger, Sugar Land, TX 77478, United States

Oilfield fluids are used to help transport and suspend solids, reduce friction pressure and prevent fluid loss. Key to these fluid performance metrics is the fluid rheology. Depending upon the composition and flow condition, the fluid can behave as a purely viscous or viscoelastic fluid. By choosing the right composition, the flow properties can be optimized for a specific function. Mechanical rheometers are used extensively for rheological measurements of fluids. However, mechanical rheometers cannot always provide accurate measurements for all the systems. Misinterpretation of rheological data may provide underestimated or exaggerated fluid features, which may in turn lead to the failure of a specific task. In addition, many of the fluids are heterogeneous, thereof change in macrorheology does not reflect the microstructure evolution of the material. Further, high-pressure measurements can be challenging for mechanical rheometers.

To address these shortcomings, we developed a passive microrheology experiment to measure the linear viscoelasticity of complex fluids at high pressures. The apparatus incorporates a sealed steel sample chamber with dual sapphire windows into a simple diffusing-wave spectroscopy (light-scattering) setup and is capable of both transmission and backscattering geometries. The measured light intensity correlation arising from the Brownian motion of polystyrene probe particles dispersed in the sample is interpreted using the generalized Stokes-Einstein relation to determine the material creep compliance. We validate this high-pressure microrheology technique with ethanol and poly(ethylene oxide) aqueous solutions and extend the measurement to stimulation fluids containing a crosslinked guar biopolymer. We investigate the effect of crosslinker density on

rheological properties at frequencies up to 1 MHz and pressures of 200 MPa, expanding the accessible range of experimental conditions beyond those of existing rheological measurement techniques.

Tuesday 5:00 Aspen

MM17

**An algebraic approach for determining viscoelastic moduli from creep compliance through application of the Generalised Stokes-Einstein Relation and Burgers model**

John Duffy<sup>1</sup>, Fred Mazzeo<sup>2</sup>, Samiul Amin<sup>1</sup>, Akubaru Minegishi<sup>3</sup>, and Philip Rolfe<sup>2</sup>

<sup>1</sup>Malvern Instruments, Malvern, United Kingdom; <sup>2</sup>Malvern Instruments, Westborough, MA 01581, United States; <sup>3</sup>Malvern Instruments, Tokyo, Japan

DLS Microrheology involves tracking the time dependent motion or mean square displacement of dispersed tracer particles of known size using Dynamic Light Scattering (DLS) in order to determine viscoelastic properties of the dispersion medium. The viscoelastic moduli are then calculated using a generalised form of the Stokes-Einstein equation which requires Fourier Transformation of the MSD. An alternative approach for estimating the viscoelastic moduli uses a modified algebraic form of the generalized Stokes-Einstein equation, which employs a power law expression to describe the local change in MSD with time. Since the mean square displacement is linearly related to the creep compliance, it can be shown that the same algebraic approach can also be applied to creep measurements made on a rotational rheometer, giving access to the low frequency moduli in a fraction of the time required for oscillatory testing. Furthermore, the quality of the conversion process can be improved by fitting a Burgers model to the time domain data prior to conversion thus minimising errors associated with local differentiation, which is fundamental to the conversion approach.

## Wednesday Morning

### Symposium PL Plenary Lectures

Wednesday 8:30 Cripple Creek Ballroom

PL3

#### **Understanding and probing the dynamics of cell-material interactions in four dimensions**

Kristi Anseth

*Chemical and Biological Engineering, University of Colorado, Boulder, CO 80303, United States*

Our group is interested in the development of biomaterials to serve as in vitro cell culture systems and decipher critical extracellular matrix (ECM) signals that are relevant in tissue development, regeneration, and disease. We design synthetic ECM analogs that capture key features of the unique chemistry and physical properties of a cell's niche—an environment that is not only tissue specific, but can be strikingly heterogeneous and dynamic. Unique to our approach is the creation of cell-laden matrices in which the matrix properties can be changed on demand—so-called 4D biology. We use these chemistries to create hydrogels functionalized with peptides, proteins and small molecules, and then monitor cell migration, protease activity, and paracrine signaling, all of which depend strongly on the surrounding microenvironment. But the approach is not without confounding complexities of its own. While it is now routine to assess how initial material signals alter cellular machinery in the short term, it is more difficult, without new techniques, to decipher dynamic and reciprocal remodeling processes that influence cell function over longer time scales. Advances in real-time tracking of cells are critical, but need to be complemented with methods to characterize local changes in material properties (e.g., deposition of matrix molecules, degradation, and local mechanical properties)—all of which occur on multiple time and size scales and in 3D. This talk will provide examples using cell-degradable hydrogels to study how cells proliferate, migrate and differentiate in response to changes in matrix density, degradability, elasticity, and adhesivity. However, beyond simply observing cells, rheological techniques allow real time measurements of the local and global hydrogel properties and monitoring of cell activity in situ. This talk aims to place these results in the broader context of opportunities for new characterization methods in tissue engineering applications.

### Symposium BB Biomaterials and Biological Systems

Organizers: Keith Neeves and Kelly Schultz

Wednesday 9:50 Crystal A

BB1

#### **Modeling the transient rheology of human blood**

Jeffrey S. Horner<sup>1</sup>, Antony N. Beris<sup>1</sup>, Norman J. Wagner<sup>1</sup>, and Donna S. Woulfe<sup>2</sup>

*<sup>1</sup>Chemical and Biological Engineering, University of Delaware, Newark, DE, United States; <sup>2</sup>Biological Sciences, University of Delaware, Newark, DE 19716, United States*

Modeling blood flow is an active area of research due to its potential in improving clinical issues such as drug delivery or bypass surgery. However, most current models for blood flow are limited by an oversimplification of the rheology of blood, with the most advanced accounting for only the steady shear behavior. In reality, blood demonstrates, in addition to the shear thinning nature under steady flow, a nonzero yield stress, viscoelasticity, and thixotropy. These phenomena occur due to the rouleaux microstructures that suspended erythrocytes form under stasis and low shear. Since blood naturally flows under pulsatile conditions, an accurate model for blood flow must address the thixotropy that blood exhibits. In addition to improving blood flow models, by accurately modeling transient blood rheology, we can obtain a better understanding of the mechanics of rouleaux formation that can lead to improved diagnosis and treatment of disease. Using experimental data that were previously presented and newly collected data for transient tests on well characterized blood samples, we offer a new thixotropic model that is able to capture the behavior of blood in response to a variety of transient experiments. Novel unidirectional large amplitude oscillatory shear tests (UD-LAOS) were performed for a range of amplitudes and frequencies. These measurements better mimic peristaltic flows in vivo and allow for transient measurements without flow reversal. Additionally, measurement considerations for blood rheology are discussed with a focus on the handling techniques and the interactions that can lead to sample inhomogeneities in the measurement geometry during testing. To account for these inhomogeneities, a model for the formation of erythrocyte free layers near the walls of the measurement device is proposed and incorporated into the thixotropic model. This overall model provides an improved representation of the transient blood rheology and enables insight into the mechanics behind rouleaux formation.

Wednesday 10:15 Crystal A

BB2

**The state of contemporary modeling and analysis of human blood rheology**Matthew J. Armstrong, Evan Ousley, Tyler Helton, and Michael Deegan*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States*

Recent work modeling the rheological behavior of blood indicates that blood has all of the hallmark features of a complex material, including shear-thinning, viscoelastic behavior, a yield stress and thixotropy. After decades of modeling steady state blood data, and the development of steady state models, like the Casson, Carreau-Yasuda, Herschel-Bulkley, etc. the advancement and evolution of blood modeling to transient flow conditions now has a renewed interest. Using published data by Sousa et al. and Moreno et al. we show and compare modeling efforts with the simple models. We first show the strengths of the simple models, then discuss potential weaknesses. This effort is followed with an evolution into using models that can handle the transient flow conditions to include fitting to published step-up/step-down experiments and Large Amplitude Oscillatory Shear (LAOS) flow [2]. The family of models that can handle the transient flows involve the recently published Modified Delaware Thixotropic Model (MDTM), the Apostolidis Thixotropic Blood Model and the Bautista-Monero-Puig Model (BMP) [5,9,13]. We first discuss the development of the scalar, structure parameter evolution models and we compare fitting results with all of these published models and transient data. In addition we propose a new term for, similar to what has been used in MDTM, for the Apostolidis model using a structural viscosity term, that has the potential to also be used in a more viscoelastic mode if necessary. The new term is compared to the original model, and the BMP model to demonstrate its effectiveness. Lastly we demonstrate a novel approach to analyzing transient blood data by incorporating the novel Series of Physical Phenomena (SPP) framework. Recent work with blood using LAOS has shown that its unique rheological signature can be used as a pseudo- "fingerprint", able to clearly show and delineate elastic and viscous regions of the LAOS cycle.

Wednesday 10:40 Crystal A

BB3

**Measurement of blood rheology using RheoSpec viscometer with EMS method**Taichi Hirano and Keiji Sakai*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, Japan*

We introduce an originally developed system for viscosity measurement, together with evaluation of rheological properties, of lowly viscous fluids such as ionic liquids, alcohol solutions, and biological fluids. In addition, we report the results of rheological measurements for human whole bloods observed in wide range of the shear rate. This system will be a powerful tool for general use in medical and biological fields, in which contamination to/from the sample specimens is a serious problem. The system is equipped with the electromagnetically spinning (EMS) technique, which was developed by us. The EMS technique can apply a driving torque to a rotor probe in a noncontact manner, and therefore, has an advantage of the sealed condition and the disposable usage; these features are outstanding when compared with the conventional viscometers or rheometers. To make the best use of these features, we have manufactured a rheometer named Rheology-Spectrometer (RheoSpec). In this study, we used an advanced-type of RheoSpec system developed especially for the accurate measurement of low viscosity. The newly developed system employs a thin disk rotor attached to a spindle as the probe for detecting the viscous torque of the sample liquid, and the rotor is designed so that it stands by the support of the buoyancy. Since the reduction of the mechanical friction is essential for the high accuracy in measuring low viscosity, the advanced-type system could achieve the accuracy better than 1%. The geometry of this probe is similar to that in a parallel-plate system, and then, we already validated a numerical procedure to obtain the exact flow curve via the measured data. Recently, we have aimed to investigate the rheological properties of fresh human bloods from the viewpoint of not only individual differences but also daily or hourly variations in each person. These rheological approach would be an interesting topic for flow mechanics in body circulation and medical check of health condition.

Wednesday 11:05 Crystal A

BB4

**Microrheological study of plasma coagulation triggered by intrinsic pathway**Yating Mao<sup>1</sup>, Mingyang Tan<sup>1</sup>, Owen J. McCarty<sup>2</sup>, and Travis W. Walker<sup>1</sup><sup>1</sup>*CBE, Oregon State University, Corvallis, OR 97331, United States;* <sup>2</sup>*Biomedical Engineering, Oregon Health & Science University, Portland, OR 97239, United States*

Both the extrinsic pathway, caused by tissue injury, and the intrinsic pathway, initiated by the exposure to a negatively charged surface, can initiate fibrin clot formation. At the early stages of the intrinsic pathway, FXII is converted to FXIIa, which then activates FXI. The structure of the fibrin is crucial for the kinetics and stability of thrombus formation, controlling the strength of the clot and its susceptibility to lysis. To measure the role of FXI in the coagulation kinetics and the fibrin clot structure, standard microrheology is performed on platelet-poor plasma to extract the transient rheological properties of the fibrin clots that are formed with and without the inhibition of FXI. The rheological change of fibrin gel is indicated by the decreasing diffusivity of probe particles that are dispersed in the plasma. At the late stage of the coagulation, a sub-diffusive region becomes notable, and a static mean squared displacement indicates the completion of the coagulation.

Wednesday 11:30 Crystal A

BB5

**Continuum modeling of nanoparticles transport in the vasculature**Rekha Rao<sup>1</sup>, Kimberly Butler<sup>2</sup>, Jonathan Clausen<sup>1</sup>, Scott A. Roberts<sup>1</sup>, Justin Wagner<sup>1</sup>, Zixiang Liu<sup>3</sup>, and Cyrus Aidun<sup>3</sup><sup>1</sup>*Sandia National Laboratories, Albuquerque, NM, United States;* <sup>2</sup>*Nanobiology, Sandia National Laboratories, Albuquerque, NM 87185, United States;* <sup>3</sup>*Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, United States*

We are developing a multiscale modeling approach to elucidate the underlying mechanisms of nanoparticle (NP) transport in vivo. In this presentation, we will discuss our work to develop a model of NP transport in the larger blood vessels where there are enough red blood cells across

the vein or arteriole to form a continuum. We compare two types of rheological models for the blood: one using a Casson model with a yield stress and another where we track the concentration of red blood cells explicitly and use this for the generalized Newtonian viscosity model. The continuum model for transport of the NPs is coupled to the rheology of the blood through the velocity field and a diffusivity tensor. The NP diffusion tensor is informed through experiment, literature review, and particle-scale modeling of the red blood cell-NP interactions. The diffusion can depend on the local shear rate and NP size as well as properties associated with the red blood cells. Following Zydny and Colton [Physicochemical hydrodynamics, 10(1), 77-96. (1988)], we developed a NP transport equation including these effects and the local hematocrit. We compare this approach to the standard method using an isotropic diffusivity tensor for dilute small particles in a continuous fluid. The predictions for blood flow and particle transport are compared in the vasculature of a chicken embryo model (CAM) system. We use stacked 2D two-photon imaging data from the large blood vessels in the CAM to create the 3D finite element mesh. Particle imaging velocimetry from high speed videos of confocal microscopy of fluorescent NP in these vessels is also discussed.

\* Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

## Symposium SM Polymer Solutions and Melts

Organizers: Suraj Deshmukh and Reza Foudazi

Wednesday 9:50 Crystal B

SM27

### **Effect of extensional flow on immiscible polymer blend/nanoparticle composites**

George Shebert and Yong Lak Joo

*Cornell University, Ithaca, NY 14850, United States*

We use coarse-grained nonequilibrium molecular dynamics to simulate a nanocomposite system of immiscible polymers and nanoparticles (NPs) under planar elongational flow. Polymer nanocomposites are increasingly used as high-performance materials due to their improved thermal, mechanical, and electrical properties, which vary with the placement of the nanoscale additive in the polymer bulk. Our goal is to investigate the effect of planar elongational flow on NP placement in a nanocomposite blend system and an analogous symmetric block copolymer (BCP) system. A comparison of the blend and BCP systems reveals that for selective NP, the blend system shows a much broader NP distribution in the selective phase than the BCP phase. For nonselective NP, the blend and BCP systems show similar results for low strain rates, but the NP peak in the BCP system broadens as strain rates approach the order-disorder transition. To better simulate polymer processing techniques like electrospinning, we add cylindrical confinement to blend and BCP systems under uniaxial extensional flow. We find that the combination of confinement and flow can create transient morphologies and inhibit ordered assembly.

Wednesday 10:15 Crystal B

SM28

### **Blends of disentangled UHMWPE and HDPE: Oscillatory & extensional rheology, optimized processing conditions for dissolution, and model development**

Krishnaroop Chaudhuri<sup>1</sup>, Suparna Poddar<sup>1</sup>, Ashish K. Lele<sup>1</sup>, Harshawardhan V. Pol<sup>1</sup>, Ajit Mathur<sup>2</sup>, and Rakshvir Jasra<sup>2</sup>

<sup>1</sup>*Polymer Science & Engineering Division, CSIR - National Chemical Laboratory, Pune, Maharashtra 411008, India;* <sup>2</sup>*Reliance Industries Ltd., Baroda, India*

Addition of Ultra High Molecular Weight Polyethylene (UHMWPE) into High Density Polyethylene (HDPE) has been explored recently in order to improve the mechanical properties of the latter. While there is no enthalpic barrier preventing these two species of (chemically identical) polyethylene to blend, the dispersion of molten droplets of UHMWPE in HDPE melt, followed by diffusion of long UHMWPE chains in the HDPE network, act as formidable kinetic obstacles to this process. In our work an entangled UHMWPE (ePE) and a disentangled UHMWPE (dPE) were blended in HDPE matrix in varying compositions in a twin-screw microcompounder. Using oscillatory rheology, we show that dPE dissolves much faster and more extensively in HDPE than the ePE over time scales that are representative of industrial processing. This is attributed to the disentangled UHMWPE long chains not being dynamically restricted by the topological network of entanglements. The effects of blend composition, time of mixing, and rotation speed of the screws on linear rheology were studied. Further, we investigated the extensional rheology of the UHMWPE/HDPE blends. We show that the blends exhibit strain hardening even though the constituent HDPE does not in the pure state. This is because pure UHMWPE is seen to have significant strain hardening characteristics. A preliminary model, based on constraint release theory, is used to quantify the rheological observations.

Wednesday 10:40 Crystal B

SM29

### **Predictions of flow-induced demixing and shear banding in polydisperse polymer melts**

Joseph D. Peterson, Glenn H. Fredrickson, and Gary Leal

*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93117, United States*

In our research group, we have recently shown that flow-induced phase separation in an entangled monodisperse polymer solution can lead to macroscopic concentration non-uniformities, and these in turn can produce major changes in the flow. For planar shear flow, the coupling of stress and polymer concentration leads to regions of shear rate where the homogeneous shear flow is linearly unstable. This leads ultimately to a steady

shear banded velocity and concentration profile. The same is also true for Taylor-Couette and LAOS flows. An important related question is whether the same physics can lead to banded flows as a consequence of spatially nonhomogeneous molecular weight profiles in a polydisperse polymer melt? To answer this question, we consider an entangled melt with two distinct molecular weights, both significantly above the entanglement molecular weight. The blend rheology is modelled using a new approximate constitutive model that generalizes the concept of double reptation to all the non-linear stress relaxation mechanisms of a Rolie-Poly polymer. This reduces to a double reptation model in the linear viscoelastic limit, and is consistent with the more detailed molecular model of Read et. al. in the nonlinear flow regime. Combining this constitutive framework with a two-fluid model, we have found that for well-entangled polymer blends, entropic forces favoring mixing can be very small compared to elastic stresses within the system. For deformation rates near the inverse long chain reptation time, only a modest contrast between the molecular weight of long and short chains is needed to produce an instability in compositionally homogeneous shear flow. Following such an instability, the system evolves towards a compositionally inhomogeneous steady state comprising a high shear band of lower average molecular weight, and a low shear band of higher average molecular weight.

Wednesday 11:05 Crystal B

SM30

### **Influence of long-chain branching on thermorheology of a metallocene polyethylene**

Jorge M. Silva

*Polymer Science, Braskem, Triunfo, RS, Brazil*

It is well-known that long-chain branching (LCB) affects the processing behavior of polyolefin. Despite its importance and all the considerable efforts made, a complete characterization of LCB is still not possible. In recent years, the thermorheology has emerged as one of the techniques that can provide an additional insight into the branching structure. In fact, the analyses of thermorheological complexity, which is often observed in branched polyolefin, seems to carry valuable information about LCB. The position of the peak in graph of the apparent activation energy versus phase angle is particularly relevant [1], but still it reflects the combined effect of molar mass distribution (MMD) and LCB. In this work, two polyethylenes, with and without LCB, but with identical MMD and comonomer content are physically blended at different ratios. Hence, the effect of LCB concentration in the position of  $E_a(\delta)$  peak can be observed. Additionally, the influence of crosslinking generated by thermo-oxidative degradation is also evaluated.

[1] Stadler *et al.*, "Deriving comprehensive structural information on long-chain branched polyethylenes from analysis of thermo-rheological complexity," *Polymer* **104**, 170-192 (2016).

Wednesday 11:30 Crystal B

SM31

### **Tailored polyolefin interfaces via rheological and process modelling**

Alex M. Jordan<sup>1</sup>, Kyungtae Kim<sup>1</sup>, Frank S. Bates<sup>1</sup>, Shaffiq Jaffer<sup>2</sup>, Olivier Lhost<sup>2</sup>, and Christopher W. Macosko<sup>1</sup>

<sup>1</sup>*Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States;* <sup>2</sup>*Total, S.A., Paris, France*

While isotactic polypropylene (iPP) and polyethylene (PE) are chemically similar, poor interfacial adhesion between these polyolefin pairs has been repeatedly demonstrated in the literature. Here, we utilize rheological measurements and modelling to determine the molecular structure of multiple commercial grades of iPP, high density polyethylene (HDPE), and linear low density polyethylene (LLDPE), which arise from the use of heterogeneous Ziegler-Natta (z) catalysts or site-specific metallocene (m) catalysts. Further, we employ additional rheological modelling to quantify the interfacial tension between various miPP/mLLDPE, miPP/mHDPE and ziPP/zHDPE polymer pairs. The measured interfacial tension was then related back to the adhesion between each polymer pair; in brief, as interfacial tension decreased, interfacial adhesion increased. The role of post-extrusion take-up on interfacial adhesion was also examined and modeled as a transient thermal heat flow. Finally, these polymer pairs were processed into droplet/matrix blends, co-continuous blends, and multilayer films and the role of interfacial adhesion on the mechanical properties of extruded films and injection molded parts was highlighted. This work demonstrates the utility of rheological and thermal modelling to maximize adhesion between immiscible polymer pairs to achieve tailored interfaces with specific mechanical properties.

## **Symposium SC Suspensions, Colloids and Granular Systems**

Organizers: Cari Dutcher and Lilian Hsiao

Wednesday 9:50 Crystal C

SC22

### **Shear thickening in suspensions: The effects of contact model**

Helen J. Wilson and Adam K. Townsend

*Mathematics Department, University College London, London WC1E 6BT, United Kingdom*

We all know the phenomenon of shear thickening in concentrated cornstarch suspensions; indeed most of us will have used it as a hands-on demonstration experiments in our public engagement activity. Recently there has been a lot of research trying to understand the underlying mechanism of shear thickening. Some researchers have successfully replicated the phenomenon using a combination of inter-particle contact and a friction force that applies above some critical load [e.g. Mari et al, *JRheol* 58:1693, 2014; Seto et al, *PRL* 111:218301, 2014]. But it is still not entirely clear which properties of the inter-particle contact force are critical for shear thickening, and indeed whether these models really capture the local physics of the particle interactions. Using Stokesian Dynamics, we experiment with a variety of contact models, including the very simple

model we first used in 2000 [Wilson & Davis, JFM 421:339-367, 2000] and some more sophisticated modifications to it. We find, perhaps surprisingly, that pure hard-contact asperities are not capable of predicting Discontinuous Shear Thickening; the compressibility used elsewhere is a critical component of the thickening behaviour.

Wednesday 10:15 Crystal C

SC23

### **A system-spanning dynamically jammed region in response to impact of cornstarch and water**

Rijan Maharjan<sup>1</sup>, Shomeek Mukhopadhyay<sup>1</sup>, Benjamin Sokol<sup>1</sup>, Benjamin Allen<sup>2</sup>, Tobias Storz<sup>1</sup>, and Eric Brown<sup>1</sup>

<sup>1</sup>*Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06511, United States;* <sup>2</sup>*Clark University, Worcester, MA, United States*

We experimentally study the impact response of concentrated suspensions consisting of cornstarch and water. We observe that the suspensions support a large normal stress - on the order of MPa - with a delay after the impactor hits the suspension surface. We show that neither the delay nor the magnitude of the stress can be explained by either standard rheological models of shear thickening in terms of steady-state viscosities, or impact models based on added mass or other inertial effects. Through surface imaging and particle tracking, we show that the stress increase occurs shortly after a solid-like region of the suspension in front of the impactor propagates to the opposite boundary of the container, which can support large stresses when it spans between solid boundaries. We present a constitutive impact rheology in terms of the delay and an effective modulus of the solidlike region while it spans between solid boundaries, both as a function of impact velocity, fluid height, and weight fraction. We show that this constitutive model can be used to quantitatively predict, for example, the trajectory and penetration depth of the foot of a person walking or running on cornstarch and water. We also present a detailed calculation of the added mass contribution to impact response to compare its range of applicability to that of the system-spanning solid-like region.

Wednesday 10:40 Crystal C

SC24

### **Controlling shear thickening in colloidal suspensions by adding shaped, non-colloidal particles**

Norman J. Wagner

*Chemical and Biological Engineering, University of Delaware, Newark, DE, United States*

Colloidal dispersions exhibit shear thickening and it is often desirable to control the onset and extent of this rheological response. While tailoring particle size, shape, surface interactions, and solvent properties can all be used to systematically and predictively vary the shear thickening behavior of a suspension, it has been shown that confinement can also affect suspension rheology due to the enhanced hydrodynamic interactions propagated by the confining surfaces (Swan & Brady, JFM 2011). Simulations of non-Brownian particles with models for hydrodynamic interactions have also shown that confinement can induce shear thickening (Bian et al. JNNFM 2014). Here, we exploit these results to control reversible shear thickening in colloidal dispersions by inducing confinement within the suspension by adding non-colloidal particles. For example, it has also been demonstrated experimentally that shear thickening in colloidal dispersions can be dramatically altered by the addition of non-colloidal spherical and cubic particles to the suspension (Cwalina et al. JOR 2015, AIChE 2017). At low volume fractions, the addition of non-colloidal spherical particles to the colloidal dispersion leads to an increase in the steady shear viscosity as well as the dynamic moduli. At higher volume fractions of non-colloidal spheres, the shear thickening power law exponent increases with the addition of non-colloidal particles. At higher concentrations of added, cubic particles, deviations from this shifting procedure are apparent as depletion attractions and confinement of the underlying colloidal dispersion lead to larger increases in the viscosity at both low and high applied shear stresses. Further effects are induced by the greater confinement afforded by adding large plate-like clay particles. The results of this study provide guidance for formulating suspensions through control of particle shape and mixture concentration. Examples of the use of this in technologies in health care and sports will be given.

Wednesday 11:05 Crystal C

SC25

### **Hydrodynamic stress in a discontinuous shear thickening colloidal suspension**

Kevin J. Whitcomb and Norman J. Wagner

*Chemical and Biological Engineering, University of Delaware, Newark, DE, United States*

The role of hydrodynamic interactions in the onset and stress levels achieved in discontinuous shear thickening in colloidal suspensions is explored. A discontinuous shear thickening colloidal suspension consisting of alkane coated silica particles (nominal size 57.8 nm) is dispersed in a near-index matched Newtonian medium consisting of ( 69.7% deuterated ethylene glycol and 30.3% polyethylene glycol by volume). The system has been studied previously<sup>1,2</sup> and has been shown to transition from continuous to discontinuous shear thickening at 0.54 volume fraction.<sup>3</sup> Rheology shows discontinuous shear thickening occurring at shear stresses of 250 Pa and shear rates of 200 s<sup>-1</sup>. Stress jumps are performed to resolve the relative importance of hydrodynamic and non-hydrodynamic forces through the shear thickening transition. Microstructure measurements are performed using small angle neutron scattering under flow in rheo-SANS and 1-2 plane flow SANS geometries. The analysis<sup>1</sup> of Gurnon et al. was used to determine the hydrodynamic and non-hydrodynamic contributions to the shear stress and normal stress differences. This work will help clarify the role of hydrodynamic interactions in discontinuous shear thickening in colloidal dispersions and is important for engineering colloidal dispersions for specific technological applications.

[1] Gurnon, A.; Wagner, N., Microstructure and rheology relationships for shear thickening colloidal dispersions. *Journal of Fluid Mechanics* 2015, 769, 242-276. [2] Kalman, D., Microstructure and Rheology of Concentrated Suspensions of Near Hard-Sphere Colloids. Available from ProQuest Dissertations and Theses A and I.: 2010; Vol. Order No. 3423338. [3] Cwalina, C.; Wagner, N., Material properties of the shear-thickened state in concentrated near hard-sphere colloidal dispersions. *Journal of Rheology* 2014, 58 (4), 949-967.

Wednesday 11:30 Crystal C

SC26

### Rheology and microstructure of dense deformable colloidal suspensions: Interplay between elasto-hydrodynamic and frictional interactions

Joao Maia, Arman Boromand, Shaghayegh Khani, and Brandy Grove*Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

Understanding the physical origin of the rheological response of colloidal suspensions, namely the shear thickening phenomenon, has been the subject of numerous recent studies, with both lubrication hydrodynamic and friction theories having been used to explain the shear rate dependent behavior of these complex fluids. However, neither has been able to replicate by itself the whole range of rheological responses in the continuous and discontinuous shear thickening regimens. Recently, using numerical simulations, our group investigated the role of hydrodynamic and frictional interactions in rheological properties of dense and semi-dense colloidal suspensions and showed that the formation of a frictional percolating network at high stresses is essential for obtaining discontinuous shear thickening behavior and positive N1; however, it is also necessary for hydroclusters to form at low stresses in order to bring particles together and nucleate the frictional contacts. Deformable colloidal particles will change the flow response of colloidal suspensions. Herein we discuss the effect of elasto-hydrodynamic deformation of the particles on the microstructures formed under external shear flows and on the corresponding rheological response, i.e., shear-thickening and normal-stress differences. We will use a mesoscale model that includes lubrication and frictional forces in addition to a contact force developed based on the elasto-hydrodynamic theory. Monitoring the structure and rheology of soft to rigid suspensions, we explore the interplay between the elasto-hydrodynamic and frictional interactions.

## Symposium GS Gels and Self-Assembled Systems

Organizers: Kendra Erk and Simon Rogers

Wednesday 9:50 Crestone A

GS14

### Can rheology distinguish between gelation and glass transition in soft matter?

H. Henning Winter*Dept. of Chem. Eng. & Dept. of Polymer Sci. and Eng., University of Massachusetts Amherst, Amherst, MA 01003, United States*

Superficially, soft matter behaves very much alike, whether it is a gel or a soft glass. Rheological experiments will be shown for both classes of materials in search for universal differences between the two. Chemical gels are solids because of their permanent network connectivity; they cannot be dissolved in a good solvent, for instance. In this way, chemical gels are fairly straight forward to identify. This is different for physical gels and soft glasses. Both are liquids, however, with very long relaxation time constants and trapped non-equilibrium states. Even then, their dynamics is distinctly different as will be shown.

Wednesday 10:15 Crestone A

GS15

### Viscoelastic behaviour of a colloidal gel at the critical point

Khushboo Suman and Yogesh M. Joshi*Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India*

We investigate the rheological behaviour of a colloidal dispersion of charged disk like particles of Laponite XLG undergoing sol-gel transition as a function of time. We observe that, while undergoing gelation, Laponite suspension passes through the critical state wherein percolated space-spanning fractal network of particles give rise to power law dependence of relaxation time on frequency ( $G' \sim G'' \sim \omega^{-n}$ ). In this work we study stress relaxation, creep and start up shear behaviour of Laponite dispersion in the critical-gel state. The creep and stress relaxation experiments started at the critical point very interestingly show power law evolution in accordance with the Winter criterion ( $G(t) \sim t^{-n}$  and  $J(t) \sim t^n$ ). For the pre-gel and post-gel states, the dynamics is respectively less and more sluggish than that of at the critical state for both creep as well as stress relaxation experiments. We also solve quasi-linear integral model with  $G(t) \sim t^{-n}$  for creep-recovery and start-up of shear flow. Very interestingly in the linear response regime, creep and strain recovery predicted by the model matches the experimental behaviour very well. In shear start-up experiments, it is observed that, in a linear response regime, the stress growth function ( $\eta^+$ ) depends only on shear strain ( $\gamma$ ) irrespective of the strain rate, and the dependence is given by:  $\eta^+ \sim \gamma^{1-n}$ . Again, the quasi-linear integral model predicts the identical behaviour of  $\eta^+$  validating the consistency of linear viscoelastic framework for various flow fields for an attractive fractal network. Beyond the linear regime, for higher values of stresses and strain rates, the experimental behaviour deviates from the model prediction, which we attribute to the breakage of the fractal network.

Wednesday 10:40 Crestone A

GS16

**Using creep testing as an alternative to Multiwave Oscillation for determining the true gel point of network polymers**Mats Larsson<sup>1</sup>, John Duffy<sup>2</sup>, Shona Murphy<sup>2</sup>, Adrian Hill<sup>2</sup>, and Philip Rolfe<sup>3</sup><sup>1</sup>Malvern Nordic, Uppsala, Sweden; <sup>2</sup>Malvern Instruments, Malvern, United Kingdom; <sup>3</sup>Malvern Instruments, Westborough, MA 01581, United States

The common method for monitoring gelation dynamics with a rheometer is to perform Small Amplitude Oscillatory Shear (SAOS) at a single frequency while monitoring the evolution of  $G'$  &  $G''$  with time or temperature. The point of gelation defined as the time or temp at which  $G'$  and  $G''$  cross. Winter shows, that with exception of stoichiometrically balanced network polymers & networks with excess cross-linker true gel point does not coincide with the intersection of the dynamic moduli and is more accurately identified as the time or temperature at which  $G'$  and  $G''$  become parallel and the loss tangent ( $\tan \delta$ ) independent of frequency, AKA the Winter-Chambon criteria. Hence, to accurately determine the gel point using SAOS testing requires measurements to be made at multiple frequencies and at various stages of the gel process. A common approach is to perform Fourier Transform Mechanical Spectroscopy (FTMS) or Multiwave Oscillation whereby the frequency dependent moduli are determined simultaneously at several discrete frequencies by applying a complex waveform consisting of a fundamental frequency and several harmonics. While this approach reduces time needed to obtain a frequency spectrum the determination of the true gel point is still limited by the time to perform the lowest frequency, which can be long. Hence, the approach is only really valid for relatively slow curing systems. Furthermore, the sum of the stress or strains applied at each freq must be within the Linear Viscoelastic Region (LVR) thereby increasing noise to signal ratio compared with a single freq test. This alternate to Multiwave overcomes many limitations cited above. The approach, based on creep testing and transformation of  $J(t)$  to  $G'(\omega)$  and  $G''(\omega)$ , since  $J(t)$  contains information of all oscillation frequencies, not just the discrete harmonics as in multiwave. It's possible to quickly determine a frequency spectrum vs. multiwave without the same limitations. We will show that it is possible to determine true gel point for many network polymers

Wednesday 11:05 Crestone A

GS17

**Relaxation times and "self-healing" recovery of entangled and unentangled supramolecular systems**

Zachary R. Hinton and Nicolas J. Alvarez

*Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States*

Supramolecular molecules show increase in relaxation times as a function of increased association strength and number of associations. However, several questions remain on how these associations form and are distributed as a function of time. The timescale of the association process (i.e. the time required to achieve maximum equilibrium stress) is dependent upon many fundamental physics including reptation, entanglements, and association. In this work, an extensional rheometer is employed to probe the effects of temperature and contact time on the equilibrium stresses of model associating systems, including poly-(n-butyl acrylate) (PnBA), poly-(acrylic acid) (PAA), and 2-ureido-4[1H]-pyrimidinone (UPy) containing macromolecules. The slope of the equilibrium stress as a function of healing time is examined for polymers with and without associations to show the compound effects of entanglement and hydrogen bonding on the healing timescale. The effect of degree of association and temperature on the adhesion timescale are explored.

Wednesday 11:30 Crestone A

GS18

**Stress induced abrupt sol-gel transition in associating polymer solutions**

Indravadan Parmar, Ashish K. Lele, Manohar Badiger, and Prakash Wadgaonkar

*Polymer Science & Engineering Division, CSIR - National Chemical Laboratory, Pune, Maharashtra 411008, India*

Recently, we demonstrated that semi-dilute aqueous solutions of hydrophobically modified high molecular weight associating polymers show an abrupt sol-gel transition upon cooling (Parmar et al, RSC Adv., 7, 5101 (2017)). The low shear viscosity showed an abrupt increase by several orders of magnitude at a critical temperature, which was dependent on polymer concentration. The phenomenon was shown to be caused by percolation of chains due to swelling upon cooling together with conversion of intra-molecular hydrophobic associations to inter-molecular associations. A temperature shift factor that accounts for chain swelling due to cooling enables superimposing viscosity-temperature curves for various polymer concentrations onto a mastercurve. We have also shown in the past that similar polymers exhibit a shear induced sol-gel transition (Lele et al, Macromolecules 43, 10055 (2010)). In the present work, we show that an abrupt sol-gel transition can be induced by a combination of cooling and imposed shear. The critical temperature for sol-gel transition increases with increase in imposed shear stress. A stress shift factor, which accounts for expansion of coil dimensions due to imposed shear, can be calculated from superposition of viscosity-temperature data at various imposed stresses. The shift factor is seen to be linearly dependent on shear rate, in disagreement with theories of polymer solutions but in agreement in data of Lee et al (Macromolecules, 30, 7313 (1997)) for polystyrene solutions.

## Symposium NF Non-Newtonian Fluid Mechanics

Organizers: Paulo Arratia and Chris Dimitriou

Wednesday 9:50 Crestone B

NF22

### Edge fracture in complex fluids

Suzanne M. Fielding, Ewan J. Hemingway, and Halim Kusumaatmaja  
*Department of Physics, Durham University, Durham, United Kingdom*

We study the edge fracture instability using linear stability analysis and direct nonlinear simulations. We derive an exact expression for the onset of edge fracture in terms of the shear-rate derivative of the fluid's second normal stress difference, the shear-rate derivative of the shear stress, the jump in shear stress across the interface between the fluid and the outside medium (usually air), the surface tension of that interface, and the rheometer gap size. We provide a mechanistic understanding of the edge fracture instability, validated against our simulations. These findings, which are robust with respect to choice of rheological constitutive model, also suggest a possible route to mitigating the effect, potentially allowing experimentalists to achieve and accurately measure stronger flows.

Wednesday 10:15 Crestone B

NF23

### Comparison of impulsively induced viscoelastic jets having different shear-rate dependent viscosities

Emre Turkoz, Antonio Perazzo, Hyungsoo Kim, Craig B. Arnold, and Howard A. Stone  
*Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, United States*

Jet formation is very important in ink-jet printing and dispensing techniques, where well-defined and robust single droplet generation is desirable. In this study, "impulsive" jet formation from viscoelastic inks, which exhibit different non-Newtonian behavior, are investigated using a novel nozzle-less printing technique called blister-actuated laser-induced forward transfer (BA-LIFT). Extensional and shear rheometry are used to evaluate material properties, and the relationship between the jet rheology and the printing outcomes are discussed. We show that a specific range of the Deborah and Ohnesorge numbers provide a robust single-droplet morphology thus highlighting a way to tailor the rheological properties of the inks in order to obtain optimum printing material parameters.

Wednesday 10:40 Crestone B

NF24

### Computational study of melt fracture

Youngdon Kwon  
*School of Chemical Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Republic of Korea*

Numerically modeling the Poiseuille flow along and outside a straight channel with a differential viscoelastic constitutive equation, we illustrate unstable dynamics involving a bifurcation from steady to periodic melt fracture (sharkskin instability) and its further transition to a chaotic regime. The first Hopf bifurcation results from the high stress along the streamlines and their finite curvature near the die lip. Its succeeding chaotic transition at higher level of flow elasticity that results in gross melt fracture, seems to take a period doubling as well as quasiperiodic route. Current study suggests another possible cause for the onset of sharkskin instability and conceivably provides a robust methodology to portray various types of melt fracture if combined with an appropriate model of wall slip.

Wednesday 11:05 Crestone B

NF25

### Liquid rope coiling in a power-law fluid: Simulation and observation of the structuration at the impact

Anselmo S. Pereira, Alexandre Antoniotti, Romain Castellani, and Rudy Valette  
*CEMEF, MINES ParisTech, PSL Research University, Sophia Antipolis, PACA 06904, France*

In multiple industrial applications where a fluid jet impacts a surface, coiling instabilities are observed. Such instabilities are critical as they will have an influence on end-use properties that are themselves affected by the structuration originating in the way the coils collapse. Potential gradients of composition in the jet, and air bubbles entrapping, lead to complex structures in the bulk. It is known that a jet of fluid will spread or form different types of coils depending on its velocity and diameter. For Newtonian fluids, the diameter of these coils, the winding frequency and the jet radius at impact are well known for a large range of flow rates and falling heights [1]. Multiple regimes were found, depending on the balance of gravity, inertial and viscous forces (and thus fluid characteristics as viscosity or density). However, in the case of fluids possessing a different rheology, many other issues arise.

In this communication, we study coiling instabilities for concentrated suspensions, considered here obeying a power-law behavior (at least locally). Simulations are performed (i) in the case of a Newtonian fluid and (ii) for a shear-thickening suspension. The results, appearing consistent to those obtained in the literature for the Newtonian case, highlight the changes in coiling frequencies and diameters when the fluid rheology is different. In parallel, experiments were conducted using transparent silicon oils and simple spheres suspensions, close to the packing fraction. Analysis and comparison with simulations were done using a high-speed camera. We also address how, for these different cases, fluid rheology affects structuration after the impact and bubbles entrapping, when the different coils collapse.

[1] Neil M. Ribe et al., Liquid Rope Coiling, Annual Review of Fluid Mechanics Vol. 44: 249-266 (2012)

Wednesday 11:30 Crestone B

NF26

**Capillary break-up of liquid-liquid interfaces**Susanna Formenti<sup>1</sup>, Karel Verbeke<sup>2</sup>, Francesco Briatico Vangosa<sup>1</sup>, Naveen K. Reddy<sup>3</sup>, and Christian Clasen<sup>2</sup><sup>1</sup>Politecnico di Milano, Milano, Italy; <sup>2</sup>KU Leuven, Heverlee, Belgium; <sup>3</sup>Hasselt University, Hasselt, Belgium

Studies of capillary breakup phenomena of liquid filaments are classically related to liquid-air interface; however, there is a variety of applications where liquid-liquid interfaces are involved. The presence of a surrounding medium of different (often similar or even higher) viscosity and an altered interfacial tension change the thinning dynamics significantly, so that classical descriptions need to be reconsidered. Pioneering studies focused mainly on the late-stage thinning and breakup dynamics close to pinch-off in dripping experiments, exploiting a large range of viscosity ratios of inner to outer fluid. For this, different similarity solutions were proposed to describe the universal pinch-off for well-defined regimes of the Navier-Stokes equations.

Here we explore the thinning behaviour away from the self-similar final stage of pinch-off for a wide range of inner and outer fluids, combining inertia controlled, viscous and intermediate fluids. To this end, the capillary thinning of filaments with Liquid-liquid interfaces is investigated, using a high-resolution optical setup together with a modified version of a capillary breakup setup. Using this novel Liquid-in-liquid technique allows to accurately control the wavelengths of the instability induced in the filament. Due to the slowed-down dynamics arising from the lower interfacial tension, capillary thinning can now be investigated in higher detail: results reveal clear transitions between different thinning regimes. In particular, we experimentally highlight a pronounced presence of the inertial-viscous regime, possibly followed by a final two-fluids viscous regime. Contrary to previous observations, the similarity prefactor, as well as the transition radii, are found to be a function of the viscosity ratio in all regimes. This dependence is compared with results from linear stability analysis considering the actual imposed wavelength.

## Symposium SG Solids, Glasses, and Composites

Organizers: Xiaolong Yin and Jonathan Stickel

Wednesday 9:50 Aspen

SG5

**Fluidization and yielding of soft glassy solids**Vishwas V. Vasisht<sup>1</sup>, Gabrielle Roberts<sup>2</sup>, and Emanuela Del Gado<sup>3</sup><sup>1</sup>University Grenoble Alpes, Grenoble, France; <sup>2</sup>Yale, New Haven CT, CT, United States; <sup>3</sup>Georgetown University, Washington, DC, United States

We investigate the yielding and fluidization of soft solids by means of 3D computer simulations of a model non-Brownian jammed suspension. Consistent with previous results, we find that a significant shear banding can persist even in an apparently steady-state flow, when the deformation is imposed at sufficiently low rate. More importantly and at odd with general understanding, we provide evidence that, in such conditions, the flow inhomogeneities are not simply controlled by the deformation rate. Our analysis reveals in fact that the stresses accumulated upon yielding and at the origin of the shear banding relax on a timescale that is not just set by  $1/\dot{\gamma}$  but rather increases as  $1/\dot{\gamma}^\alpha$  with  $\gamma > 1$ . The exponent  $\alpha$  dramatically depends on the sample history and in particular on the local energy minima closest to its initial jammed state. While supporting recent experimental findings, our results provide novel insight indicating that frozen-in stresses in the initially solid state select the relevant sub-portion of the energy landscape and hence the pathways available to relaxation under shear.

Wednesday 10:15 Aspen

SG6

**Elasto-plastic models for soft glasses: The role of load transfer mechanism**Botond Tyukodi<sup>1</sup>, Damien Vandembroucq<sup>2</sup>, and Craig E. Maloney<sup>1</sup><sup>1</sup>Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States; <sup>2</sup>PMMH, ESPCI, Paris, France

Visco-plastic flow in amorphous solids (metallic/polymeric glasses, dense suspensions, emulsions/pastes/foams, granular materials) is governed by local plastic rearrangements of atoms/particles/droplets/bubbles. When these materials are driven in shear at vanishing rate near their yield stress, the stress relaxation proceeds via avalanches of local shear events with a broad spectrum of stress relaxation and duration. Lin et. al. [1] have proposed a relation between the rheological response and avalanche spectrum. In this work, we present results on various types of meso-scale stochastic elasto-plastic models for amorphous plasticity with varying microscopic models for time dependent load transfer. We discuss how the details of the time-dependent load transfer model (how viscous stresses from the suspending fluid are incorporated, whether inertia is considered, whether local yielding is immediate or delayed) affect the scaling parameters for the avalanche size spectrum, the avalanche size-duration relation, and the associated rheological response and flow curves.

[1] Lin, J., Lerner, E., Rosso, A., & Wyart, M. Scaling description of the yielding transition in soft amorphous solids at zero temperature. PNAS 2014.

Wednesday 11:05 Aspen

SG8

**Rheology in hydrate formation at atmospheric pressure**Paulo H. de Lima Silva, Mônica F. Naccache, and Paulo R. de Souza Mendes*Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22451900, Brazil*

One of the big issues of the oil industry is the blockage of pipeline due to hydrate formation. Hydrates of natural gas are formed by the association of water and light hydrocarbon molecules in a given organized structure, in conditions of high pressure and low temperature. The hydrates are crystalline solids that resemble ice. Depending on the amount of hydrates formed, the pipeline may become fully blocked. Since the cost to remove hydrates is very high, an alternative commonly employed is to use anti-agglomerants to operate the pipeline with hydrate slurries. Therefore, it is important to know the rheology of these hydrate slurries, in order to better understand and optimize the flow throughout the pipelines. We study the rheology of hydrate slurries, formed at atmospheric pressure in a mixture of water and tetrahydrofuran (C<sub>4</sub>H<sub>8</sub>O, hereinafter THF). THF form hydrates at atmospheric pressures, even at temperatures above 0 °C. Rheological tests are carried out for different fluid compositions. Transient and steady state results are obtained, showing that the rheology is strongly affected by agglomeration and breakdown of hydrate crystals that happen simultaneously, as hydrate is forming.?

Wednesday 11:30 Aspen

SG9

**Measurements and modeling of the viscosity of gas hydrate slurries formed from model water-in-oil and oil-in-water emulsions**Ahmad A. A. Majid<sup>1</sup>, Carolyn A. Koh<sup>1</sup>, and David T. Wu<sup>2</sup><sup>1</sup>*Chemical & Biological Engineering, Colorado School of Mines, Golden, CO, United States;* <sup>2</sup>*Department of Chemistry, Colorado School of Mines, Golden, CO, United States*

Gas hydrates are crystalline structures that contain small gas molecules such as methane, ethane and propane. These gas molecules are trapped inside hydrogen bonded water cages. Gas hydrates form at high pressure and low temperature and thus could form and plug oil and gas flowlines. This is a major concern in the oil and gas industry since it can be costly and a safety concern to remove these hydrate plugs. The traditional method of preventing flowline plugging from hydrates is complete avoidance, which is uneconomical for maturing fields. A relatively new strategy, called hydrate management, allows hydrates to form but manages them to prevent hydrate plugging. An important parameter that is needed in a hydrate management strategy is the viscosity profile of gas hydrate slurries at various conditions. In this work, in situ viscosity profiles of gas hydrate slurries were measured using a high pressure rheometer. Viscosity was measured using a four-blade vane impeller. Model emulsions consisting of a mixture of mineral oil 350T and surfactants (Span 80 and AOT) were used in this investigation. Tests were conducted at constant pressure and temperature (1500 psig and 1 °C). The water content was varied from 10 to 80 vol.% water cut. Additionally, ramping tests where the shear rate of the system was changed in a cycle were conducted to evaluate hydrate agglomeration. Results of this investigation showed that the relative viscosity of a hydrate slurry increases with increasing water content until an inversion of the emulsion occurred. After the emulsion changed from oil continuous to water continuous, the relative viscosity decreases with increasing water content. The ramping tests conducted showed that for oil continuous emulsion systems, agglomeration of hydrate particles occurred at high water cut (above 25 vol.%) and low shear rates (= 800 s<sup>-1</sup>). With these results, an initial model to predict the relative viscosity of a hydrate slurry at various hydrate concentrations was developed.

## Wednesday Afternoon

### Symposium BB Biomaterials and Biological Systems

Organizers: Keith Neeves and Kelly Schultz

Wednesday 1:30 Crystal A

BB6

#### **Mechanical characterization of living tissues: the Live Cell Monolayer Rheometer (LCMR)**

Gerald G. Fuller, Maria C. Merola, and Juho Pokki

*Chemical Engineering, Stanford University, Stanford, CA 94305, United States*

During the last decades several techniques have been developed to investigate mechanical properties of living tissues. At the cellular level, the experimental methods currently used for measuring mechanical properties include atomic force microscopy, magnetic twisting and pulling cytometry, micropipette aspiration, optical particle trapping and optical tweezers, the two micro-plates method, and traction force microscopy. While they present a great interest, however, for a better understanding of the cell as a physical system, multiple cell approaches must be considered.

In order to overcome the challenges with the biological variation between individual cells, new technologies are thus necessary.

In this work, we present rheological measurements using a purpose-built Live Cell Monolayer Rheometer (LCMR) that can characterize averaged cell mechanics or averaged cell adhesion. The LCMR enables the investigation of biologically active layers: controlled amounts of live cells with or without artificial materials (e.g., contact lenses), and in presence of inflammation, which is known to cause endothelial cell membrane stiffening, due to cytoskeletal rearrangement.

The LCMR is used in this study to measure: i) the adhesion of corneal epithelial cells with contact lenses and ii) the role of inflammation on the endothelial cell membrane stiffening. To simulate physiological conditions, the cell monolayer is deformed tangentially during experiments. Time-dependent step-strain tests are used to determine the mechanical relaxation of the cell layers.

Wednesday 1:55 Crystal A

BB7

#### **Determining the role of tissue inhibitors of metalloproteinases in matrix remodeling during 3D human mesenchymal stem cells motility in cell-degradable hydrogel**

Maryam Daviran, Sarah M. Longwill, and Kelly M. Schultz

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

Cells actively reengineer and remodel their microenvironment using chemical degradation from cell-secreted enzymes and cellular traction. Specifically, during wound healing human mesenchymal stem cells (hMSCs) migrate from their native tissue to the injury site. A process partially regulated by cell-secreted enzymes. But, little is known about the interplay between the material and the cell during these processes, which has important implications biomaterials design to promote wound healing. Here, we encapsulate hMSCs in peptide-functionalized poly(ethylene glycol) (PEG) hydrogels to characterize cellular remodeling during migration. This hydrogel consists of 4-arm PEG end functionalized with norbornene cross-linked with a matrix metalloproteinase (MMP) degradable peptide. Dynamic cell-mediated scaffold degradation is measured using multiple particle tracking (MPT) microrheology. MPT measures the Brownian motion of fluorescent particles embedded in the hydrogel. Measurements show that prior to motility there is no scaffold degradation directly under the hMSC, allowing the cell to spread and attach. The greatest degradation occurs 160  $\mu\text{m}$  from the cell center, at the end of our measurable window. We hypothesize that hMSCs are secreting a second set of enzymes, tissue inhibitors of metalloproteinases (TIMPs). TIMPs inhibit the activity of the MMPs and, therefore, scaffold degradation. We determine the role of TIMPs by neutralizing them. Four TIMPs have been identified and hMSCs secrete only TIMP-1 and TIMP-2. By inhibiting both TIMPs, hMSCs reverse the degradation profile resulting in a reaction-diffusion gradient; where the greatest degradation is closest to the cells. TIMP inhibition results in upregulation of MMPs that aggressively degrade the matrix. Due to this, cells do not have enough time to spread and attach to the network and instead migrate to stiffer regions. This motility can be harnessed to enhance hMSC delivery to injuries during the wound healing process.

Wednesday 2:20 Crystal A

BB8

#### **The rheology of type II diabetes – transport of insulin granules in pancreatic beta cells**

Adam S. Burbidge<sup>1</sup>, El-Hadji M. Dioum<sup>2</sup>, and Fotis Christakopoulos<sup>2</sup>

<sup>1</sup>*Physics and Processing, Nestlé Research Center, Vers-chez-Les Blanc, Vaud 1000 L 26, Switzerland;* <sup>2</sup>*Nestlé Institute of Health Sciences, Ecublens, Vaud 1015, Switzerland*

Type II diabetes is one of the most important non-communicable diseases (NCDs) and is an epidemic resulting in staggering human and economic costs. Epidemiology suggests strong links between diet, exercise and disease prevalence, but in itself it does not address the question of mechanistic causality. One potential bottom up mechanism of type II progression is via amyloid plaque driven pancreatic beta cell death. In this case, glucose

supply kinetics and subsequent insulin transcription, granule formation and trafficking are key processes controlling the risk of amyloid nucleation and growth. We explore the possibilities for particle tracking in live, in-vitro beta cells and discuss potential issues related to cell motion on comparable timescales to the cytoplasm relaxation. Furthermore we derive measures of the apparent cell matrix microrheology via classical generalised Stokes-Einstein equations. If time permits, the links between dynamical remodeling of the cell's actin/tubulin network in the cell will also be discussed.

Wednesday 2:45 Crystal A

BB9

### **Rheology reveals pro-metastatic lung stiffening following exposure to tumor-derived microparticles**

Tamar Barenholz-Cohen<sup>1</sup>, Yulia Merkher<sup>1</sup>, Dvir Shechter<sup>2</sup>, Yuval Shaked<sup>2</sup>, and Daphne Weihs<sup>1</sup>

<sup>1</sup>*Biomedical Engineering, Technion-Israel Institute of Technology, Haifa 3200003, Israel;* <sup>2</sup>*Medicine, Technion-Israel Institute of Technology, Haifa, Israel*

The mechanics of the tumor microenvironment greatly affects the tumor growth rate, its invasive capacity, and the survival of tumor cells following treatment. Following chemotherapy, tumor cells respond by shedding increased numbers of tumor-derived microparticles (TMPs), i.e. 0.1-1 $\mu$ m extracellular vesicles. These TMPs have been shown to support tumor growth, for example by contributing to a rapid mobilization of bone marrow derived proangiogenic cells (BMDCs) towards the treated tumor site and likely also to potential metastatic sites. The BMDCs, with other local cells, are able to modify the microenvironment, making it more favorable to tumor cell seeding. However, the physical and mechanobiological changes in the pre-metastatic sites which support tumor cell seeding have not been evaluated.

Here, we have evaluated the effects of TMPs shed from paclitaxel chemotherapy-treated breast cancer cells on their metastatic capacity towards the lungs and correlated with the lung rheology. We show that TMPs from invasive cells exposed to chemotherapy, increase the metastatic capacity of single cells making them more migratory and invasive. As a result, when such TMPs were injected into mice, the metastatic burden in the lungs increased, as compared to TMPs from control cells. To evaluate the rheology of the lung tissue in this context, mice injected with TMPs from control cells or cells exposed to paclitaxel, and the rheology of the entire lungs and lung slices was evaluated using a shear rheometer. We observe that the lungs are viscoelastic, and lung-slice rheology was sensitive to changes in the lung mechanics, revealing local stiffening in different conditions. These results further support the understanding how chemotherapy may induce a survival-driven response in tumors that may lead to tumor spreading.

Wednesday 3:45 Crystal A

BB10

### **Shear-dependent microgel processing for efficient encapsulation of functional nanoparticles**

Robert K. Prud'homme<sup>1</sup> and Brian K. Wilson<sup>2</sup>

<sup>1</sup>*Dept. Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States;* <sup>2</sup>*Princeton University, Princeton, NJ 08544, United States*

Sustained release depot delivery reduces dosing frequency and increases patient compliance. Poly(ethylene glycol) (PEG) based hydrogel microparticles are an attractive vehicle for this application due to their biocompatibility and tunable mechanical properties. We report on a water-in-oil shear emulsion process to produce microparticles of uniform size where the size distribution is controlled by the shear emulsification processing parameters and not the internal aqueous phase composition. Shear rates from 1000 s<sup>-1</sup> to 2500 s<sup>-1</sup> produce particle diameters between 180  $\mu$ m and 40  $\mu$ m. A pulsed shear history leads to a narrower size distribution of emulsion drops. Nanoparticles added to the internal aqueous phase produce composite hydrogel microparticles where the PEG gel encapsulates nanoparticles in the microparticle matrix. Fluorescent dye loaded nanoparticles are used to show both the encapsulation of nanoparticles in the microparticle matrix and the co-loading of multiple nanoparticles in one microparticle. This work highlights the ability to prepare microparticles of flexible composition and physical properties using a single PEG hydrogel chemistry and processing technique. The delivery of these microgel particles to the lungs was demonstrated and the optimal particle size is shown, as well as the clearance rates from the lungs as the gel degrades.

Wednesday 4:10 Crystal A

BB11

### **Mechanistic action of weak acid drugs on biofilms**

Binu Kundukad<sup>1</sup>, Megan Schussman<sup>2</sup>, Kaiyuan Yang<sup>3</sup>, Thomas Seviour<sup>4</sup>, Liang Yang<sup>4</sup>, Scott Rice<sup>4</sup>, Kjelleberg Staffan<sup>4</sup>, and Patrick S. Doyle<sup>5</sup>

<sup>1</sup>*Biosystems and Micromechanics, Singapore MIT Alliance for Research and Technology, Singapore, Singapore;* <sup>2</sup>*Massachusetts Institute of Technology, Cambridge, MA, United States;* <sup>3</sup>*National University of Singapore, Singapore, Singapore;* <sup>4</sup>*Nanyang Technological University, Singapore, Singapore;* <sup>5</sup>*Massachusetts Institute of Technology, Cambridge, MA, United States*

Selective permeability of a biofilm matrix to some drugs has resulted in the development of drug tolerant bacteria. Here we studied the efficacy of a weak organic acid drug, N-acetyl-L-cysteine (NAC), on the eradication of biofilms formed by the mucoid strain of *Pseudomonas aeruginosa* and investigated the commonality of this drug with that of acetic acid. We showed that NAC and acetic acid at pH < pKa can penetrate the matrix and eventually kill 100% of the bacteria embedded in the biofilm. Once the bacteria are killed, the microcolonies swell in size and passively shed bacteria, suggesting that the bacteria act as crosslinkers within the extracellular matrix. Despite shedding of the bacteria, the remnant matrix remains intact and behaves as a pH-responsive hydrogel. These studies not only have implications for drug design but also offer a route to generate robust soft matter materials.

Wednesday 4:35 Crystal A

BB12

**Flagellar thrust and motor torques in two-dimensional bacterial motility**Pushkar Lele*Chemical Engineering, Texas A&M University, College Station, TX, United States*

Planktonic cells of *Escherichia coli* swim with the aid of multiple flagellar filaments that switch repeatedly between clockwise (CW) and counter-clockwise (CCW) directions of rotation. When grown on semi-soft agar substrates, cells undergo subtle morphological changes and transition into swarmer cells that exhibit 2D surface motility. Mechanical forces arising from contact with the surface likely trigger this transition. The cell lengths and the number of filaments in swarmer cells are twice those found in planktonic cells. We are interested in determining the interplay between cell lengths, filament forms, the direction of flagellar rotation and hydrodynamic interactions with the substrates during swarming. We will present our latest findings that suggest that mutants that swim exclusively CCW fail to swarm. Motility can be rescued by simply wetting the agar surface, in agreement with earlier reports. However, swarming in mutants that swim exclusively CW cannot be rescued. To determine the underlying reason for this difference, we measured the torque generated by individual flagellar motors in the CCW and CW mutants. Results suggested anisotropic torque generation in the two directions, consistent with our previous observations with *C. crescentus* motors. However the torque-anisotropy by itself was found to be inadequate in explaining the inhibition of swarming in the CW-mutants. Fluorescent-labeling experiments were carried out to determine the predominant polymorphic flagellar forms in the two types of mutants. We will discuss the insights revealed by the fluorescence-based experiments and the resulting effects on the thrust developed by each cell. The implications of these phenotypes in swarm-initiation will also be discussed.

Wednesday 5:00 Crystal A

BB13

**Controlling the properties of planar large area lipid bilayers**Jan Vermant, Peter Beltramo, and Laura Scheidegger*Materials, ETH Zürich, Zürich, Switzerland*

Lipid bilayers constitute an important aspect of the cell. Most commonly the bending rigidity of the membrane is investigated. In the present work, we report on the development of methods to study large area bilayers, in which the composition, tension and temperature can be controlled. The thickness of the bilayers is measured using optical or dielectric methods, and the composition is controlled using the surrounding phases. Effects of cholesterol and block-copolymers on the membrane compressibility are studied.

## Symposium SM Polymer Solutions and Melts

Organizers: Suraj Deshmukh and Reza Foudazi

Wednesday 1:30 Crystal B

SM32

**Characterization of commercial polybutadiene and the effects of microstructure on processing**Jon A. Bielby<sup>1</sup> and Saeid Kheirandish<sup>2</sup><sup>1</sup>*Tire and Specialty Rubbers Business Unit, ARLANXEO Inc., London, Canada;* <sup>2</sup>*Tire & Specialty Rubbers Business Unit, ARLANXEO Deutschland GmbH, Dormagen, Germany*

The need for improved dynamic performance in tires has pushed the design of new polymers with exact structures. Awareness of the differences in rheological properties of polybutadiene is crucial as they can have a significant impact on industrial processing as well as the intended application. The rheology was studied of various commercially available neodymium, lithium and cobalt catalyzed polybutadiene elastomers. The linear and extensional rheological properties were determined, as well as the rheological properties of the polymers after reinforcement with carbon black.

Long-chain branching of the polymers was qualitatively determined by the shape of their van Gurp-Palmen plot, zero shear viscosity and extensional strain hardening.

Increases in long-chain branching resulted in an improvement in carbon black dispersion as determined by rheology and atomic force microscopy.

Wednesday 1:55 Crystal B

SM33

**Rheological properties of plasticized polyacrylonitrile copolymers**Jianger Yu<sup>1</sup>, Gregory C. Miller<sup>2</sup>, Donald G. Baird<sup>1</sup>, and Judy S. Riffle<sup>2</sup><sup>1</sup>*Chemical Engineering, Virginia Tech, Blacksburg, VA 24060, United States;* <sup>2</sup>*Macromolecules Innovation Institute, Virginia Tech, Blacksburg, VA, United States*

Polyacrylonitrile (PAN) fiber is currently one of the most important synthetic fibers and approximately 90% of carbon fiber is made from PAN fibers as a precursor. PAN-based carbon fiber plays a significant role in many modern industries, such as the aerospace and automobile industries, because it has low density, high thermal stability, high tensile strength and high tensile modulus. However, due to the limitations of the current PAN spinning processes, the cost is relatively high and the relevant solvents are environmental unfriendly. The development of PAN melt spinning has the potential to significantly reduce the cost of carbon fiber. The melting point of PAN polymer is as high as 320C, but PAN starts to suffer a

cyclization reaction around 180C. This degradation reaction is undesirable in the spinning process (but desirable in the carbon fiber conversion process). So the major challenge of PAN melt spinning is to decrease the melting point of PAN to avoid degradation reaction during the melt spinning process. Coxe first discovered that by adding water into PAN as plasticizers, the melting point of PAN could be significantly reduced to below 200C, which made the PAN melt spinning technically feasible. Later, further research had been performed and more potential plasticizers has been discovered. BASF claimed in their patent that a mixture of water and acetonitrile (AC) could be used as plasticizer for the PAN melt spinning. However, due to the economic consideration, the melt spinning PAN process with has not been commercialized yet. Several potential plasticizers, including water and acetonitrile, are considered in this study. The relevant rheological behavior of PAN with those plasticizers is reported. The steady-shear rheological data shows the presence of acetonitrile can further decrease the processing temperature of PAN melt spinning. The time-dependent rheological stability data show that PAN could hold its viscosity stable without significant degradation for a sufficient period of time below 180C.

Wednesday 2:20 Crystal B

SM34

### **Glass transition temperature and chain entanglement in conjugated polymers**

Renxuan Xie<sup>1</sup>, Enrique D. Gomez<sup>1</sup>, and Ralph H. Colby<sup>2</sup>

<sup>1</sup>Chemical Engineering, Penn State University, University Park, PA 16802, United States; <sup>2</sup>Materials Science and Engineering, Penn State University, University Park, PA 16802, United States

Linear viscoelastic methods are used to probe the glass transition temperatures, plateau modulus and entanglement molecular weight of linear semiflexible conjugated polymers in their bulk state. Various molecular weights of regioregular poly(3-hexylthiophene-2,5-diyl) (RR P3HT), regiorandom (RRa) P3HT, and poly((9,9-bis(2-octyl)-fluorene-2,7-diyl)-alt-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5'-diyl) (PFTBT) are studied from below their lowest glass transition to above any melting temperature. RR and RRa P3HT both show two glass transitions: At very low temperature of order -100 oC, there is a T<sub>g</sub> associated with the alkyl side chains and there is a second backbone T<sub>g</sub> between 0 oC and 20 oC, depending on molecular weight in the usual way. In contrast PFTBT only exhibits one T<sub>g</sub> between 130 oC and 144 oC, depending on molecular weight. Entanglement of semicrystalline polymers is challenging and the various methods utilized will be discussed and compared.

Wednesday 2:45 Crystal B

SM35

### **Anomalous temperature dependence of rheological properties of star telechelic PDLA ionomer melt**

Amruta Kulkarni<sup>1</sup>, Ashish K. Lele<sup>1</sup>, Pragati Sharma<sup>2</sup>, and Suman Chakrabarty<sup>3</sup>

<sup>1</sup>Polymer Science & Engineering Division, CSIR - National Chemical Laboratory, Pune, Maharashtra 411008, India; <sup>2</sup>Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune 411008, India; <sup>3</sup>Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, India

Viscoelastic material functions of polymer melts typically decrease with increasing temperature due to enhancement in chain mobility. The temperature dependence of relaxation time can be described by the WLF equation or the Arrhenius equation. This enables time-temperature superposition (TTS) of viscoelastic functions onto mastercurves. While ionomer melts are known to show higher viscoelastic moduli and long relaxation time compared to the base non-ionic polymer, there are varied results in the literature on temperature dependence of viscoelastic properties. For instance, while TTS is known to work for some ionomers (e.g., Shohamy and Eisenberg, J. Appl. Polym. Sci., 1976) except perhaps in an intermediate range of frequency (Ruymbeke et al, Macromolecules, 2010), the TTS principle is reported to break down for other ionomers, especially those containing high ionic concentration (e.g., Eisenberg and Navratil, Polym. Lett., 1972; Weiss and Zao, J. Rheol., 2009). Temperature ramp experiments for ionomer melts show linear increase of G' with temperature that accompanied with a peak in G'' indicating an additional relaxation phenomenon caused most likely by dissolution of nano-sized dipolar clusters that hold matrix chains into a transient network (Weiss et al, Macromolecules, 1991). We report here unusual temperature dependence of viscoelastic properties of an unentangled star telechelic ionomer of poly(D, L- lactide) melt. We show that the steady shear viscosity and dynamic moduli of this ionomer increase non-linearly with temperature over a wide range of temperatures. However, beyond a certain temperature the viscoelastic properties start decreasing rapidly with further increase in temperature. We also show using atomistic MD simulations that this unusual rheology of the star telechelic PDLA ionomer may be attributed to increased cluster formation and strengthening of the transient network of matrix chains with increasing temperature.

Wednesday 3:45 Crystal B

SM36

### **Wide angle X-ray study of nematic interactions in a bi-disperse polystyrene melt**

Anine Borger<sup>1</sup>, Kell Mortensen<sup>1</sup>, Jacob Kirkensgaard<sup>1</sup>, Kristoffer Almdal<sup>2</sup>, Qian Huang<sup>3</sup>, and Ole Hassager<sup>3</sup>

<sup>1</sup>Niels Bohr Institute, University of Copenhagen, Copenhagen 2100 Kbh O, Denmark; <sup>2</sup>Department of Micro- and Nanotechnology, Technical University of Denmark, Kgs. Lyngby 2800, Denmark; <sup>3</sup>Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

Commercial polymer materials are polydisperse. This study investigates the effects of such dispersity by probing how the presence of longer chains affects the response to deformation of a short-chain model system, i.e. a bi-disperse melt of well-defined long and short chains compared to a monodisperse model system of short chains. The experiment is carried out in two steps: The first step is to stretch the sample and allow it to relax while measuring its response using a Filament Stretch Rheometer, which both makes the deformation and measures the rheological parameters. After the response measurement, the sample is quenched below its glass-transition temperature, with the aim to preserve the molecular conformation for the further studies. The second step is to measure the molecular alignment of the polymer molecules in the quenched samples using Small-Angle Neutron Scattering (SANS) for the overall coil conformation, and Wide-Angle X-ray Scattering (WAXS) to probe the structure on the length scale of the monomers. The previous SANS study showed that in the presence of the long chains, the short chains are stretched ~50

% more due to the nematic field from the long chains. The current WAXS study shows that the correlations on the scale of the monomers are strongly enhanced in the bidisperse melt, which supports the conclusion of a nematic field from the long chains.

Wednesday 4:10 Crystal B

SM37

### **SAXS/WAXS studies of flow-induced crystallization of LDPE under uniaxial extensional flow**

Mu Sung Kweon and Wesley R. Burghardt

*Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, United States*

We report flow-induced crystallization studies of low density polyethylene under uniaxial extensional flow. Flow was applied using an SER housed in a custom-built oven designed to facilitate *in situ* synchrotron x-ray experiments. Samples loaded onto the fixture were first heated well into the melt, and then cooled to a selected crystallization temperature under which negligible quiescent crystallization occurred on reasonable time scales. Two types of flow protocols were employed: short-term and continuous. Under short-term flow, a short burst of flow was applied at temperatures where samples crystallized isothermally *after* the application of flow under varied extension rates and Hencky strains. Under continuous flow, samples crystallized isothermally at desired temperatures *during* the application of flow under varied extension rates. Extent of crystallization, orientation of crystallites, and extensional viscosity were monitored using simultaneous small- and wide-angle x-ray scattering (SAXS and WAXS, respectively) and torque measurements. WAXS peaks generally indicate strong alignment of unit cells along the flow direction in both short-term and continuous flows. SAXS patterns under short term flow span a wide range of morphologies that show signs of evolution in lamellae ordering; those under continuous flow show distinct features of shish-kebab crystalline structure.

Wednesday 4:35 Crystal B

SM38

### **A new approach to polymer rheology via spatially-dependent structural response functions**

Yangyang Wang<sup>1</sup>, Zhe Wang<sup>2</sup>, Christopher Lam<sup>1</sup>, and Wei-Ren Chen<sup>2</sup>

<sup>1</sup>*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States;* <sup>2</sup>*Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

A central problem in polymer rheology is to understand how the chain conformation is transformed by the macroscopic deformation. The rheo-small-angle-neutron-scattering (rheo-SANS) technique has long held the promise of offering a molecular perspective on this issue. However, the existing investigations have primarily focused on the analysis of the radius of gyration tensor, which renders only a coarse-grained description of the polymer shape on the whole chain level. Here we describe a new framework for molecular rheology of polymeric liquids, by combining and extending several key concepts in the literature, and drawing upon our recent development of the spherical harmonic expansion technique. We show how several spatially-dependent structural response functions, such as the anisotropic single-chain structure factor and pair distribution function, can serve a bridge between rheo-SANS experiments on the one hand and theoretical studies on the other, providing a convenient ground for molecular rheology of polymers. To demonstrate the power of this idea, we will discuss in this talk our recent rheo-SANS experiments as well as computational investigations on entangled and unentangled polymer melts.

Wednesday 5:00 Crystal B

SM39

### **A Rheo-SANS investigation of a star-linear polymer blend**

Nino Ruocco, Luke T. Andriano, and Gary Leal

*Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106, United States*

We investigate the dynamic mechanisms in a blend composed of a four-arm star polymer and a linear matrix of the same polymer in the presence of a simple shear flow. The molecular weight of the linear matrix (MW= 89kg/mol) is approximately the same as the span (MW= 88kg/mol) of the star polymer (overall MW= 176kg/mol). Our main focus is to obtain an understanding of the non-linear relaxation processes of the star polymer. We coupled a mechanical device (i.e. Couette cell geometry device) with a small-angle neutron scattering (SANS) instrument in order to access the chain configuration of the star polymer (probe) dispersed in the linear deuterated matrix chain. To the best of our knowledge, the in-situ rheo-SANS method is the most successful approach to connecting macroscopic rheological properties with the structure of polymeric materials at the molecular level. Indeed, we show how in a simple rheological treatment that the average macroscopic rheological properties of the bimodal polymer blend are mainly determined by the majority component of the system and properties of the minority component are not measurable in a rheological characterization. In steady-state flow SANS experiments, the structure factor provides a variety of information in how the chains are oriented and aligned and is related to the minority component (star polymer), which acts as a natural probe chain. We have interpreted the scattering data by using the well-established neutron scattering version of the GLaMM model for entangled polymer melts, but specialized to eliminate relaxation of the star arms by reptation. We have also observed a synergic contribution of the two components towards the presence of nonlinear effects such as convective constraint release (CCR).

## Symposium SC Suspensions, Colloids and Granular Systems

Organizers: Cari Dutcher and Lilian Hsiao

Wednesday 1:30 Crystal C

SC27

### **Does the Huggins coefficient describe the thermodynamics & rheology of concentrated monoclonal antibody formulations?**

Jai A. Pathak<sup>1</sup>, Sean Nugent<sup>1</sup>, Michael Bender<sup>1</sup>, Mahlet Woldeyes<sup>2</sup>, Daniel Corbett<sup>3</sup>, Robin Curtis<sup>3</sup>, Eric M. Furst<sup>2</sup>, Christopher J. Roberts<sup>2</sup>, and Jack F. Douglas<sup>4</sup>

<sup>1</sup>Vaccine Production Program, NIAID NIH, Gaithersburg, MD 20878, United States; <sup>2</sup>Dept. of Chemical & Biomolecular Engineering, Univ. of Delaware, Newark, DE, United States; <sup>3</sup>Chemical Engineering & Analytical Science, Univ. of Manchester, Manchester, United Kingdom; <sup>4</sup>Materials Science & Engineering Division, NIST, Gaithersburg, MD, United States

Monoclonal Antibodies (mAbs) are prolifically used to vaccinate against various infectious diseases and as therapeutics for numerous clinical indications. Shear viscosity of mAb formulations is both a constituent engineering input for delivery device design, and a sensitive metric of protein aggregation at (supra-)molecular lengthscales, e.g. reversible self-association, and sub-visible particle formation. Therefore, mAb formulation development requires facile high-throughput measurement and prediction/ranking of formulation shear viscosity. We first show in this talk that the leading virial diffusion interaction parameter,  $k_D$ , is unsurprisingly a poor predictor of concentrated formulation viscosity, since it ignores hydrodynamic interactions in concentrated systems. In the quest for appropriate holistic descriptors of concentrated mAb solution rheology and thermodynamics, we test the seminal theory of Russel, who derived a prediction for the Huggins coefficient  $k_H$  of sticky spheres interacting with a short-range attraction and long-range repulsion in terms of the osmotic second virial coefficient,  $B_{22}$  (normalized by its hard sphere value). While globular proteins and monoclonal antibodies can be readily mapped as sticky spheres due to the presence of charged surface patches, surprisingly this elegant theory of Russel has not been interrogated in these systems. We are currently measuring  $k_H$  and  $B_{22}$  for various NIH Vaccine Research Center mAb molecules in different solution conditions. In this talk these data, and data on other molecules studied by this team, will be presented and their implications for Russel's model will be critically examined, along with that of the predictions of Kholodenko and Douglas, who derived a Generalized Stokes-Einstein relation for concentrated suspensions and proposed the sum rule:  $k_D = B_{22} - [\eta]$ ;  $[\eta]$  denotes intrinsic viscosity.

Wednesday 1:55 Crystal C

SC28

### **Predicting the time-dependent rheological behavior of irreversible materials: Cement and waxy crude oil examples**

Flavio H. Marchesini and Paulo R. de Souza Mendes

Department of Mechanical Engineering, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453 900, Brazil

Along the last decades a lot of effort has been put into investigating the reversible rheological behavior of thixotropic materials. However, few attempts have been made to describe the rheology of irreversible time-dependent materials. Thus, in this work, the time-dependent rheological behavior of materials undergoing an irreversible process is investigated. A recently proposed thixotropic elasto-viscoplastic model (de Souza Mendes, *Soft Matter*, 2011, 7, 2471-2483) is modified to account for irreversible effects, which are either due to chemical reactions or shear degradation. The model is employed in step-change flows in both shear rate and shear stress, and the predictions of the model are compared to experimental data available. Two different materials are analyzed, namely cement slurry and waxy crude oil. It is shown that the model successfully describes the experimental data obtained. The predictive capability of the model includes: non-monotonic flow curves, viscosity bifurcation, stress overshoots, effects of chemical reactions, and irreversible shear degradation.

Wednesday 2:20 Crystal C

SC29

### **Yield stress and structure recovery of flocculated micro and nanofibrillated cellulose (MNFC) suspensions**

Emily G. Facchine<sup>1</sup>, Koushik Ghosh<sup>2</sup>, Pruthesh Vargantwar<sup>2</sup>, Richard J. Spontak<sup>1</sup>, Orlando J. Rojas<sup>1</sup>, and Saad A. Khan<sup>1</sup>

<sup>1</sup>Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, United States; <sup>2</sup>Eastman, Kingsport, TN, United States

Aqueous suspensions of micro and nanofibrillated cellulose (MNFC) are known to exhibit gel-like behavior even at low concentrations. In this work, they were studied to determine their apparent yield stress and structure recovery behavior. Yield stress measurements were found to be highly susceptible to wall slip and shear banding, which can be mitigated somewhat by the use of serrated geometries. Yield stress values obtained by oscillatory and steady shear stress sweep were compared, and the effect of geometry on each method was evaluated. Experimental parameters such as the stress sweep frequency were found to have dramatic effects on the apparent yield behavior. Additionally, the microstructure recovery of the gel-like suspensions after breakdown was evaluated via oscillatory time sweeps under different conditions. These experiments demonstrated that the applied level of stress during structure breakdown has a pronounced effect on the extent of recovery of the gel structure, with a minimum recovery window observed at intermediate stress values in the range of the apparent yield stress. The observations are consistent with the presence of a network structure composed of interconnected flocs.

Wednesday 2:45 Crystal C

SC30

**The effect of carboxymethyl cellulose (CMC) on Large Amplitude Oscillatory Shear (LAOS) behavior of corn starch suspensions**Menglu Gao<sup>1</sup>, Rohollah Sadeghi<sup>1</sup>, Ozlem Duvarci<sup>2</sup>, and Jozef Kokini<sup>1</sup><sup>1</sup>Purdue University, West Lafayette, IN, United States; <sup>2</sup>Izmir Institute of Technology, Urla Izmir, Turkey

During different kinds of processing, food products are often subjected to large deformations, where LAOS offers a good understanding of the structural change of food materials during processing. The aim of this study is to investigate the change in LAOS behavior of a shear thickening fluid (cornstarch suspension) by adding CMC, which is a widely used polysaccharide gum in food industry which exhibit shear thinning behavior. This study includes determination of change in LAOS behavior of 50% wt. corn starch suspensions with different concentrations of CMC (0.3%, 0.5%, and 0.7% wt) to understand how they affect flow behavior of a suspension with high solid content. The rheological parameters ( $G'$ ,  $G''$ ,  $\tau^*$ ,  $\tau^*$ ,  $e_3/e_1$ , and  $v_3/v_1$ ) (Ewoldt, Hosoi, and McKinley, 2008) were evaluated for the samples at a strain in the range of 0.01-200%. Lissajous-Bowditch curves were utilized to evaluate the elastic component and viscous component of the strain separately, to provide a visualized and qualitative study of the transition of the material's viscoelasticity under increasing strain. All the samples we studied (50% wt cornstarch suspension + 0, 0.3%, 0.5%, and 0.7% CMC) showed predominately elastic behavior in small strain region, and predominately viscous behavior in large strain region. Cornstarch suspension without CMC showed strong nonlinearity, with yield stress which can be visualized from Lissajous-Bowditch plots, and the behavior is similar to a Bingham model. Cornstarch suspension with CMC addition, however, showed less nonlinearity, more viscous behavior, and much less dissipated energy in oscillation cycles in large strain, which can be described as closer to a modified Bingham model as the definition was ideal Hookean elastic behavior followed by ideal Newtonian flow (Rogers and Lettinga, 2012).

Wednesday 3:45 Crystal C

SC31

**Rheological properties of cellulose nanocrystal aqueous suspensions prepared via ultrasonication**Quentin Beuguel, Jason R Tavares, Pierre J. Carreau, and Marie-Claude Heuzey

Chemical Engineering, Polytechnique Montreal, Montreal H3C3A7, Canada

The structural and rheological properties of aqueous suspensions of spray-dried cellulose nanocrystals (CNCs) were investigated after various ultrasonication processes, in terms of both power (ranging from 10 W to 90 W) and energy (ranging from 2,500 to 10,000 joules per gram of CNC). The CNCs were obtained from sulfuric acid hydrolysis of wood pulp, leading to 3.4 sulfate half-ester groups per 100 bulk anhydroglucose units on the CNC surface. While a pH decrease was measured after ultrasonication, energy dispersive X-Ray spectroscopy (EDX) demonstrated that there was no desulfation following dialysis. Diffusion light scattering (DLS) measurements showed a decrease of the Z-average equivalent diameter of the particles, down to a limit of 75 nm, indicating agglomerate break-up. For an equivalent energy level, a higher ultrasonication power accelerated this size decrease. Accordingly, the viscosity of CNC suspensions in the dilute and semi-dilute regimes decreased with increasing ultrasonication power or energy. The relative viscosity variations of CNC aqueous suspensions as a function of concentration were fitted using the Fedors model. The strongest ultrasonication methods caused the increase of maximum packing concentration and the decrease of intrinsic viscosity. This rheological behavior could be the result of trapped water being released during agglomerate break-up, as well as the increased number of deprotonated sulfate half-ester groups available in the suspensions - consequently reducing the effective CNC concentration in the suspension and compressing the electrostatic double layer thickness surrounding the particles.

Wednesday 4:10 Crystal C

SC32

**Effects of shape on the rheology of polymer-grafted nanoparticles in solution**Daniele Parisi<sup>1</sup>, Dimitris Vlassopoulos<sup>1</sup>, Benoit Loppinet<sup>1</sup>, Chen-Yang Liu<sup>2</sup>, and Ying-Bo Ruan<sup>2</sup><sup>1</sup>FORTH-IESL, HERAKLION, Greece; <sup>2</sup>Institute of Chemistry Chinese Academy of Science, Beijing, China

The large majority of rheological investigations with soft colloids involve spherical particles. However, in several applications the particles are anisotropic. Here, we focus on polymer-grafted nanoparticles in solution and compare three soft systems with different core shape (spheres, cylinders and lamellas) but identical chemistry and molar mass of the graft, and very similar grafting density. These systems have different overlap fractions and spatial organization. Concentrated solutions at the same mass concentration have been investigated by means of dynamic light scattering and rheology in both linear and nonlinear regime. We find that shape affects substantially the relaxation time, yielding mechanism and residual stresses, which reflect different particles arrangement in solution. We compare against relevant data in the literature with hard spheres, ellipsoids and other soft spheres, and attempt at extracting a generic phenomenological picture of rheology vs. shape and concentration. These results show that advantages of shape in tailoring the flow properties of dense soft colloids and provides guidelines for understanding its role in the mechanisms of viscoelasticity and yielding.

Wednesday 4:35 Crystal C

SC33

**The microstructural origin of the rheo-dielectric behavior of carbon black suspensions in propylene carbonate**Jeffrey J. Richards<sup>1</sup>, Julie B. Hipp<sup>2</sup>, John K. Riley<sup>1</sup>, Paul D. Butler<sup>1</sup>, and Norman J. Wagner<sup>2</sup><sup>1</sup>NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States;<sup>2</sup>Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

The lack of efficient and economical methods for large-scale energy storage has become a significant barrier to meeting the rising demand for integration of renewable energy sources into the electricity grid. Recently, energy storage technology has been advanced with the development of a high energy density semi-solid flow battery (SSFB). Rather than a traditional liquid electrolyte, SSFBs use a flowable slurry of lithium-based

active particles and network-forming conductive nanoparticles suspended in a liquid electrolyte. While these flowable electrodes contribute to improved electrical properties, the addition of particles to the suspension leads to adverse rheological properties such as high viscosities and a yield stress that cause energy losses due to pumping. By understanding the relationship between the electrical and rheological properties of flowable electrodes, suspensions with more favorable properties can be designed. In this work, the microstructural origin of the rheo-dielectric properties of the network-forming conductive carbon black nanoparticles found in SSFBs is studied. The structural hierarchies of two commercially available conductive carbon blacks, Vulcan XC-72 and KetjenBlack EC-600JD, have been studied in propylene carbonate using electron microscopy, dynamic light scattering, and small angle neutron scattering (SANS). The onset of mechanical percolation in these suspensions has been measured using small amplitude oscillatory shear measurements as a function of volume fraction. While the mechanical percolation threshold is often associated with the onset of electrical percolation, we have found that these carbon black suspensions electrically percolate at volume fractions far below the mechanical percolation threshold. This percolation is maintained even under shear. Using a combination of Dielectric RheoSANS, RheoUSANS, and steady shear rheology, we identify structural transitions in the suspensions under shear flow and relate them to the macroscopic electrical and rheological response.

Wednesday 5:00 Crystal C

SC34

### **The impact of colloidal suspension rheology on battery performance**

Samantha L. Morelly, Maureen H. Tang, and Nicolas J. Alvarez

*Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States*

Battery slurries are made through a complex mixing process that combines active material, conductive additive, polymer binder and solvent. The effect of the mixing process on battery performance is acknowledged, but not fully understood. In recent years, the rheology of battery slurries has become a characterization technique used when varying mixing processes. Slurry microstructure is argued to have a large impact on battery performance due to the persisting structure (particle dispersion) from the wet to the dry state. Before making the slurry, dry-mixing of conductive additive (carbon black) and active material is documented to impact viscoelastic behavior, e.g. change a colloidal gel to a viscoelastic fluid [1,2]. Dry-mixing is done to increase carbon on the surface of the micron-sized active material, with the intent of increasing the overall electronic conductivity of the electrode. The goal of this work is to decouple whether the initial electrode microstructure (particle dispersion), electronic conductivity, or a synergism of the two is responsible for increases in battery performance. By maintaining the total concentration of carbon, we generate electrode slurries with different degrees of free carbon, i.e. carbon that is available to form a volume spanning colloidal network (gel) and surface carbon. Our data suggests that at low carbon concentrations dry-mixing does not have a beneficial impact on battery performance.

References [1]W. Bauer, D. Noetzel, *Ceram. Int.* 40 (2014) 4591. [2]G.-W. Lee, J.H. Ryu, W. Han, K.H. Ahn, S.M. *Journal of Power Sources* 195 (2010) 6049-6054.

## **Symposium GS Gels and Self-Assembled Systems**

Organizers: Kendra Erk and Simon Rogers

Wednesday 1:30 Crestone A

GS19

### **Effect of normal stresses on the determination of the yield strength**

Roney L. Thompson<sup>1</sup>, Luiz R. Sica<sup>2</sup>, and Paulo R. de Souza Mendes<sup>2</sup>

<sup>1</sup>*Mechanical Engineering, COPPE-UFRJ, Rio de Janeiro, RJ, Brazil;* <sup>2</sup>*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, RJ 22451-900, Brazil*

It is usual practice to measure the yield strength in simple shear flow. In these measurements, the yield strength is identified as the maximum value of the shear stress below which no irreversible flow occurs. Then, the thus determined yield strength is used in conjunction with the von Mises criterion in any complex flow. The von Mises criterion compares the yield strength with the intensity of the deviatoric stress, i.e. the square root of the second invariant. It happens that for simple shear flow the intensity of the deviatoric stress is composed of both the shear stress and the normal stress differences, but the contribution of the latter is never considered in the experimental determination of the yield strength. In this research, we performed creep tests (in simple shear flow) for several viscoplastic materials, to determine the yield strength by measuring the limiting shear stress and the corresponding first normal stress difference. These results allowed us to assess the importance of the contribution of the normal stresses to the yield strength. It was observed that for some materials the normal stress contribution is much larger than the shear stress contribution.

Wednesday 1:55 Crestone A

GS20

### **Effect of yield stress during coating of microfibrinous cellulose**

James F. Gilchrist<sup>1</sup>, Thitiporn Kaewpetch<sup>1</sup>, Jane M. Boettcher<sup>2</sup>, Jack C. Boettcher<sup>2</sup>, Jie Song<sup>3</sup>, and Patrick T. Spicer<sup>3</sup>

<sup>1</sup>*Lehigh University, Bethlehem, PA, United States;* <sup>2</sup>*Naperville North High School, Bethlehem, PA, United States;* <sup>3</sup>*School of Chemical Engineering, University of New South Wales, Sydney, Australia*

Microfibrinous cellulose (MFC) is a renewable, edible, and biodegradable system that holds promise for development of sustainable, functional materials. MFC forms low viscosity, high yield stress fluids due to the interaction of their high aspect ratio attractive fibers. Viscosity and yield stress can be tuned through MFC concentration and addition of xanthan gum which serves to reduce the fiber-fiber affinity. Through various

deposition rates and fluid properties, the effect of yield stress on coating homogeneity and fiber alignment is explored. Using confocal laser scanning microscopy, the fiber alignment in the dried film is quantified. Flow alignment generally occurs for lower yield stress samples deposited under higher shear conditions. Other signatures of the microstructure that result during coating are explored.

Wednesday 2:20 Crestone A

GS21

### **Effect of counter anion sizes on polymer dynamics and morphologies for polymerized ionic liquids**

Atsushi Matsumoto<sup>1</sup>, Takeru Noda<sup>2</sup>, Ciprian Iacob<sup>3</sup>, Osamu Urakawa<sup>2</sup>, James Runt<sup>3</sup>, and Tadashi Inoue<sup>2</sup>

<sup>1</sup>*MicroBioNanofluidics Unit, Okinawa Institute of Science and Technology, Onna, Okinawa 904-0495, Japan;* <sup>2</sup>*Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan;* <sup>3</sup>*Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States*

Polymerized ionic liquids have been attracting significant attention in the last two decades because they potentially have properties of both polymers, such as high elasticity, and ionic liquids, such as high ionic conductivity. Polymerized ionic liquids are polymers having a structure of ionic liquids on their repeating units and can be chemically classified as a type of polyelectrolytes. In the current study, poly(1-butyl-3-vinylimidazolium)-based ionic liquids with bis(perfluoroalkylsulfonyl)imide-based counter anions having ionic sizes larger than those of polycations were synthesized to clarify the effect of relatively larger counter anions on their morphologies and viscoelastic properties. We previously found that they have amorphous structure and show linear viscoelasticities almost like those of polystyrene when ionic sizes of counter anions are smaller than those of polycations. However, once ionic sizes of counter anions exceed those of polycations, it has turned out that the segmental motion of polymer chains are highly restricted based on the results of linear viscoelastic measurements. This is presumably because larger counter ions cannot diffuse freely in polymeric media. Furthermore, structure observation by polarizing microscope revealed the existence of a thermally stable nematic-like mesophase in these polymerized ionic liquids. The formation of this mesophase structure was strongly affected by the preparation history. A phase transition from the isotropic to mesomorphic state was achieved only when external force was applied by hot press molding, and did not occur only by thermal treatment below the thermal decomposition temperature. This ordered structure could be stabilized by several factors, such as Coulomb forces and excluded volume effects caused by the incompatibility of fluoride atoms. In this presentation, the relationship between the mesomorphic structure and the viscoelastic behavior of some polymerized ionic liquids will be discussed.

Wednesday 2:45 Crestone A

GS22

### **Effect of platelet in a soft nanocomposite: Physical gelation and yielding**

Vijesh Tanna<sup>1</sup> and H. Henning Winter<sup>2</sup>

<sup>1</sup>*Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01002, United States;* <sup>2</sup>*Dept. of Chem. Eng. & Dept. of Polymer Sci. and Eng., University of Massachusetts Amherst, Amherst, MA 01003, United States*

The size of clay platelets in a nanocomposite plays a key role in their rheological response. To study this, we use a model system, an exfoliated polybutadiene/clay composite, which undergoes a liquid to solid transition associated with the exfoliation of clay. The internal connectivity of the system was found to reduce drastically with smaller sizes of the clay platelets. Sample preparation plays a critical role in these experimental findings. A carefully chosen sequence of steps was able to suspend clay particles in polybutadiene (PB), reduce their size by fluid grinding, and then exfoliate the reduced clay particles. Two polybutadienes were used, one regular polybutadiene (PB) and one end-functionalized polybutadiene (sPB). For size reduction via flow treatment, the clay particles were suspended in PB, which is a non-interacting liquid polybutadiene and allows size reduction without exfoliation/gelation. After size reduction, sPB was added to cause the clay to exfoliate so that the composite forms a physical gel. Large strain induces yielding (after sample deformation) caused irreversible change of the composite structure. For samples with small platelets, the yielding caused an irreversible solid to liquid transition. The rheological effects of platelet reduction and yielding will be shown for nanocomposites.

Wednesday 3:45 Crestone A

GS23

### **Embedding memories in colloidal gels through oscillatory shear**

Eric M. Schwen<sup>1</sup>, Meera Ramaswamy<sup>1</sup>, Chieh-Min Cheng<sup>2</sup>, Linda Jan<sup>2</sup>, and Itai Cohen<sup>1</sup>

<sup>1</sup>*Physics, Cornell University, Ithaca, NY 14850, United States;* <sup>2</sup>*Xerox, Rochester, NY, United States*

While gels are ubiquitous in applications from food products to filtration, their mechanical properties are usually determined by self-assembly. We use oscillatory shear to train colloidal gels, embedding memories of the training protocol in rheological responses such as the yield strain and in the gel network structures. When our gels undergo shear, the particles are forced to rearrange until they organize into structures that can locally undergo reversible shear cycles. We utilize a high-speed confocal microscope and a shear cell to image a colloidal gel while simultaneously straining the gel and measuring its shear stresses. By comparing stroboscopic images of the gel, we quantify the decrease in particle rearrangement as the gel develops reversible structures. We determine the structural origins of these shear training memories by characterizing the gel network and identifying regions that rearrange between shear cycles. These results may allow us to use shear training protocols to produce gels with controllable yield strains and to better understand changes in the microstructure and rheology of gels that undergo repeated shear through mixing or flowing.

Wednesday 4:10 Crestone A

GS24

**Photoinduced viscoelasticity in hydrogels to study cellular mechanotransduction**Ian A. Marozas<sup>1</sup>, Tobin E. Brown<sup>1</sup>, Justin J. Cooper-White<sup>2</sup>, and Kristi Anseth<sup>1</sup><sup>1</sup>Department of Chemical and Biological Engineering, University of Colorado, Boulder, Boulder, CO, United States; <sup>2</sup>Australian Institute for Bioengineering and Nanotechnology, Brisbane, QLD 4066, Australia

Hydrogels are water swollen polymer networks that have found use as biomaterials in a wide range of applications. Hydrogels can easily be functionalized with a variety of biologically relevant signals and the material properties can be tuned due to the synthetic nature of the hydrogel macromers. The storage modulus ( $G'$ ) of hydrogels can be modified by changing the crosslinking density, while the loss modulus ( $G''$ ) can be modified by incorporating physical or dynamic-covalent crosslinks into the structure. With a growing appreciation for the influence that viscoelasticity has on cellular processes, it is important to have a tool to probe the spatial and temporal effects of viscoelasticity on cellular behavior. To address this niche, we designed a hydrogel system that is capable of rapid photoinduced viscoelasticity. The poly(ethylene glycol) (PEG) based hydrogels are formed through a strain promoted alkyne-azide cycloaddition (SPAAC) crosslinking reaction and contain an allyl sulfide functionality in the core of the crosslink. Irgacure 2959 photoinitiator was tethered to the backbone of the network allowing the crosslinks to reorganize through a photoinitiated addition fragmentation chain-transfer (AFCT) reaction upon exposure to light. Specifically, the allyl sulfide group reacts with a photogenerated thiyl radical and generates another allyl sulfide crosslink and thiyl radical. Consequently the crosslinks are covalently adaptable, and thus the material is viscoelastic, only where and when the light is exposed. The system recovers elasticity upon removal of the light and can become viscoelastic again with a reproducible  $G''$  during subsequent exposures to light. Furthermore, the magnitude of  $G''$  can be modified by increasing the intensity of light and also by increasing the concentration of 8-arm PEG-thiol in the system. In preliminary experiments, user-directed detachment of cellular adhesion sites was accomplished by exposing portions of the cell to 405nm light on a confocal laser scanning microscope.

Wednesday 4:35 Crestone A

GS25

**Hydrogel materials as rheometer tooling for the transient delivery of additives during mechanical rheometry**Tianhui M. Ma<sup>1</sup>, Megan Szakasits<sup>1</sup>, Peng-Kai Kao<sup>1</sup>, J. Scott Van Epps<sup>2</sup>, and Michael J. Solomon<sup>1</sup><sup>1</sup>Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI 48105, United States; <sup>2</sup>Emergency Medicine, University of Michigan, Ann Arbor, Ann Arbor, MI 48105, United States

Mechanical rheology is widely applied to study self-assembled soft matter; however, the transient rheological properties of these materials are often sensitive to additives in a way that is difficult to study. It is therefore of interest to study the transient rheology of self-assembled materials as such additives diffuse into the material and generate microstructural and physicochemical changes. We have developed rheometer tooling comprised of a porous hydrogel that allows us to dose solvents and other additives to materials as their mechanical response is measured. We synthesize a disposable hydrogel rheometer plate through photopolymerization of an aqueous polymer solution. We control the precision of the tooling by fixing the mold to a five-axis optomechanical stage, which controls the pitch, yaw, and translational position of the tool relative to its rotational axis. We demonstrate the performance of the tooling by measuring viscoelastic properties of aqueous polyethylene oxide (PEO) solutions and comparing the values to those obtained using standard fixtures. We further offer examples of self-assembled and gel soft matter that demonstrate that the tooling can be used to study the kinetics of material property variation due to the diffusion of molecular additives through the hydrogel plate. The examples addressed include solutions of colloids, polymers, and proteins, with additive dosing that includes salts, surfactants, and enzymes.

Wednesday 5:00 Crestone A

GS26

**Rheological properties and swelling behavior of host-guest gels**

Tadashi Inoue, Takuya Katashima, and Yu Kashiwagi

Macromolecular Science, Osaka University, Toyonaka 5600041, Japan

A Host-Guest polymer was prepared through the radical polymerization of  $\beta$ -cyclodextrin-acrylamide ( $\beta$ CD-AAm) and adamantane-acrylamide (Ad-AAm) in addition to conventional vinyl monomers as main components. Although the HG polymer is a linear chain and is expected to have only temporary crosslinkings based on the host-guest interaction between  $\beta$ -cyclodextrin and adamantane, they exhibit very long relaxation modes and the swelling behavior like a gel. In addition, the Host-Guest Gel shows very strong mechanical toughness and self-healing property. In this study, we examine the viscoelastic properties and swelling behavior of the HG gel to elucidate the effect of the temporary crosslinkings. The linear viscoelastic measurements of the HG gels indicated that the HG gels have long relaxation modes due to the associative Host-Guest complex, and behave as a solid in the time scale we examined. Further measurements on the HG gels with partly capped host-guest inclusions revealed that the transient crosslinkings retard the chain dynamics and have no contribution to the rubbery plateau modulus. We found that this slow relaxation dynamics can be explained by the concept of the "sticky reptation model". In this concept, the HG gels have entanglement-dominant networks with sticky points, which intensively retard the segmental and reptation dynamics, resulting in the solid-like behavior in the time scale we examined. This concept suggests that the HG gels have the energy dissipation mechanism due to entanglements and the transient crosslinkings.

## Symposium NF Non-Newtonian Fluid Mechanics

Organizers: Paulo Arratia and Chris Dimitriou

Wednesday 1:30 Crestone B

NF27

### Numerical simulations of viscoelastic film retraction

Massimiliano M. Villone<sup>1</sup>, Gaetano D'Avino<sup>1</sup>, Ernesto Di Maio<sup>1</sup>, Martien A. Hulsen<sup>2</sup>, and Pier Luca Maffettone<sup>1</sup>

<sup>1</sup>*DICMaPI, University of Naples Federico II, Napoli, Italy;* <sup>2</sup>*Eindhoven University of Technology, Eindhoven, The Netherlands*

The retraction of a circular viscoelastic liquid film with a hole initially present in its center is studied by means of finite element numerical simulations. The results are discussed and interpreted through a simple heuristic model. Three different viscoelastic constitutive equations, namely, Oldroyd-B, Giesekus, and Phan Thien-Tanner models, are considered, and several system geometries, in terms of the film initial radius and thickness, are investigated. For each given geometry, the effects on the dynamics of the hole opening of liquid inertia, elasticity, flow-dependent viscosity, and wall slip are analyzed. Depending on the relative strength of such parameters, qualitatively different features can appear in the retracting film shape and dynamics, e.g., the formation of rims at the edge of the retracting film or hole radius/opening velocity oscillations.

Wednesday 1:55 Crestone B

NF28

### An attempt to measure the yield stress of microbial polysaccharides in aqueous solution

Ernest E. S. Ong and Jong-Leng Liow

*School of Engineering and Information Technology, University of New South Wales, Canberra, ACT 2600, Australia*

Yield stress measurements have long been considered to be difficult and inconsistent, especially for a thixotropic colloid since the thixotropic behaviour gives rise to time-dependent rheological properties. In our present study, we conducted both steady and oscillatory shear measurements of microbial polysaccharides in aqueous solution at different concentrations. Prior to the yield stress measurement, a time independence study was conducted to ensure that the measurement results are not greatly affected by the ongoing aging process in the solution. There is an intriguing phenomenon in our steady shear measurements whereby there is a resistance to the avalanche of shear-thinning flow when the shear stress is steadily increased. The observed resistance is likely to be caused by the occurrence of elastic turbulence during the yield stress measurements. From our results, the yield stress values obtained from both methods are well matched with less than 3% difference.

Wednesday 2:20 Crestone B

NF29

### Visco-plastic sculpting in stable triple layer heavy oil transport flow

Parisa Sarmadi<sup>1</sup>, Sarah Hormozi<sup>2</sup>, and Ian Frigaard<sup>3</sup>

<sup>1</sup>*Mechanical Engineering, University of British Columbia, Vancouver, Canada;* <sup>2</sup>*Department of Mechanical Engineering, Ohio University, Athens, OH, United States;* <sup>3</sup>*University of British Columbia, Vancouver, Canada*

In [1] we introduced a novel methodology for efficient transport of heavy oil via a triple layer core-annular flow. Pumping pressures are significantly reduced by concentrating high shear rates to a lubricating layer, while ideas from Visco-plastic lubrication [2,3] are used to eliminate interfacial instabilities. We purposefully position a shaped unyielded skin of a visco-plastic fluid between the transported oil and the lubricating fluid layer. The shaping of the skin layer allows for lubrication forces to develop and balance the density difference between the fluids. Here we address the sculpting of the shaped skin within a concentric inflow manifold. First we present the results of a long-wavelength/ quasi-steady analysis, which allows for us to predict maximal and minimal variations in skin thickness, while maintaining a constant flow rate of the transported oil. Secondly, we use the simple model to provide inputs to an axisymmetric triple layer computation, showing development of the streamwise skin profile and establishment of the flow. For this we use a finite element discretization with the augmented-Lagrangian method to represent the yield surface behaviour accurately and a PLIC method to track the interface motion.

[1] P. Sarmadi, S. Hormozi and I.A. Frigaard, "Triple-layer configuration for stable high-speed lubricated pipeline transport", *Phys. Rev. Fluids*, 2 pp 044302, (2017). [2] M. Moyers-Gonzalez, I.A. Frigaard and C. Nouar, "Nonlinear stability of a visco-plastically lubricated shear flow." *Journal of Fluid Mechanics*, 506, pp.117-146, (2004). [3] S. Hormozi, G. Dunbrack, I. Frigaard, "Visco-plastic sculpting", *Phys. Fluids*, 26 pp. 093101 (2014).

Wednesday 2:45 Crestone B

NF30

### Can we elongate a yield stress fluid?

Xiao Zhang, Oumar Fadoul, and Philippe Coussot

*Laboratoire Navier, University Paris-Est, Champs sur Marne 77420, France*

In general an attempt to elongate a small heap of yield stress fluid by moving away two solid surfaces in contact with it, rapidly leads to the separation of the heap in two conical volumes on each surface. During the process it seems that the fluid close to the surfaces progressively stops flowing while the central region, which thins, concentrates the flow before breakage. It was suggested that due to the symmetry of the problem a uniaxial elongational flow occurs in this central region, which may be used to determine the normal stress and validate the usual Herschel-Bulkley 3D formulation of the constitutive equation. However contradictory results have been found [1]. Here we show that it is possible to obtain a uniaxial elongational flow in the bulk at a constant rate. This is achieved by using smooth solid surfaces and a sufficiently small rate of separation

to remain at any time in the slip regime along the solid surfaces. For larger rates we can observe a transition from an elongational regime to a lubricational regime (associated with adherence to the walls in some region). The normal stress deduced from such measurements appears in agreement with that predicted by the usual theory. On the contrary it seems that simple planar elongational flows are always unstable: when one forces, an annular layer of yield stress fluid placed between two smooth plates at a constant distance, to grow in diameter, a few fractures tend to open along the inner interface, which induces a local adherence to the wall because the local stress concentrates at these points and preclude the expected elongational flow to occur. This might be an effect inherent to the jammed structure associated with the yielding behavior.

[1] G. German, V. Bertola, *Phys. Fluids*, 2010, 22, 033101; K. Niedzwiedz, H. Buggisch, N. Willenbacher, *Rheol. Acta*, 2011, 49, 1103 ; P. Coussot, F. Gaulard, *Phys. Rev. E*, 2005, 72, 031409; L. Martinie, H. Buggisch, and N. Willenbacher, *J. Rheol.*, 2013, 57, 627; J. Boujlel, P. Coussot, *Soft Matter*, 9, 5898 (2013).

Wednesday 3:45 Crestone B

NF31

### **Sinking bubbles**

Jeremy A. Koch and Randy H. Ewoldt

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

Intuition tells us that air bubbles will rise and steel objects will sink in liquids, though here we describe the opposite. With experimental demonstration and theoretical rationale, we describe how the motion of containers of liquid with immersed solid objects and air bubbles can cause curious behaviors: sinking bubbles and rising high-density particles. Bubbles and solid spheres of diameter on the order of a few millimeters are introduced into dramatically shear-thinning fluids with an effective yield stress (aqueous Carbopol microgel particle suspensions). Imposed motion of the rigid container allows for control of the trajectories of the immersed particles -- without the container imparting direct shearing motion on the fluid. Particle displacements are measured and compared to predictions from a theoretical model, based on a newly-proposed modification to the dimensionless yield-gravity parameter, and relying on drag laws found in literature. Considerations are made for the highly-transient accelerations imposed on the system, with LAOS measurements used to build a Pipkin space demonstrating a possible dependence of the material's yield stress on the transient timescale (Ewoldt & McKinley 2017). We suggest that, with proper considerations, the system can be used as an "impact rheometer" for characterizing short timescales inaccessible to standard rheometry.

Reference: Ewoldt, R.H., and G.H. McKinley. "Mapping thixo-elasto-visco-plastic behavior," *Rheologica Acta* (2017).

Wednesday 4:10 Crestone B

NF32

### **The role of surface charge convection in the electrohydrodynamics and breakup of prolate drops**

Rajarshi Sengupta, Lynn M. Walker, and Aditya S. Khair

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, United States*

The deformation of a weakly conducting, 'leaky dielectric,' drop in a density matched, immiscible, weakly conducting medium under a uniform DC electric field is quantified computationally. We exclusively consider prolate drops, for which the drop elongates in the direction of the applied field. Furthermore, we assume the drop and medium to have equal viscosities. Using axisymmetric boundary integral computations, we delineate drop deformation and breakup regimes in the  $Ca_E - Re_E$  parameter space, where  $Ca_E$  is the electric Capillary number (ratio of the electric to capillary stresses); and  $Re_E$  is the electric Reynolds number (ratio of charge relaxation to flow time scales), which characterizes the strength of surface charge convection along the interface. For so-called 'prolate A' drops, where the surface charge is convected towards the 'poles' of the drop, we demonstrate that increasing  $Re_E$  reduces the critical capillary number for breakup. Moreover, surface charge convection is the cause of an abrupt transition in the breakup mode of a drop from end-pinch, where the drop elongates and develops bulbs at its ends that eventually detach, to a breakup mode characterized by the formation of conical ends. On the contrary, the deformation of 'prolate B' drops, where the surface charge is convected away from the poles, is essentially unaffected by the magnitude of  $Re_E$ .

Wednesday 4:35 Crestone B

NF33

### **Chain stretch dynamics and rheology of entangled polymer liquids under continuous startup shear deformation**

Shi-Jie Xie and Ken S. Schweizer

*Dept. Materials Science, University of Illinois at Urbana-Champaign, Urbana, IL, United States*

We construct a theory for chain stretch dynamics and the stress-strain response under continuous startup shear deformation that builds on our new dynamic scaling deduced grip force and delayed chain retraction model in conjunction with an argument that in the absence of entanglements the effective Rouse relaxation rate is enhanced at high Rouse Weissenberg numbers ( $Wi_R > 1$ ). The chain-retraction-driven convective constraint release (CCR) idea is modified and integrated with the delayed retraction picture guided by the physical idea the overshoot is an elastic-viscous crossover. Calculations are performed for the evolution with strain of the primitive path step length and orientation, dynamic tube diameter, effective relaxation time, and stress in entangled polymer melts. At low  $Wi_R < 1$ , classic tube model behavior is recovered including a stress plateau in the flow curve. However, under strong stretching conditions ( $Wi_R > 1$ ) qualitatively different results are predicted compared to standard tube models for the shear rate dependence of the overshoot stress and strain, degree of chain stretch and tube diameter at the overshoot and in the steady state, and the long time orientational and total stresses. An apparent fractional power law growth of the steady state stress with deformation rate is predicted for  $Wi_R \gg 1$ . Strong connections between chain stretching at the overshoot and at long times are found suggesting common physics is involved in determining the elastic-viscous crossover and nonequilibrium flow state. The theoretical results will be compared with experiments, recent simulations and tube models which do not contain the grip force and delayed retraction concept.

Wednesday 5:00 Crestone B

NF34

**Modeling microstructural inertia effects in material flow**Paul M. Mwasame, Norman J. Wagner, and Antony N. Beris*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Conformation tensor-based constitutive models are important in describing the rheology of complex fluids including polymers and emulsions at the macroscopic level of description [1,2,3]. Previous authors [3,4] have considered how to incorporate inertial effects into material flow models by introducing a structural momentum tensor into the description of the complex fluid. In this work, we present a general systematic application of non-equilibrium thermodynamics [3] to incorporate inertia effects into conformation tensor based models. Our work reveals at least two ways to formulate inertial conformation tensor based models with further specialization strongly dependent on system-specific physics. By using theoretical results by Eriksen-Leslie (LE) theory [4] and microscopic theory by Raja et al. [5], for liquid crystalline systems and emulsions respectively, we show how one may select the correct corresponding inertial formulation. For these two materials, the resulting inertial formulations are distinct, highlighting the importance of using microscopic theory in elucidating the correct inertial model select. A second major result of this work is the identification of a regime at small particle Reynolds numbers in emulsion flows where the lowest order micro-inertia effects can be accommodated through an extended Gordon-Schowalter non-affine time derivative for the conformation tensor representing the emulsion droplet, without the need to introduce a structural momentum tensor. Predictions from the inertial models will also be compared against simulation results.

[1] G. Batchelor, *J. Fluid Mech.* 41, (1970). [2] M. Doi and T. Ohta, *J. Chem. Phys.* 95, (1991). [3] A. N. Beris and B. J. Edwards, *Thermodynamics of flowing systems* (Oxford University Press, New York, 1994). [4] Leslie, F. M., *Adv. Liq. Cryst.*, 4, (1979). [5] R. V. Raja, G. Subramanian, and D. L. Koch, *J. Fluid Mech.* 646, (2010). [6] X. Li and K. Sarkar, *J. Rheol.* 49, (2005).

## Symposium SG Solids, Glasses, and Composites

Organizers: Xiaolong Yin and Jonathan Stickel

Wednesday 1:30 Aspen

SG10

**Understanding the effect of attractive forces on rheology in dense slurries: Toward better understanding of complex correlations between scales**Jaehun Chun<sup>1</sup>, Sidhant Pednekar<sup>2</sup>, and Jeffrey Morris<sup>2</sup><sup>1</sup>*Pacific Northwest National Lab, Richland, WA, United States;* <sup>2</sup>*Chemical Engineering, The City College of New York, New York, NY, United States*

Understanding rheology is critical to control flows of dense slurries in various processing such as nuclear waste treatment plant at Hanford where the processing involves slurries with high salts and particle volume fraction, often giving rise to a yield stress. Rheology is a mesoscopic phenomenon, involving chemical physics at smaller length scales; it can be determined by a delicate balance between repulsive and attractive forces between solid particles, coupled with hydrodynamics, and details on microstructure of aggregates. We studied the effects of attractive van der Waals forces between particles on rheology based on a numerical simulation called the Lubricated Flow-Discrete Element Method (LF-DEM). We found that an existence of sufficient attractive force obscures shear thickening and leads to a significant increase in the apparent viscosity at small shear rates, giving rise to the development of a yield stress. Further insights were obtained by relative contributions of different forces to the bulk stress and the attractive force-dependent contact networks. Our study can be a starting point to understand complex correlations between chemical physics at different scales which are necessary for rigorous understanding of rheology.

Wednesday 1:55 Aspen

SG11

**Rheological characterization of ballistic witness materials**Ran Tao<sup>1</sup>, Kirk D. Rice<sup>1</sup>, Aaron M. Forster<sup>1</sup>, Randy A. Mrozek<sup>2</sup>, Shawn T. Cole<sup>2</sup>, and Reygan M. Freaney<sup>3</sup><sup>1</sup>*Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, United States;* <sup>2</sup>*U.S. Army Research Laboratory, Aberdeen Proving Grd, MD, United States;* <sup>3</sup>*U.S. Army Aberdeen Test Center, Aberdeen Proving Grd, MD, United States*

Clay and clay-like materials are used as a backing support for body armor during standards-based ballistic resistance tests. The backing material is also known as a ballistic witness material (BWM). Due to the complex thermomechanical behavior, unspecified formulation, and temperature sensitivity of the current standard material, Roma Plastilina No. 1 (RP1), the ballistic testing community has begun to look for an alternative BWM to replace RP1. Rheology is relied upon to characterize different candidate BWMs that are in development and to develop an understanding of mechanisms that control their behavior during the verification process of the BWM and ballistic testing of body armor. Test methods employed in this study include dynamic frequency sweep, stress relaxation, dynamic time sweep, and large amplitude oscillatory shear (LAOS). The rheology results offer fundamental information on structure-property relationships for different BWMs in an effort to guide the long-term goal of developing a replacement backing material as the standard.

Wednesday 2:20 Aspen

SG12

**Cold spray deposition of polymer powders – a novel additive manufacturing technique for polymers**Zahra Khalkhali, Jonathan Rothstein, and David P. Schmidt*Mechanical Engineering, University of Massachusetts Amherst, Amherst, MA 01002, United States*

For the last two decades, the Cold Spray process has been attracting increased research interests for its remarkable advantages over other additive manufacturing techniques and its promising industrial applications. In this technique, solid micro-particles are accelerated in a warm gas through a converging-diverging nozzle up to a supersonic velocity. Upon impacting a substrate, these solid particles deform and in some cases melt and mix locally within the high shear zones to form a strong bond with the substrate. This process has been fully developed for a number of metallic materials. Yet little research on the cold spray of polymers has been conducted. In this presentation, the necessary spray conditions for an efficient deposition of a number of different polymers will be presented. A series of particles consisting of High density polyethylene (HDPE), polyurethane, polyamide 12, polystyrene, and polyether ether ketone and some composites of HDPE were cold sprayed on an array of substrate materials including low density polyethylene, HDPE, polyvinyl chloride, polyoxymethylene, glass and aluminum. Like-on-like depositions were also implemented by cold spraying on a melt cast piece of each powder material. Deposition maps will be presented for each particle/substrate choice to demonstrate the particle impact velocity required for successful deposition. The effect of particle properties including size, shape, flowability, melting point, glass transition temperature as well as particle rheological properties on the feasibility of deposition will also be presented. In addition, variation in a number of spray conditions including particle velocity, substrate temperature and stand-off distance will also be presented. SEM images will be presented to characterize the porosity and defects of the surfaces deposited through cold spray. Finally, the mechanical properties of the surfaces deposited through cold spray will be presented and compared to melt-cast surfaces of the same polymer.

Wednesday 2:45 Aspen

SG13

**Thermal and mechanical response of battery insulation materials**Scott A. Roberts, Alexander Headley, Kevin N. Long, Adam D. Martinez, Christine C. Roberts, and Mark E. Stavig*Sandia National Laboratories, Albuquerque, NM 87185-0836, United States*

Insulation materials are critical components of molten salt batteries, retaining heat within the battery and providing mechanical constraint while other internal components deform during activation. These materials are composites comprised of bundles of ceramic fibers and void space. Modeling the thermal and mechanical response of these materials is a critical part of predicting battery performance, yet to date these materials have been relatively poorly characterized.

We present mechanical and thermal characterization and modeling of these insulation materials. Long-time fixed-strain mechanical load tests show stress relaxation over time scales of months, with significant sample-to-sample variability and nonlinear rebound behavior. Thermal conductivity depends on both the gas environment and on the state of internal mechanical deformation. We present experimental characterization and constitutive modeling of these phenomena, along with exploring the effect of the variability on battery cell performance. Additionally, mesoscale imaging and modeling are used to provide additional insights into the material performance.

*Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525*

Wednesday 3:45 Aspen

SG14

**Obtaining and evaluating fiber orientation model parameters using nonlubricated squeeze flow**Gregory M. Lambert, Hongyu Chen, and Donald G. Baird*Chemical Engineering, Virginia Tech, Blacksburg, VA, United States*

Accurate modeling of the orientation dynamics of fiber fillers in polymeric matrices during the processing of fiber-reinforced thermoplastics remains a significant challenge for a variety of reasons. This work seeks to address the problem of obtaining empirical parameters from the proposed orientation models independently of processing conditions. Here, a suspension of long-glass-fiber-reinforced (average length > 1mm) polypropylene is subjected to nonlubricated squeeze flow in a rectangular channel. Parameters for a rigid and a semiflexible fiber model are obtained in two ways: first, parameters are chosen to fit to experimental orientation data; second, a stress tensor is coupled to the orientation models and parameters are obtained by fitting to the stress growth during nonlubricated squeeze flow. The parameters are then used to predict orientation in an injection-molded center-gated disk made from the same material.

Wednesday 4:10 Aspen

SG15

**Shear and elongational-induced crystallization of branched poly (lactic acid)**Amirjalal Jalali*Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario M5S 3G8, Canada*

Abstract - We report the effect of shear and extensional flows on the crystallization of branched poly (lactic acid), B-PLA, using rheometry. To investigate the effect of weak shear flow, the samples were first heated up to 190 °C to erase the thermal history. Next, molten polymers were rapidly cooled to a determined temperature and subjected to continuous shear flow varying from 0.01 to 0.1 s<sup>-1</sup>. Although B-PLA exhibited faster crystallization kinetics, compared with linear PLA, the effect of shear flow was more pronounced on the crystallization kinetics of linear PLA. In a bid to examine the effect of strong shear flow on the crystallization of B-PLA, the samples were pre-sheared and then crystallized at the same

temperature. Evolution of the crystallization was monitored by the variation of storage modulus,  $G'$ , versus time,  $t$ . To study the effect of elongational flow, the same thermal protocol as used for shear-induced crystallization was employed. It was found out that the elongational flow showed a more impactful role on B-PLA crystallization compared to shear flow. Thermal behavior and the microstructures of the sheared and stretched samples were studied by Differential Scanning Calorimetry, and X-ray Diffraction, respectively.

Wednesday 4:35 Aspen

SG16

### **Complex viscosity of small polymer grafted nanoparticles dispersed in entangled matrices**

Marissa Giovino and Linda Schadler

*Materials Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

Polymer nanocomposites have been shown to display improved thermal, mechanical and electrical properties over polymer matrices even at low loadings. Dispersion has proven to be a key factor in property enhancement for these materials. To achieve good dispersion a short brush is densely grafted to prevent enthalpic attraction and a long brush is sparsely grafted to provide entanglements with the matrix. The complex rheology of these brush modified / polymer nanocomposites needs to be understood to effectively use them for commercial melt processing. Currently there are no equations to predict the viscosity of polymer grafted nanoparticle composites. Towards this end, the viscosity of a model system has been measured. The model system consists of  $ZrO_2$  nanoparticles grafted with two populations of polydimethylsiloxane (PDMS) brushes: one short brush and one long brush. These were dispersed into three homopolymer matrices (36 kg/mol, 49 kg/mol and 77 kg/mol) at different loadings. The composite viscosity was measured for each sample using oscillatory rheology. The data was compared to the Batchelor model which is ineffective. By including the grafted polymer as part of the filler volume fraction, the data can be fit reasonably well to a curve.



## Thursday Morning

### Symposium AP Award Presentations

#### *Metzner Award Presentation*

Thursday 8:00 Crystal C

AP1

#### **Drift redux**

Aditya S. Khair

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, United States*

One of the first problems that a student of fluid mechanics encounters is inviscid flow past a stationary sphere. Here, fluid elements simply follow streamlines. The situation is more interesting if, instead, the sphere moves steadily in a fluid that is quiescent at large distances; fluid elements undergo complex looping trajectories and can be permanently displaced. This displacement is known as "drift." The "drift volume" is the volume of fluid between the initial and final positions of an unbounded, marked (as in with dye) set of fluid elements that is initially far ahead of the body and perpendicular to its path of travel. Physically, the drift volume is a measure of the amount of fluid entrained by the body. In 1953, Sir Charles Darwin (grandson of the naturalist) calculated that the drift volume induced by a sphere in inviscid flow equals one half of its own volume. Recent interest in quantifying drift in *viscous* fluids is motivated by applications to pool boiling; stratified flows; protein transport in membranes; and mixing by swimming organisms. In this talk, a framework to compute the drift volume in viscous flows will be presented, which interprets the drift volume as the time-integrated flux of fluid between streamlines via a conservation-of-mass argument. This enables computation of the drift volume without the need to resolve the trajectories of fluid elements. It will be demonstrated that viscosity has a dramatic influence on drift. For instance, if a body is towed by an external force (e.g. a sedimenting particle) the drift volume can be orders of magnitude larger than the volume of the body and diverges with the travel time of the body. Remarkably, this conclusion holds at all (finite) Reynolds numbers. Finally, the drift volume induced by a self-propelled swimmer is shown to be fundamentally different from that due to a towed body. The implications of this finding on the ability of intermediate Reynolds number (milli-meter sized) swimmers to transport fluid via drift will be discussed.

### Symposium SG

#### **Solids, Glasses, and Composites**

Organizers: Xiaolong Yin and Jonathan Stickel

Thursday 8:40 Crystal A

SG18

#### **Natural fiber surface treatment determined by rheological methods: A case study of hemp in linear medium density polyethylene**

Denis Rodrigue<sup>1</sup>, Désiré Yomeni Chimeni<sup>1</sup>, and Charles Dubois<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Université Laval, Quebec, QC - Quebec g1v0a6, Canada;* <sup>2</sup>*Chemical Engineering, Polytechnique Montreal, Montreal, QC - Quebec, Canada*

It is well known that the adhesion between a fiber and the matrix is of the utmost importance to improve the mechanical properties of polymer composites. This is especially true when using lignocellulosic fibres in polyolefins due to their very different chemical and physical properties. In most cases, fiber surface treatment, coupling agent addition or a combination of both methods can be used. Nevertheless, there is still interest to determine the efficiency of these methods by other means than standard mechanical properties measurement. In this work, several methods are combined to understand the interactions involved at the interface. In particular, morphological analyses via scanning electron microscopy (SEM) are combined with dynamic mechanical analyses (DMA) in the solid state as well as small amplitude oscillatory shear (SAOS) in the melt state. From the results obtained, several methods are proposed to infer the interfacial adhesion, but van Gurp-Palmen plots are found to be very sensitive as they present a maximum which can be related to interfacial strength.

Thursday 9:05 Crystal A

SG19

#### **Rheological properties of biopolymers filled with cellulose nanofibers**

Fatemeh Safdari<sup>1</sup>, Pierre J. Carreau<sup>1</sup>, Marie-Claude Heuzey<sup>1</sup>, and Musa R. Kamal<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Polytechnique Montreal, Montreal, Quebec H3C3A7, Canada;* <sup>2</sup>*Chemical Engineering, McGill University, Montreal, Quebec H3A0C5, Canada*

Cellulose nanofibers (CNFs) are highly flexible and hydrophilic fibers that tend to entangle and form agglomerates, especially when mixed with hydrophobic matrices. In this work we have examined the rheological properties of two bio-thermoplastics, i.e., polylactide (PLA) and poly(ethylene oxide) (PEO), filled with CNFs. Initially, PLA/CNF and PEO/CNF biocomposites were prepared separately via solution methods.

Subsequently, the compatibilization effects of poly(ethylene glycol) (PEG), a low molecular weight PEO, were investigated. Scanning electron microscopy and rheological data confirmed that the CNFs were well dispersed in the PLA and PEO matrices, and the dispersion is improved when using PEG as a compatibilizer. The complex viscosity and storage modulus of PLA and PEO increased substantially by incorporating CNFs. The increases were one order of magnitude larger for the compatibilized PLA/CNF composites. The storage modulus of the PLA/2wt%CNF/4wt%PEG biocomposite obtained in dynamic mechanical thermal analysis (DMTA) at room temperature and 80 °C, increased by 42 and 553%, respectively, relative to the neat PLA.

Thursday 9:30 Crystal A

SG20

### **Influence of formulation on morphology and rheology of polypropylene/polyamide blends filled with nanoclay mineral particles**

Quentin Beuguel<sup>1</sup>, Julien Ville<sup>2</sup>, Jérôme Crépin-Leblond<sup>3</sup>, Pascal Médéric<sup>2</sup>, and Thierry Aubry<sup>2</sup>

<sup>1</sup>*Polytechnique Montreal, Montreal, Canada;* <sup>2</sup>*IRDL, Université de Bretagne Occidentale, Brest, France;* <sup>3</sup>*IMERYS TALC, Toulouse, France*

The effect of formulation on the morphological and rheological properties of clay polypropylene/polyamide 12 nanocomposites is investigated. Two clay minerals, organically modified montmorillonite and synthetic talc, and two polypropylenes matrices, a low viscosity polypropylene and a high viscosity polypropylene, are used. The higher polypropylene matrix viscosity strongly influences the interfacial coverage of polyamide nodules, by slowing down the migration of fillers from polypropylene matrix to polyamide nodules. The nature of clay minerals as well as the polypropylene matrix viscosity are shown to influence the change from nodular to non-nodular morphology of nanocomposites. A comparative study of the viscoelastic properties of montmorillonite or synthetic talc high viscosity polypropylene/polyamide 12 nanocomposites is performed through the use of Palierné's model. Surprisingly, the results show that a developed montmorillonite interphase behaves like a weakly developed synthetic talc interphase suggesting that the nature and structure of clay particles located at the interface play a key role in interphase viscoelastic properties.

Thursday 10:25 Crystal A

SG21

### **Effect of nano-particles and flow induced crystallization kinetics in polymer nanocomposites**

Debjani Roy<sup>1</sup>, Anthony P. Kotula<sup>2</sup>, Jeff Gilman<sup>1</sup>, Kalman Migler<sup>1</sup>, and Doug Fox<sup>3</sup>

<sup>1</sup>*Polymers, NIST, Gaithersburg, MD 20899, United States;* <sup>2</sup>*Materials Science and Engineering, NIST, Gaithersburg, MD 20899, United States;* <sup>3</sup>*Chemistry, American University, Gaithersburg, MD 20899, United States*

It is well known that either flow or nanoparticles can greatly increase the crystallization kinetics in thermoplastics, presumably by increasing the nucleation rate. Here we study the case of combined flow and nanoparticles to understand how these two effects interact. We utilize a recently developed rheo-Raman microscope to quantitatively correlate the elastic modulus and the crystalline structures associated with the conformational changes during crystallization subject to a combination of shear and nanoparticles in polycaprolactone (PCL) with cellulose nanocrystals (CNCs). First we demonstrate that PCL and cellulose nanocrystals CNCs can be well-compatibilized by replacing the Na<sup>+</sup> of sulfated cellulose nanocrystals (Na-CNCs) with tetra-butyl ammonium cations and then melt mixing via twin-screw extrusion. Transmission electron microscope and high temperature melt rheology show that the modified CNCs were dispersed in the polymer matrix. Combining rheo-Raman measurements we establish a correlation between mechanical, chemical and structural properties. For the present studies we have used a kinetic parameter defined by Lichtenecker's equation, a two phase composite model, to correlate the mechanical and Raman data, indicative of structural changes with addition of the filler particles.

## **Symposium SM Polymer Solutions and Melts**

Organizers: Suraj Deshmukh and Reza Foudazi

Thursday 8:40 Crystal B

SM40

### **Squeezing deformation of entangled melts along with particle-tracking velocimetry**

Xianggang Li<sup>1</sup> and Shi-Qing Wang<sup>2</sup>

<sup>1</sup>*Key Laboratory of Advanced Materials and Technology, Hunan University of Technology, Zhuzhou, China;* <sup>2</sup>*Polymer Science, University of Akron, Akron, OH 44325, United States*

The subject of strain localization in polymer melt deformation is challenging to investigate in available commercial rotational rheometry due to a) edge failure and b) torque and normal force tolerances. We design a squeezing device where a sheet-like sample maintains a constant width and decreases its thickness while increasing its length. We use either a step-motor or air cylinder to displace the plunger onto the sample. The travel of the plunger reduces the sample's thickness in either rate-controlled or pressure-controlled squeezing. Particle-tracking velocimetry (PTV) observations are carried out along with the measurements of stress or strain response. Albeit more intricate than simple-shear geometry, the squeezing produces large melt deformation in absence of any interference from meniscus. Under constant pressure, we observe an entanglement-disentanglement transition that may be accompanied by shear strain localization. In presence of lubrication, we study planar extension. With stepwise squeezing, we also examine whether the relaxation is quiescent or not.

Thursday 9:05 Crystal B

SM41

**Reconstruction of three-dimensional anisotropic structure from scattering experiments**Guan-Rong Huang<sup>1</sup>, Yangyang Wang<sup>2</sup>, Bin Wu<sup>1</sup>, Zhe Wang<sup>1</sup>, Changwoo Do<sup>1</sup>, Gregory S. Smith<sup>1</sup>, Lionel Porcar<sup>3</sup>, and Wei-Ren Chen<sup>1</sup><sup>1</sup>Biology and Soft Matter, Oak Ridge National Laboratory, Oak Ridge, TN, United States; <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States; <sup>3</sup>Institut Laue-Langevin, Grenoble, France

When subject to flow, the structures of many soft matter systems become anisotropic due to the symmetry breaking of the spatial arrangements of constituent particles at microscopic level. While it has now been a common practice of using various small angle scattering techniques to explore the flow-induced micro-structural distortion, how the three-dimensional asymmetric structure can be unbiasedly reconstructed from the two-dimensional scattering spectra has not been thoroughly discussed in the documented literature. In this work, we rigorously addressed this issue by a mathematical perspective based on the real spherical harmonic expansion analysis. We first show that, under the steady shear condition, except for the cases where the mechanical perturbation is sufficiently small, the existing small angle scattering technique in general does not provide the complete information of structural distortion. This limitation is caused by the linear dependence of certain spherical harmonic basis on the flow-vorticity and flow-velocity gradient planes, where the flow structures are probed by currently available annular shear cells. To circumvent this constraint imposed by the cell geometry, a proposition of using a parallel-plate shear cell with a central rotary axis extending in parallel with the flow direction is proposed. From the calculation of rotation of reference frame, we further demonstrate the feasibility of this experimental implementation for fully resolving three-dimensional anisotropic structure via a case study of sheared polymer solutions.

Thursday 9:30 Crystal B

SM42

**Monitoring phase transitions with simultaneous rheology and Raman spectroscopy**Nathan C. Crawford<sup>1</sup>, David Drapcho<sup>2</sup>, Massimiliano Rocchia<sup>3</sup>, and Jan P. Plog<sup>4</sup><sup>1</sup>Thermo Fisher Scientific, Denver, CO, United States; <sup>2</sup>Thermo Fisher Scientific, Madison, WI, United States; <sup>3</sup>Thermo Fisher Scientific, Rodano, Italy; <sup>4</sup>Thermo Fisher Scientific, Karlsruhe, Germany

Rheology is an analytical tool that examines or induces bulk physical material changes, such as melting, crystallization, gelation, and/or polymerization (to name a few). Unfortunately, rheological measurements cannot directly measure the underlying chemistry which drives these physical transformations. Raman spectroscopy, on the other hand, is a complementary vibrational spectroscopic technique that provides insight to these processes at the molecular level, both chemically and morphologically. Until recent, rheology and Raman studies (deemed rheoRaman) were often conducted *ex situ*, whereby Raman spectra were acquired prior to and after the observed physical transformation. The true chemical/morphological changes driving these processes were largely left uncaptured, leaving much room for data interpretation and speculation surrounding these dynamic physicochemical relationships.

Here, we examine the recrystallization behavior of polypropylene using a rheometer coupled with an *in situ* Raman spectrometer (Thermo Fisher Scientific MARS<sub>XR</sub> system). The recrystallization process was examined isothermally, both with and without the influence of imposed shear. This multimodal analytical tool allowed the bulk structural properties of polypropylene ( $G'$  and  $G''$ ) to be directly correlated with conformational changes at the molecular level (i.e., helical chain vibrations and CH stretching) in real-time. The data revealed that the rate of crystallization (indicated by rapid increases in  $G'$ ,  $G''$ , and helical chain formation) could be directly correlated with crystallite concentration (signified by a decrease in the Raman spectral intensity). While this work focused on crystallization behavior, the underlying principles applied here should be applicable for a wide range of material processes including gelation, polymerization, curing behavior, as well as other shear-induced phenomena.

Thursday 10:25 Crystal B

SM43

**Influence of automated algorithms on the quality of TTS shift factors**Bharath Rajaram and Aly Franck

TA Instruments, New Castle, DE 19720, United States

The application of the Time-Temperature Superposition (TTS) principles to shift frequency- and time- dependent modulus and compliance data is well known and extensively documented. These principles allow the generation of a unique master curve for materials such as polymer by collecting data over a wide range of temperatures and provides access to data at time scales and frequencies unencumbered by mechanical and experimental limitations. Briefly, the data collected at temperature  $T$  can be superposed with data collected at an arbitrary reference temperature  $T_0$  through shift factors  $aT$  and  $bT$ . Here,  $aT$  is the horizontal shift factor that describes the material's temperature dependence while  $bT$  represents the vertical shift factor that scales with the temperature and density. Traditionally, the data were manually shifted along the time or frequency axes till they superpose. However, manually shifting the data is prone to introducing a subjective bias in the master curve. These limitations can be overcome through the use of mathematical procedures that can provide reproducible shift factors. In this study, the shift factors generated during TTS analysis using five different shift algorithms are compared and evaluated. Frequency sweep data on commercial polystyrene and low density polyethylene materials were collected over the temperature range from 130 °C to 240 °C using an ARES-G2 rheometer equipped with a Forced Convection Oven; all tests were performed under an inert Nitrogen gas atmosphere to avoid sample degradation. The quality of shift factors were evaluated using the same data set on all the algorithms. The algorithms investigated include polynomial fitting, arc length minimization, closed form shifting, and an interpolation based method. Results comparing the algorithm's sensitivity to initial starting point, influence of temperature, and the robustness of the shift factor curve are discussed.

Thursday 10:50 Crystal B

SM44

**Various aspects of melt extension to test standard models**Jianning Liu<sup>1</sup>, Yi Feng<sup>1</sup>, Zhichen Zhao<sup>1</sup>, Apostolos Avgeropoulos<sup>2</sup>, and Shi-Qing Wang<sup>3</sup><sup>1</sup>University of Akron, Akron, OH 44325, United States; <sup>2</sup>University of Ioannina, Ioannina, Greece; <sup>3</sup>Polymer Science, University of Akron, Akron, OH 44325, United States

Despite decades of research our understanding of melt extension remains highly tentative. The presentation selects a few examples, based on either a series of 3,4-polyisoprene melt or polystyrene and poly(methyl methacrylate), to indicate the limitation of available models for large deformation of entangled melts. A) Uniaxial extension produces various forms of tensile strain localization to terminate homogeneous melt stretching. B) Slow stepwise extension cannot insure quiescent relaxation. C) Ordinary melt extension produces significant energetic effects associated with conformational distortion. Existing molecular models do not prepare us to anticipate these features.

This work was supported, in part, by a grant from the National Science Foundation (DMR-1105135).

Thursday 11:15 Crystal B

SM45

**The melt rheology of poly(ethylene oxide) powder mixtures of varying initial molecular weight distribution subject to non-oxidative thermal degradation**Craig D. Mansfield<sup>1</sup>, Donald G. Baird<sup>1</sup>, and Christopher J. Pino<sup>2</sup><sup>1</sup>Chemical Engineering, Virginia Tech, Blacksburg, VA, United States; <sup>2</sup>Innovative BioTherapies, Ann Arbor, MI 48108, United States

The chemical kinetics of the non-oxidative thermal degradation of (poly(ethylene oxide) (PEO) are well described in the literature. However, the rheological behavior of PEO subject to these conditions has not been well characterized. The rheology of melt material streams plays an important role in predicting the optimal performance of melt processes, such as the co-extrusion process. Connecting the rheology of degrading PEO to the governing kinetics is of fundamental importance to predicting composition and rheological behavior as a function of processing conditions. In this work, the rheological behavior of melts formed from PEO powder mixtures of varying molecular weight was characterized using a combination of dynamic small amplitude oscillatory shear (SAOS) tests and inception of steady shear tests. SAOS tests were used to eliminate shear induced mixing, which was studied separately with inception of shear tests. The SAOS test scheme used allowed for isolation of thermal degradation effects during data analysis. The effect of degradation on the rheology of PEO will be discussed. In addition, updates for a previously introduced model for non-oxidative thermal degradation connecting the observed rheological behavior to the governing chemical kinetics will be discussed.

## Symposium SC Suspensions, Colloids and Granular Systems

Organizers: Cari Dutcher and Lilian Hsiao

Thursday 8:40 Crystal C

SC35

**Transient and steady shear rheology of aqueous graphene oxide dispersions**Francesco Del Giudice<sup>1</sup>, Ben Cunning<sup>2</sup>, Rodney S. Ruoff<sup>3</sup>, and Amy Q. Shen<sup>1</sup><sup>1</sup>Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan; <sup>2</sup>Center for Multidimensional Carbon Materials, Institute for, Ulsan, Republic of Korea; <sup>3</sup>Center for Multidimensional Carbon Materials, Institute for, Ulsan, Republic of Korea

Graphene Oxide (G-O) dispersions in water are aqueous suspensions containing chemically modified graphene sheets. G-O sheets or aqueous G-O dispersions have found applications in hydrogen storage, sensing, and biomedical devices. Understanding the rheological behavior of aqueous (and other) G-O dispersions is fundamentally interesting and important for various processing operations. However, conflicting information of rheological behavior of G-O dispersions was reported in the literature. In this work, we present transient and steady shear rheology of aqueous graphene oxide (G-O) dispersions. Aqueous G-O dispersions in the volume concentration range  $0.0030 < \phi < 2.7$  vol% are characterized under oscillatory linear shear flow, transient shear flow, and steady shear flow. Steady shear measurements have been performed after the evaluation of transient properties, to assure steady-state conditions. Linear oscillatory shear measurements have been used to evaluate viscous and elastic properties of the dispersions, and for the determination of the critical concentration  $f_c$ , where G-O sheets start to interact with each other. Prior to each measurement, a preshear has been applied to the dispersion in order to impose a defined shear-history. When  $f/f_c > 1$ , aqueous G-O dispersions show both strong elastic components and a yield stress, due to the formation of clusters made of G-O sheets. In transient measurements, different trends are displayed at different shear rates due to the competition between Brownian diffusion and convection, quantified by the Peclet number  $Pe$ . At  $Pe=0.001$ , transient viscosity shows fluctuations over time, and steady-state is not clearly reached. At higher  $Pe$ , steady state is reached after  $\sim 200$  s ( $0.01 < Pe < 1$ ) or  $\sim 100$  s ( $Pe > 1$ ). Stress-imposed measurements confirm the existence of the yield stress when  $f/f_c > 1$ , in agreement with literature reports. Steady-shear measurements exhibit a monotonic behavior of the shear viscosity with the concentration, in agreement with reported findings.

Thursday 9:05 Crystal C

SC36

**Orientation dynamics of dilute graphene suspensions: Dichroism and modeling**Gioviannantonio Natale<sup>1</sup>, Naveen K. Reddy<sup>2</sup>, and Jan Vermant<sup>3</sup><sup>1</sup>*University of Calgary, Calgary, Canada;* <sup>2</sup>*Hasselt University, Hasselt, Belgium;* <sup>3</sup>*ETH Zurich, Zurich, Switzerland*

Graphene sheets are two-dimensional structures made of carbon atoms, which are electrically and thermally conductive and have unique mechanical properties. They have potential applications in many fields, including organic electronics, reinforced and electrically conducting composites and even new types of biological sensors and devices. Promising processing routes involve suspensions of graphene flakes. However, to fully exploit graphene suspensions, control of the microstructure evolution during flow is required. Specifically, a full understanding of the orientation behaviour of the graphene flakes during flow is necessary. In this work, we analyse the orientation dynamics of graphene suspensions in the dilute regime by examining their rheo-optical response. Dichroism is obtained in a Couette flow geometry which allows direct measurement of the average orientation angle ( $\chi$ ) of the particles with respect to the flow direction. Micrometer sized and functionalized graphene flakes were dispersed in a Newtonian mineral oil. The orientation of the system is studied in simple shear flow at steady state and using large amplitude oscillatory shear (LAOS) as a prototype transient flows. In LAOS, the suspensions present an interesting double peaked  $\chi$  response at large strains during oscillation. To explain flow behaviour of graphene suspensions in simple steady shear and in LAOS, the particles are modelled as oblate spheroids and the suspension orientation dynamics are captured by a single particle Smoluchowski equation. This simple model captures surprisingly well, especially given the strong approximation of particle shape, the suspensions dynamics without the need of additional fitting parameters.

Thursday 9:30 Crystal C

SC37

**Free surface flows of particle suspensions**Ivan R. Siqueira and Marcio S. Carvalho*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Brazil*

Free surface flows are common in many manufacturing processes such as injection molding, extrusion, printing and coating. In many applications, the liquid is a complex fluid composed by particles suspended in a viscous or viscoelastic continuous phase. The effect of suspended particles on free surface flows is still not fully understood. Local variation of particle concentration may lead to viscosity and surface tension gradients, which can change the flow pattern and final particle structure in the final product. If the particles are elongated, the liquid stress will depend not only on the local particle concentration but also on its orientation with respect to the flow. The main goal of this work is to study the effect of particle suspensions in two important free surface, process flows: extrusion and slot coating. We present a flow model that describes a non-colloidal suspension as a Newtonian liquid but with the viscosity being a function of the local concentration and particle axis aspect ratio (in the case of elongated particles). If the particles are non-spherical, their average orientation leads to an additional stress, which is written as a function of the conformation tensor. The well-known Diffusive Flux Model describes particle migration. In extrusion flow, we show that that particle migration dramatically changes the shape of the free surface when the suspension flow is compared to a Newtonian liquid with the same bulk properties. Remarkably, we observed the expected extrudate expansion in the Newtonian and dilute suspension flows; in turn, at high concentrations, extrudate contraction appears a phenomenon that has been observed in some experiments. In the case of slot coating, the results show how process conditions affect particle distribution and orientation in the final coated film. These findings shed light on the possibility of optimizing process conditions in order to achieve the desired particle structure.

Thursday 10:25 Crystal C

SC38

**Comparison of different flow assessments for Selective Laser Sintering powders illustrated on a rotational rheometer**Abhishek Shetty<sup>1</sup> and Denis Schütz<sup>2</sup><sup>1</sup>*Rheology, Anton Paar USA, Ashland, VA 23005, United States;* <sup>2</sup>*Anton Paar, Graz, Austria*

Selective Laser Sintering (SLS) is a rapidly expanding field of manufacturing technology. Its raw materials are manifold spanning both high density as well as low density metal powders and extending into polymers and ceramics as well. While currently strict criteria are applied towards the sphericity of the particles as well as having an extremely narrow size distribution, this puts a considerable strain on the manufacturers of such powders, especially cost wise, and severely limits the availability of exotic materials for high performance engineering purposes. Ring shear testers are a well-developed and standardized method for the characterization of flow behavior, it is often found to be lacking with especially free flowing powders such as the raw materials for SLS machines. We have successfully demonstrated the viability of a rotational rheometer with different peripherals to characterize different SLS powders. Several alternative methods (Tensile strength testing, Rotational Cohesion Testing, Uniaxial testing, Penetration testing) will be compared both from the standpoint of particulate mechanics as well as the perspective of the practical process engineer. This includes an assessment of the particulate mechanics of such systems as well as extensive experimental work and application of low and high density metal and polymer powders.

Thursday 10:50 Crystal C

SC39

**Broken necklaces**Emad Chaparian, Anthony Wachs, and Ian Frigaard*University of British Columbia, Vancouver, Canada*

In Stokes flow of a particle settling within a yield stress fluid, the resistive force of the yield stress must be overcome in order for the particle to move. This leads to a critical ratio of the buoyancy stress to the yield stress: the yield number. This translates geometrically to a critical envelope around the particle in the limit of zero flow, that contains both the particle and encapsulated unyielded fluid. Such unyielded envelopes and critical yield numbers are becoming well understood for single (2D) particles, as well as the means of calculating [1,2]. Here we study multiple particles, which introduces interesting complications. Firstly, plug regions can appear between the particles and connect them together, depending on the proximity. The combination forms larger (and heavier) particle with a different yielding behaviour. Thus, small particles (that cannot move alone) can be pulled by larger particles. Increasing the number of particles leads to "necklaces" of particles, which can have interesting chain dynamics, including breaking and reforming.

[1] E. Chaparian, I.A. Frigaard, "Yield limit analysis of particle motion in a yield-stress fluid." *Journal of Fluid Mechanics*, 819, pp. 311-351, (2017). [2] E. Chaparian, I.A. Frigaard, "Cloaking: Particles in a yield-stress fluid," *Journal of Non-Newtonian Fluid Mechanics*, 243, pp. 47-55, (2017).

Thursday 11:15 Crystal C

SC40

**Flow of colloidal gels and log rolling structures of rod-like colloids**Mohan Das and George Petekidis*IESL, FORTH, Heraklion, Greece*

Suspensions of anisotropic colloids may form a variety isotropic and lyotropic liquid-crystalline phases varying the concentration and interparticle interactions. Moreover, similar with their spherical counterparts, rod-like colloids can be trapped in non-ergodic states such as glasses and gels at high volume fractions and/or with increasing interparticle attraction. Here we present the rheological response and the flow induced clustering of dilute gels of silica rods ( $L \sim 5 \mu\text{m}$ ,  $d = 0.4 \mu\text{m}$ ) in a density matching solvent. Van der Waals attractions between rods become dominant by screening repulsions due to negative surface charges through the addition of an excess amount of CsCl (65 wt%). The latter also provides a density matching solvent mixture and leads to the formation of stable isotropic gels. Using a variety of imaging techniques along with rheological experiments, we monitor structural changes under shear at different length-scales down to single particle level. We observe shear induced cluster formation in the vorticity direction that is driven by an interplay of hydrodynamic interactions, confinement and a balance of shear and attractive forces. We investigate the effect of particle volume fraction, shear rate, gap size and tool geometry as well as shear history on the dimension and the evolution of log-rolling structures. We finally compare the yielding response of these attractive gels with their glassy counterparts where frustration and liquid to solid transition is driven by increased crowding and repulsive interactions. In both cases simultaneous confocal microscopy and rheometry provide detailed structural and dynamic information that is linked with the mechanical response at different flow regimes.

Thursday 11:40 Crystal C

SC41

**Dynamics of nanoparticles in polymer nanocomposites**Pooja Nath*Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

The study of nanoparticle motion in polymer matrices has implications in melt processing and long-term stability of polymer nanocomposite materials which are useful in designing novel materials for packaging, energy storage, and biomedical devices. Another factor guiding our interest in such studies is the occurrence of non-continuum behaviors as particle sizes become comparable or smaller than the radius of gyration ( $R_g$ ) of the host polymers. The most interesting and controversial behavior among these is the superdiffusion of nanoparticles in entangled polymer hosts when the particle size is around the tube diameter ( $a$ ) of the host polymer. The conventional wisdom surrounding superdiffusive processes calls for the presence of residual stresses or force fields that can bias particle motion. While this can explain the occurrence of superdiffusion in aggregating particles or materials close to their glass transition temperatures, this argument cannot explain the occurrence of superdiffusion in non-aging, and uniform nanoparticle-laden polymer melts or solutions. Through confocal microscopy and X-ray photon correlation spectroscopy, we have highlighted the differences in dynamics of nanoparticles in polymer melts and solutions. We find that nanoparticle dynamics vary as the function of particle size relative to tube diameter in entangled polymer solutions. We discuss anomalous diffusion behaviors in polymer melts and solutions and their dependence on measurement time scales.

## Symposium GS Gels and Self-Assembled Systems

Organizers: Kendra Erk and Simon Rogers

Thursday 8:40 Crestone A

GS27

### **The influence of supramolecular bonds on the nonlinear rheology of metallo gels**

Jan Hendricks<sup>1</sup>, Jérémy Brassinne<sup>2</sup>, James D. Wilson<sup>3</sup>, Dimitris Vlassopoulos<sup>4</sup>, and Christian Clasen<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, KU Leuven, Leuven, Belgium;* <sup>2</sup>*Research and Innovation Centre Lyon, Solvay, Saint-Fons, France;* <sup>3</sup>*Research and Innovation Centre Paris, Solvay Novacare, Aubervilliers Cedex, France;* <sup>4</sup>*FORTH-IESL, HERAKLION, Greece*

The behavior of associative polymers under shear receives currently a lot of attention. Depending on the utilized association mechanism and the physical as well as chemical properties of the polymers, a range of complex material responses has been observed when the polymers are exposed to shear flow. In the current study we investigate hydrogels comprised of a polymeric backbone with ligands distributed along the chain. The addition of specific metal ions leads to supramolecular assemblies that form hydrogels if dissolved in water. The hydrogels properties are highly tunable by altering the ratio of metal ions to ligands, the polymer concentration, the density of ligands along the backbone or the metal ion species. An open question is the mechanistic origin of the observed shear thickening as well as shear thinning. This behavior is believed to be related to a flow dependent network volume that could lead to an alteration of the amount of intermolecular bonds and thus a strong rate dependency. To explain the mechanisms leading to these nonlinear shear induced effects, orthogonal superposition measurements were performed by superimposing small amplitude oscillatory shear parallel and orthogonal to a steady shear flow. Using frequency as well as time dependent data collected in both directions we demonstrate how the anisotropy of the hydrogel network structure and morphology is affected by the flow behavior, in order to elucidate the observed macroscopic flow properties. The orthogonal time dependent moduli increase above a certain shear magnitude indicating additional bond formation. The correlated stress relaxation experiments reveal two relaxation modes corresponding to the terminal and the bond breakage and reformation timescales. The later mode is accompanied by temporarily increasing stresses indicating a bond reformation.

Thursday 9:05 Crestone A

GS28

### **Viscoelastic behavior of asphalt-polyolefin physical gels**

Xiaofei Zhao<sup>1</sup>, Tharanga Dissanayaka<sup>2</sup>, Minhazur Rahman<sup>3</sup>, Gordon F. Christopher<sup>3</sup>, Sanjaya Senadheera<sup>2</sup>, and Ronald Hedden<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>2</sup>*Civil, Environmental, and Construction Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>3</sup>*Mechanical Engineering, Texas Tech, Lubbock, TX 79409, United States*

Asphalts are complex mixtures of hydrocarbons and heteroaromatics that are widely employed as binder materials in flexible pavements. In order to extend pavement lifetime, the binder material must provide resistance to both rutting (in warm weather) and cracking (in cold weather). Polymeric materials have widely been employed as modifiers, especially copolymers of styrene and butadiene. However, relatively little work has examined crystallizable polymers as modifiers for asphalts. Our recent work has revealed that a slightly crystallizable copolymer of propylene (PP) and ethylene (PE) can enhance the rheological characteristics (viscosity, stiffness, elasticity) of asphalt binders in the rutting temperature range of 50 to 70 °C without requiring major modifications to pavement mix design or processing conditions. The PP/PE copolymer is miscible with the asphalt at a concentration of 5 % by weight at the "hot mix" temperature of 163 °C, producing only a modest increase in steady shear viscosity. However, as the polymer/asphalt solution cools, a robust physical gel forms, dramatically altering rheological behavior at lower temperatures. The polymer also induces phase separation into asphaltene-rich and maltene-rich phases during cooling, while formation of semicrystalline polymer fibrils stabilizes the morphology. These materials exhibit rubber-like elastic recovery near room temperature, leading to performance enhancements in both freshly prepared and aged asphalt concretes. The rheological behavior of the polyolefin-modified asphalt binders has been characterized in steady and dynamic shear, while stiffness and creep were evaluated by bending beam rheometry at temperatures < 0 °C. Optical and fluorescence microscopy have been applied to characterize the morphological features of the gels, which govern the observed rheological phenomena.

Thursday 9:30 Crestone A

GS29

### **Phase behaviour of block copolymer Pluronic: A rheological perspective**

Khushboo Suman, Sagar Sourav, and Yogesh M. Joshi

*Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India*

We study temperature induced phase change of a block copolymer polyoxyethylene polyoxypropylene-polyoxyethelene (PEO<sub>100</sub>-PPO<sub>65</sub>-PEO<sub>100</sub>, Pluronic F127) having concentration in a range: 20 weight % to 35 weight %. While this temperature dependent phase change visually appears like a liquid-soft solid transition, and the soft solid state has been termed as gel in the literature, there is a debate regarding precise microstructure of the soft solid state. In this work, we carry out frequency sweep at various temperatures on F127 solution on different days since preparation of a solution. We observe that, irrespective of a concentration in the explored range, aqueous solution of F127 undergoes a sol-gel transition characterized by frequency independent  $\tan \delta$  at the critical state. Such behavior suggests presence of space spanning percolated fractal network at the critical state. A temperature at which the critical state is observed, on one hand, decreases with increase in time elapsed since preparation of solution. On the other hand, the same is observed to decrease with increase in concentration of F127. The value of  $\tan \delta$  at the critical point also

leads to fractal dimension of the percolated gel, which interestingly shows a minimum with respect to concentration over the explored range. We also estimate heat of gelation associated with F127 solution and find it to be in close agreement with the values reported in the literature. Finally, based on the rheological studies we construct a phase diagram, and discuss the similarities and differences with respect to various phase diagrams of F127 solution available in the literature.

Thursday 10:25 Crestone A

GS30

### **Rheological characteristics of water/oil/pluronic block copolymer mesophases**

Sahar Qavi and Reza Foudazi

*Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

Amphiphilic molecules self-assemble at water/oil interface and form mesomorphic structures, known as mesophases. The self-assembled mesophases take various forms such as lamellar, hexagonal, and bicontinuous cubic that provide a broad range of applications in drug delivery, templating synthesis, and nanostructure production. Several methods such as polarized light microscopy, small angle X-ray scattering, cryogenic microscopy, and nuclear magnetic resonance have been utilized to characterize the structure of mesophases. However, rheological techniques are essential for investigation of the in-situ evolution of structure and its relationship with processability of mesophases. The aim of this work is to provide a rheological fingerprint of such mesostructures. We study the steady-shear, small-amplitude oscillatory shear (SAOS), and small-amplitude oscillatory shear (LAOS) flow behaviors of lamellar and hexagonal mesophases of Pluronic/water/oil. While both lamellar and hexagonal mesophases show shear thinning and strain stiffening behavior, the extent of shear thinning and strain stiffening is different in these two cases. In addition, soft glassy rheology (SGR) model is used to model the rheological behavior.

Thursday 10:50 Crestone A

GS31

### **Rheological and tribological behavior of soft complex gels**

Barbara V. Farias, Lilian C. Hsiao, and Saad A. Khan

*Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, United States*

Oil-in-water (o/w) emulsions with polymers and phospholipids are widely used for personal care products due to their thickening and emulsifying properties. However, the underlying mechanism through which this complex emulsion affects rheological and tribological characteristics is not well understood. We investigate systems containing a hydrophobically modified polymer, phospholipids, and o/w emulsions and find that bulk rheology of the studied systems plays a role in frictional behavior. We used dynamic and steady shear experiments to study systems containing the hydrophobically modified polymer and found that their rheological behavior is consistent with concentrated microgel systems. For systems containing phospholipids and polymer, the elastic modulus shows a two-fold increase if compared to systems without phospholipids, leading us to hypothesize that hydrophobic interactions are occurring between the polymer and phospholipids. The yield stress for all the studied systems is similar, except for the o/w emulsion with phospholipids that shows a higher yield stress. In addition, we characterized the tribological behavior using a soft model contact consisting of polydimethylsiloxane (PDMS). In the elasto-hydrodynamic lubrication regime, which occurs at higher speeds where the contacts are fully separated by a lubricating film, the friction coefficients increase with increasing sample viscosity. Systems containing the polymer and phospholipids showed a lower friction coefficient than Newtonian fluids at the boundary regime, where the contacting asperities dictate the frictional behavior. In order to understand this behavior, adsorption studies with quartz crystal microbalance were performed. The results showed that phospholipids are being adsorbed onto the PDMS surface, with the hydrated heads causing a decrease in the friction coefficients at low entrainment speeds due to a hydration-lubrication mechanism.

Thursday 11:15 Crestone A

GS32

### **Self-assembly, structure and rheology of polyelectrolyte complex hydrogels**

Samanvaya Srivastava, Adam Levi, David Goldfeld, and Matthew Tirrell

*Institute for Molecular Engineering, The University of Chicago, Chicago, IL 60637, United States*

Polyelectrolyte complexes (PEC) form when oppositely charged polyelectrolyte chains spontaneously associate and phase separate in aqueous media. Combining one or both polyelectrolyte chains with a neutral polymer restricts bulk phase separation of the PECs, and thus leads to self-assembled structures with PEC domains surrounded by neutral polymer coronae, forming micelles and hydrogels. The PEC domains in these assemblies can encapsulate therapeutics as well as genetic materials and thus have tremendous potential in drug delivery and tissue engineering applications. We will present insights on the equilibrium structure and bulk properties of PEC hydrogel assemblages comprising oppositely charged block copolyelectrolytes. Detailed investigations of structure-rheology relationships of hydrogels comprising model block copolyelectrolytes with oppositely charged functionalized polyallyl glycidyl ethers as ionic and polyethylene glycol as neutral blocks will be discussed. X-ray scattering investigations providing a comprehensive structural description of these materials will be presented, indicating large-scale ordering of the nanoscale PEC domains at high polymer loadings, characterized by a disorder-order transition, followed by morphological transitions with increasing polymer loading. Macroscopic effects of the nanoscopic structure will be elucidated via a mapping of the hydrogel flow properties on the PEC morphology landscape. The effect of key parameters such as polymer block lengths and concentration on the relationship between the nanoscale PEC morphology and equilibrium material properties will also be discussed.

## Symposium NF Non-Newtonian Fluid Mechanics

Organizers: Paulo Arratia and Chris Dimitriou

Thursday 8:40 Crestone B

NF35

### **A theoretical framework for steady-state rheometry in generic flow conditions**

Giulio G. Giusteri and Ryohei Seto

*Mathematical Soft Matter Unit, Okinawa Institute of Science and Technology, Onna, Okinawa 9040495, Japan*

We introduce a general representation of the stress tensor for incompressible fluids in terms of its components on a tensorial basis adapted to the local flow conditions, which include extensional flows, simple shear flows, and any type of mixed flows. Such a basis is determined solely by the symmetric part of the velocity gradient and allows for a straightforward interpretation of the non-Newtonian response in any flow geometry. In steady flow conditions, the material response functions that represent the components of the stress on the adapted basis generalize and complete the classical set of viscometric functions used to characterize the response in simple shear flows. Such a general representation is effective in coherently organizing and interpreting rheological data from laboratory measurements and computational studies in non-viscometric steady flows of great importance for practical applications. We finally discuss how the decomposition of the stress in various terms with clearly distinct roles can be exploited in developing constitutive models for non-Newtonian fluids.

Thursday 9:05 Crestone B

NF36

### **Revisit the elongational viscosity of FENE dumbbell model**

Hiroshi Watanabe and Yumi Matsumiya

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

It is well known that  $\eta_E$  of the Hookean dumbbell model increases with increasing  $\dot{\epsilon}$ ; and finally diverges to infinite on approach of  $\dot{\epsilon}$  to  $1/2 \tau_{eq}^H$ , where  $\tau_{eq}^H$  is the viscoelastic relaxation time of the Hookean dumbbell that does not change with  $\dot{\epsilon}$ . This divergence of  $\eta_E$  reflects infinite extensibility of the Hookean dumbbell. Real polymer chains obviously have the maximum stretch limit, so that the dumbbell model with a finite extensibility was developed almost a half century ago as a model for those chains under strong flow. This model exhibits the FENE effect under strong flow to provide  $\eta_E$  with the strain-hardening feature but without any divergence. This FENE dumbbell model has been mathematically analyzed in detail and is now well established. Nevertheless, stiffening of the FENE dumbbell could/should largely increase the viscosity. Thus, it is still desired to explain how the stiffening suppresses the divergence of  $\eta_E$ . From this point of view, this study focuses on the effective relaxation time  $\tau_{eff}^F$  of the FENE dumbbell under steady elongational flow. It turned out that the stiffening of the FENE dumbbell leads to a decrease of  $\tau_{eff}^F$  in proportion to  $\dot{\epsilon}^{-1}$  at  $\dot{\epsilon} > 1/2 \tau_{eq}^H$ , and this decrease of  $\tau_{eff}^F$  allows the effective Weissenberg number of the FENE dumbbell under flow,  $Wi_{eff}^F = \dot{\epsilon} \tau_{eff}^F$ , to stay below a critical value of  $\sim 1/2$  even for  $\dot{\epsilon} \rightarrow \infty$ . This limited increase of  $Wi_{eff}^F$  allows the FENE dumbbell to change its conformation just slightly even for a large increase of  $\dot{\epsilon}$ ; from  $1/2 \tau_{eq}^H$  to any higher value, which naturally leads to the lack of divergence of  $\eta_E$ .

Thursday 9:30 Crestone B

NF37

### **Out-of-plane rotational motion in shear flow of polymer melts and solutions**

Mohammad H. Nafar Sefiddashti, Carl N. Edwards, Brian J. Edwards, and Bamin Khomami

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

This presentation focuses on the rotational motion of linear chain molecules undergoing strong shear flow in both dense melts and dilute solutions. Nonequilibrium molecular dynamics and Brownian dynamics simulations of these apparently very different liquids reveal startlingly similar behavior under strong shear. Namely, the molecules experience cycles of extension and retraction at characteristic timescales that are determined by the strength of the imposed shear; however, contrary to expectations, the molecules prefer to rotate in the flow-neutral direction rather than in the shear-gradient plane. The reason for this appears to be that in the flow-neutral plane the velocity is constant, reducing the effective shear force from the chain constituents and thereby allowing the molecules to assume more statistically probable configurations. In the flow-gradient plane, on the other hand, the effectively strong shear forces induce stretching and alignment, as one would expect from the numerous flow-aligning models of rheological behavior that have been developed over the years. In essence, random Brownian fluctuation of the chain ends result in different effects, on average, depending on the flow plane into which they are nudged: chain ends pushed into the flow-gradient plane experience shear forces that tend to stretch and reorient the chains, whereas chain ends pushed into the flow-neutral plane retract towards highly coiled configurations because they experience reduced shear forces. These effects are similarly manifested by the conformation and radius of gyration tensors of both melts and dilute solutions, and give rise to non-zero first and second normal stress differences that show almost identical trends. These and further results will be discussed in detail in this presentation.

Thursday 10:25 Crestone B

NF38

**Open-ended problems in flow of complex fluids**Suraj S. Deshmukh*The Dow Chemical Company, Lake Jackson, TX 77566, United States*

Many chemical products that we use everyday are highly complex fluids that contain dispersed solids, flow modifiers, surface active agents, fillers, polymers, colorants, solvents etc. This concoction of materials leads to a complex flow behavior under various usage, shipping, storage and environmental conditions, many of which are not well understood. Some examples of these products include adhesives, thermoplastics, detergents, agrochemicals, cement pastes and paints. Flow & interfacial behavior of these complex fluids can be a key factor in the application performance and consumer satisfaction with these products. In this talk, I will use videos, images and rheological characterization of these ubiquitous products to describe some of these complex flows. I will also outline some of our efforts in using a scientific and statistical approach in understanding this behavior as well as strategies used to modify flow properties to meet those needs. I will describe the use of rheology, imaging as powerful tools to characterize these systems under various time, temperature and storage conditions. However, rheological characterization of these systems is also fraught with many complications and hence I will endeavor to outline few of these open-ended flow problems that remain important but not well understood.

Thursday 10:50 Crestone B

NF39

**Exact-solution for cone-plate viscometry**A. Jeffrey Giacomin and Peter H. Gilbert*Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada*

The viscosity of a Newtonian fluid is often measured by confining the fluid to the gap between a rotating cone that is perpendicular to a fixed disk. We call this experiment cone-plate viscometry. When the cone angle approaches  $\pi/2$ , the viscometer gap is called narrow. The shear stress in the fluid, throughout a narrow gap, hardly departs from the shear stress exerted on the plate, and we thus call cone-plate flow nearly homogeneous. In this paper, we derive an exact solution for this slight heterogeneity, and from this we derive the correction factors for the shear rate on the cone and plate, for the torque, and thus, for the measured Newtonian viscosity. These factors thus allow the cone-plate viscometer to be used more accurately, and with cone-angles well below  $\pi/2$ . We find cone-plate flow field heterogeneity to be far slighter than previously thought. In this paper, we then use our exact solution to arrive at the exact solution for the temperature rise, due to viscous dissipation, in cone-plate flow subject to isothermal boundaries.

Thursday 11:15 Crestone B

NF40

**Experimental and numerical modeling of the rolling process of potato dough**Shirley O. Echendu*Department of Mechanical Engineering, Imperial College London, London, London SW7 2AZ, United Kingdom*

In the rolling process of potato dough, the material undergoes combined shearing and extension conditions which potentially leads to tearing of the material and therefore poor crisp quality. In this study, a predictive model is developed, investigating the effect of processing on the potato dough through analysis of pressure profiles and stress fields under various processing conditions. An experimental and computational simulation of the rolling process of the potato dough were performed. For the computational model, a 3D single roll setup is investigated to obtain the exit thickness and the results now forms an initial condition for a 3D double roll setup. The dough is modelled as a visco-hyperelastic homogeneous material using van der Waals strain energy function. Operating conditions were varied and analysed in the form of the effect of roll gap and speed ratio of the rollers.

Thursday 11:40 Crestone B

NF41

**A general approach on the quantification of continuous flows of non-Newtonian fluids based on the energy balance**Hye Kyeong Jang and Wook Ryol Hwang*Gyeongsang National University, Jinju, Republic of Korea*

In this work, we propose a systematic approach in quantifying the effective viscosity, effective shear rate and pumping characteristics of pressure-driven continuous flows of non-Newtonian fluids in general flow geometries based on the energy balance. Only two flow constants (i.e., the coefficient of effective shear rate and the coefficient of energy dissipation rate), which depend solely on the flow geometry, are employed to quantify flow characteristics of continuous flow systems, independent of viscosity behaviors of a shear-thinning fluid. A similar approach based on the energy dissipation rate, so-called Metzner-Otto correlation [Metzner and Otto, *AIChE J.*, vol. 3, p. 3-10] has been available for more than sixty years in a confined flow of agitator without rigorous derivation. In the present work, we extend the original Metzner-Otto correlation to continuous flows and begin with analytical derivation for this method in a circular pipe flow. Having validated analytically, we apply the present quantification method with the two flow constants to more general types of flows with various viscosity models (Newtonian, power-law, Carreau and Herschel-Bulkley models) such as an axisymmetric expansion/contraction flow with various expansion ratios and a flow in a Kenics mixer in order to show its accuracy and feasibility.

The authors acknowledge the financial supports from the National Research Foundation of Korea (NRF-2016R1A2B4014326).

## Poster Session

### Symposium PO Poster Session

Organizers: Jim Gilchrist and Scott Roberts

Wednesday 6:30 Cripple Creek Ballroom

PO2

#### **Rheological measurements for prediction of toothpaste properties: Pumping, squeezing and shape retention**

Amit Ahuja, Giannina Luisi, and Andrei Potanin  
*Colgate-Palmolive, Piscataway, NJ, United States*

In the present work, complex rheological behaviors of several commercially available and lab-made model toothpastes are examined. Narrow-gap Couette concentric cylinders and wide-gap vane-cup geometries are used to generate flow curves with different flow histories and other rheological parameters. In order to study processability of these toothpastes, a capillary rheometer equipped with pipes of different lengths is used for pressure drop measurements which are compared to the pressures calculated from the equilibrium flow curves. Evidence of wall slippage is noted which appears stronger for rheologically thinner pastes, particularly at lower flow rates. A tube extrusion apparatus is used to measure the force required to squeeze toothpaste out of their tubes. Thus, measured force correlates with the squeezing pressure calculated using the flow curves measured from rest. A custom-made experimental set up is used to quantify retention of shape of a toothpaste ribbon on a brush in a test reminiscent of slump test. It is demonstrated that the degree of shape retention correlates with the yield stress. Different definitions of the yield stress are compared of which the one based on stress overshoot in step-shear test best correlates with the shape retention.

Wednesday 6:30 Cripple Creek Ballroom

PO3

#### **Rheological enhancement of artificial sputum medium**

Mingyang Tan, Yating Mao, and Travis W. Walker  
*CBEE, Oregon State University, Corvallis, OR 97331, United States*

Microscopic rheology enables the characterization of the microenvironment of biofluids, such as sputum from cystic fibrosis (CF) patients. As noninvasive collection of mucus for fundamental research is difficult without contamination, we have created a synthetic biofluid alternative that is a combination of artificial sputum medium (ASM) and xanthan gum (XG). The macroscopic rheological study of ASM showed that the storage and loss moduli are at least two orders of magnitude lower than those values of CF sputum, and the microscopic rheology showed that ASM is a purely-viscous fluid. The addition of XG provides a tunable parameter to the synthetic recipe that enables rheological properties that are mechanically consistent with real sputum. Probe particles that were suspended in a media of ASM and XG displayed a subdiffusive behavior at short time scales with a diffusive exponent that decreased with an increase in concentration of XG. At long time scales, particles that were suspended in ASM+XG with a concentration of XG of 0.1% to 0.4% displayed diffusive behavior. While in more concentrated samples (0.5% and 1.0%), the particles were constrained inside local elastic cages. The elastic and viscous moduli that were obtained via the generalized Stokes-Einstein relation (GSER) showed consistently lower moduli than the values that were obtained from rotational rheometry. The discrepancy suggests that the solutions of XG have a hierarchical structure that better represents the weakly associated microstructure of mucus that is found in real sputum.

Wednesday 6:30 Cripple Creek Ballroom

PO4

#### **Effects of formulation and human saliva on the rheological and tribological behaviors of acid milk gels, a model yogurt system**

Helen S. Joyner and Maryam Baniasadidehkordi  
*875 Perimeter Dr., University of Idaho, MOSCOW, ID 83844, United States*

Food texture is an important factor in consumer acceptance, particularly for reduced-calorie food products. Food composition and the presence of saliva can affect food structure and rheological behaviors, thereby affecting texture perception. Thus, the objective of this study was to determine the effect of different ingredients and saliva on acid milk gel rheological and tribological behaviors. Twenty-four acid milk gels (a yogurt model system) were made by mixing skim milk, cream, skimmed milk powder (0-2.8% w/w), sweet whey protein isolate (0-2.8% w/w), and carbohydrate hydrocolloids (locust bean gum, cellulose gum, potato and corn starch, 0-1.55% w/w). The mix (total fat content of 0-3.5% w/w) was pasteurized at 85°C for 30 min, homogenized at 10,000 RPM for 1 min, and cooled down to 42.2°C. Glucono-delta-lactone was added and the mix was incubated at 42.2°C for 4 hr to reach a pH of 4.55-4.60. The gel was broken after incubation and the samples stored at 4°C overnight. Shear rate sweeps, strain sweeps and frequency sweeps were performed at 8°C and 25°C to evaluate flow and viscoelastic properties, and tribological testing was performed at 25°C with and without human whole saliva for all samples. Two-tailed t-tests and a two-way ANOVA were performed to assess saliva, temperature and hydrocolloids effects. Sample viscosity and viscoelastic moduli decreased with added saliva, increased temperature, or both but changes were not significant for samples with added saliva. Most samples tested with saliva showed significantly lower friction coefficients than samples tested without saliva. Confocal images showed fat coalescence and an aggregated protein network for samples with

hydrocolloids and added saliva. Overall, both formulation and saliva had significant impact on acid milk gel microstructures and mechanical behaviors. The results of this study will help food manufacturers design reduced-fat products with similar textures to their full-fat counterparts.

Wednesday 6:30 Cripple Creek Ballroom

PO5

### **Fibrinogen adsorption onto phospholipid monolayers: Evolution and stiffening**

Ian Williams and Todd M. Squires

*University of California Santa Barbara, Santa Barbara, CA, United States*

All mammals rely on lung surfactant (LS) to reduce surface tension at the alveolar interface and facilitate respiration. In acute respiratory distress syndrome (ARDS), LS is inactivated and elevated levels of blood plasma proteins including fibrinogen are found in the alveolar space. Motivated by the mechanical role fibrinogen may play in LS inactivation, we measure the interfacial rheology of mixed monolayers of fibrinogen and dipalmitoylphosphatidylcholine (DPPC), the main constituent of LS, and compare these to the single species monolayers. DPPC is ineffective at displacing preadsorbed fibrinogen, and the resulting mixed monolayer has a strongly elastic shear response. In contrast, the effectiveness of a pre-existing DPPC monolayer to prevent fibrinogen adsorption depends upon its surface pressure. At low surface pressures, DPPC monolayer penetration by fibrinogen results in a system with a mixed viscoelastic shear response. As initial surface pressure is increased, this response becomes increasingly viscous-dominated and the monolayer retains more of its DPPC-like character. Fluorescence microscopy reveals that the resulting mixed monolayers exhibit qualitatively different morphologies under these two mixing protocols. Insight into the mechanisms and consequences of LS inactivation by fibrinogen may suggest improved therapies for the treatment of disorders such as ARDS.

Wednesday 6:30 Cripple Creek Ballroom

PO6

### **Dynamic study of circular DNA by bulk rheology**

Dejie Kong<sup>1</sup>, Sourya Banik<sup>1</sup>, Michael J. San Francisco<sup>2</sup>, Rae M. Robertson-Anderson<sup>3</sup>, and Gregory B. McKenna<sup>1</sup>

*<sup>1</sup>Department of Chemical Engineering, Texas Tech University, Lubbock, TX, United States; <sup>2</sup>Department of Biological Sciences, Texas Tech University, Lubbock, TX, United States; <sup>3</sup>Department of Physics and Biophysics, University Of San Diego, San Diego, CA 92110, United States*

Abstract: Circular polymers behave differently from corresponding linear ones due to the absence of free chain ends. In this work we study the dynamic properties of entangled circular polymers using rheological measurements on circular DNA in solution. Compared to synthetic circular polymers, the polydispersity index of DNA is one, and a smaller amount of linear contamination can be achieved during the preparation of samples. More importantly, the circular DNAs can, in principle, achieve the entangled regime more easily than synthetic polymers due to their large size which ranges from  $10^6$  g/mol to  $10^8$  g/mol, while the maximum size of synthetic circular polymer studied so far is  $3.9 \times 10^5$  g/mol. In this work, the circular DNA of different sizes are extracted from different kinds of bacteria, such as E.Coli and BACs. In the work we are also using particle tracking microrheology because it can use less sample and broadens the frequency regime to higher frequency than achievable with conventional rotational rheology. Results of the microrheology and macrorheology are compared using the Generalized Stokes-Einstein equations. Keywords: Circular DNA; Entangled Polymers; Bulk Rheology; Microrheology Acknowledgements: The authors thank the National Science Foundation under grant CBET 1603943 and the J.R. Bradford endowment at Texas Tech University, each for partial support of this project.

Wednesday 6:30 Cripple Creek Ballroom

PO7

### **Quantifying enzymatic degradation of uterine fibroid tissue using rheology**

Ria D. Corder<sup>1</sup>, Robert B. Vachieri<sup>2</sup>, Darlene K. Taylor<sup>2</sup>, Sashi R. Gadi<sup>3</sup>, John M. Cullen<sup>3</sup>, Friederike L. Jayes<sup>4</sup>, and Saad A. Khan<sup>1</sup>

*<sup>1</sup>Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States; <sup>2</sup>Chemistry and Biochemistry, North Carolina Central University, Durham, NC 27707, United States; <sup>3</sup>Population Health and Pathobiology, North Carolina State University, Raleigh, NC 27695, United States; <sup>4</sup>Obstetrics and Gynecology, Duke University, Durham, NC 27710, United States*

Uterine fibroids are benign tumors composed of altered, disordered, and crosslinked collagens which occur in 70-80% of women before age 50, and can interfere considerably with daily life by causing bleeding and pain. Fibroids are the leading cause for hysterectomy, and \$21 billion in healthcare expenditures are spent annually in the US for treatment and management of this disease. Fertility-preserving treatment options, such as hormone or drug therapies, are currently limited in effectiveness. Highly purified collagenase *Clostridium histolyticum* (CCH) has received FDA approval for two medical indications involving digestion of interstitial collagens to reduce tissue stiffness. A previous *ex-vivo* study on posthysterectomy fibroid samples provided proof-of-principle evidence that CCH can digest collagens within uterine fibroids. In this study, we used dynamic rheology to quantify the degree of *in-vivo* degradation of uterine fibroid tissue, and then compared the rheology to histology. Fibroids were obtained from human women undergoing hysterectomies, surgically implanted into mice, and injected with either varying amounts of CCH in saline or a pure saline control. At set day intervals, fibroids were removed and bisected. Half of the sample was histologically stained and the other was frozen and saved for rheology. Fibroids were measured while under immersion in saline using 8mm crosshatched top and bottom plates on a DHR-3 rheometer. To evaluate repeatability and optimize measurement conditions, chicken breast meat was used as a model tissue. We show that comparisons can be made between bulk rheological measurements and tissue physiology. The role of enzymatic hydrolysis time on tissue rheology and physiology will also be discussed.

Wednesday 6:30 Cripple Creek Ballroom

PO8

### **Drag reducing polymers (DRPs) reduce rigid red blood cell traffic in bifurcating microchannel blood flow**

Dan Crompton, Shushma Gudla, Maritza Jimenez, Prithu Sundd, and Marina V. Kameneva

*Bioengineering, University of Pittsburgh, Pittsburgh, PA 15219, United States*

Sickle cell disease (SCD) affects over 100,000 patients in the US and involves the pathogenic polymerization of deoxygenated hemoglobin leading to the sickling of red blood cells (RBCs). Sickled RBCs have reduced deformability and higher affinity to adhere to endothelial cells, leukocytes and platelets, resulting in blood vessel occlusion (vaso-occlusion) and is the primary reason for emergency medical care among SCD patients. SCD complications stem in part from the Fåhræus effect, where less or non-deformable cells such as sickled RBCs tend to marginate toward the vessel wall and are more likely to enter daughter branches at vessel bifurcations. Conversely, normal RBCs naturally tend to shift toward the center of vessels (Fåhræus effect). Drag reducing polymers (DRPs) are a unique class of high molecular weight blood-soluble molecules which have been shown to inhibit the inward radial migration of RBCs, leading to their even distribution along vessels. We believe this would also cause a more even distribution of rigid RBCs in small vessels and will decrease the traffic of rigid RBCs into bifurcations; thereby reducing the potential for vaso-occlusion in SCD patients. Normal and rigid RBCs (rigidified via heat treatment at 52°C for 30 min) were pooled together in a 50/50 suspension by hematocrit at 30% total hematocrit. Suspensions, both with and without 10 ppm of the DRP polyethylene oxide (PEO), MW 4,000 kDa, were driven at 5-10  $\mu\text{L}/\text{min}$  (max shear rate: 1300  $\text{s}^{-1}$ , Reynolds number  $<0.5$ , pressure drop  $<6$  mmHg) through a bifurcating PDMS microchannel and the output cells analyzed using a Linkam shearing stage. The addition of DRPs caused the number of rigid RBCs entering a single branch to decrease by over 10%. We expect to significantly increase these effects with each additional bifurcation in our ongoing work.

Wednesday 6:30 Cripple Creek Ballroom

PO9

### **Using simultaneous rheology and molecular spectroscopy to evaluate melt processability for pharmaceutical hot-melt extrusion**

Nathan C. Crawford

*Thermo Fisher Scientific, Denver, CO, United States*

Hot-melt extrusion (HME) has been used as a processing technology in the plastic, rubber, and food industries for decades. More recently, HME has been adopted by the pharmaceutical industry as a continuous manufacturing technique, where polymeric excipients are pumped using a rotating screw (or screws) at temperatures above their glass transition temperature (sometimes above their melt temperature) to achieve molecular level mixing of the polymeric materials, active pharmaceutical ingredients (APIs), and other additives. This continuous molecular-level mixing process converts the entire system into a molecularly dispersed solid-solution, which can enhance drug bioavailability, stability, and dissolution of low solubility drugs. As a result, HME is an emerging drug processing technology that can produce all common dosage forms (tablets, capsules, films, implants, etc.) as well as give way for new and innovative drug-eluting products.

The melt processability of polymers and API-polymer mixtures within the HME process is governed by the rheological behavior of the materials involved. In order to properly design and optimize the HME process, the relationship between viscosity, shear rate, and temperature must be established for all polymeric components and API-polymer mixtures. Thus, rheological characterization is crucial for evaluating material processability within the extrusion process.

Here, we examine how the rheological behavior of a polymeric excipient is altered by the addition of an API using both classic rheological measurements, as well as simultaneous rheology with *in situ* molecular spectroscopy.

Wednesday 6:30 Cripple Creek Ballroom

PO10

### **Analysis of shear-induced erythrocyte deformation following intracellular content replacement**

Luke A. Ziegler, Katrina B. Zougari, Jonathan H. Waters, and Marina V. Kameneva

*Bioengineering, University of Pittsburgh, Pittsburgh, PA 15219, United States*

We have developed a method of removing erythrocyte intracellular contents and subsequently replacing them with high concentrations of exogenous protein. While this platform technology has a variety of potential applications such as encapsulation of pharmaceuticals for conversion of erythrocytes into intravascular delivery vehicles, our primary focus has been on development of treatments for hemoglobinopathies, most notably sickle cell disease. In order to be viable in circulation it is critical that the modified erythrocytes maintain the ability to deform under physiological shear stress, as membrane damage associated rigidification will prevent perfusion of the microvasculature and result in premature removal by the reticulo-endothelial system. In this poster we present proof-of-concept results of hemoglobin replacement using healthy bovine erythrocytes. Following partial hemoglobin replacement, modified erythrocytes were analyzed using rheological methods. Modified erythrocyte deformability was analyzed by a Linkam shearing stage device, with elongation index quantification performed using Image J. Viscosity was measured using Brookfield cone and plate viscometer. Preliminary results indicate relatively trivial changes in these rheological parameters following erythrocyte intracellular content replacement.

Wednesday 6:30 Cripple Creek Ballroom

PO11

**Determination of macroscopic rheological properties of human mesenchymal stem cell laden poly(ethylene glycol) hydrogels**Michelle S. Mazzeo<sup>1</sup> and Kelly M. Schultz<sup>2</sup><sup>1</sup>Bioengineering, Lehigh University, Bethlehem, PA 18015, United States; <sup>2</sup>Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Developing hydrogels that harness human mesenchymal stem cells' (hMSCs) natural tendency to migrate to wound sites and regulate healing produce implantable scaffolds that enhance wound healing and prevent the development of critical wounds. By studying the material's structure and rheological properties, we can develop hydrogels that withstand necessary stresses and maintain high cellular viability. In our work, our hydrogels, which consist of 4-arm star poly(ethylene glycol) (PEG) functionalized with norbornene and a matrix metalloproteinase (MMP) degradable peptide sequence, use thiol-ene click chemistry for 3D hMSC encapsulation. MMPs are cell-secreted enzymes that degrade the peptide cross-linker sequence. This enables cells to shape their microenvironments during basic cellular processes, such as motility. Unlike biological scaffolds, synthetic PEG hydrogels do not provide unknown complex biological cues, providing a well-defined environment to study cell-material interactions. Therefore, this work characterizes the macroscopic material properties of these hydrogels using bulk rheology, in order to optimize hydrogel design and improve its effectiveness as a wound healing material. Hydrogel stiffness is monitored as it affects cell motility. As cells degrade the scaffold, the storage moduli decreases more than twofold within the first 24 to 48 hours after cell encapsulation. Hydrogels without cells have larger storage moduli than hydrogels with cells at a given time, indicating cell laden scaffolds are degraded by cell-secreted enzymes. Additionally, viability assays show that cell viability remains high for extended periods of time within the hydrogel, and cells survive stresses applied from the rheometer. By determining material properties and cell viability over extended periods of time, these macroscopic rheological findings can be combined with microscopic rheological results to design hydrogels that are optimized for increasing the rate of wound healing.

Wednesday 6:30 Cripple Creek Ballroom

PO12

**Quantitative predictions of 2D and 3D dam-break cases using  $\mu(I)$  rheology: Quasi static or inertial regimes and scaling laws**Stéphanie Riber, Romain Castellani, Elie Hachem, and Rudy Valette

CEMEF, MINES ParisTech, PSL Research University, Sophia Antipolis, PACA 06904, France

In this work, we present a numerical method to predict granular columns collapse, for 2D or 3D cases, using the  $\mu(I)$  rheology. To do so, we solve these granular flows using a continuous approach based on the finite element method: we solve momentum and mass conservation equations, in which we introduce the  $\mu(I)$  constitutive equation. We show that the  $\mu(I)$  rheology can capture the two spreading regimes predicted by (Lajeunesse et al.) and (Lube et al.), which depend on the initial aspect ratio 'a' of the columns: first, a linear regime for small values of 'a' and second, a power-law regime (sub-linear) for higher 'a' values, that originates in the energy dissipation at the impact. In addition, recent experimental and numerical studies on high aspect ratio columns (typically, 'a' > 30) will be analyzed, showing more complex physics with, for example, the apparition of successive waves at the surface of the heap.

Finally, a sensitivity analysis of the model, for different rheological constants, is performed. We also demonstrate, introducing another length scale, that the initial aspect ratio is not the only spatial parameter accounting for column spreading dynamics.

Keywords: granular materials,  $\mu(I)$  rheology, numerical simulations, dam break.

Wednesday 6:30 Cripple Creek Ballroom

PO13

**Diffusion and equilibrium structure of bidisperse colloidal suspensions confined by a spherical cavity**Emma Gonzalez<sup>1</sup>, Christian Aponte-Rivera<sup>2</sup>, and Roseanna N. Zia<sup>1</sup><sup>1</sup>Chemical Engineering, Stanford University, Stanford, CA 94305-4125, United States; <sup>2</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Recent simulations of monodisperse colloidal suspensions confined by a spherical cavity demonstrate that both confinement and crowding produce qualitative changes in short- and long-time transport rate processes and equilibrium material properties, arising from structural and dynamical heterogeneity associated with the confining cavity<sup>[1,2,3]</sup>. The theoretical and computational framework developed in these studies set the foundation for studying the dynamics of 3D micro-confined suspensions. However, particle polydispersity in size, shape, and softness play a role in many biophysical confined systems such as the interior of eukaryotic cells<sup>[4]</sup>, but such effects in 3D confinement have received little to no attention in the literature. In the present work, we extend our theory and model to account for size polydispersity, which is known to exert pronounced effects on structure and rheology in unbound suspensions, including viscosity reductions<sup>[5]</sup>, changes in phase behavior<sup>[6]</sup>, and particle size segregation under flow. We present the hydrodynamic coupling functions and computational model for a bidisperse suspension of colloids coupled by many-body hydrodynamic and lubrication interactions to one another and to the confining cavity. We utilize our model to study the combined effects of hydrodynamic interactions, Brownian motion, crowding and particle polydispersity on the equilibrium structure and short time transport properties of spherically confined bidisperse colloidal suspensions.

[1] C. Aponte-Rivera and R. N. Zia, Phys. Rev. Fluids, vol. 1, p. 023301, Jun 2016. [2] Aponte-Rivera C, Su Y, Zia R. N., J. Fluid Mech. In review, 2017. [3] Aponte-Rivera C, Zia R. N. Accurate 2-point microrheology inside a spherical cavity. In preparation. [4] A. S. Verkman, Trends Biochem Sci, vol. 27, no. 1, p. 27, Jan 2002. [5] M. Wang and J. F. Brady, J. Comput. Phys., vol. 306, p. 2382, 2016. [6] D. Semwogerere and E. R. Weeks, Phys. Fluids, vol. 20, p. 043306, Apr 2008.

Wednesday 6:30 Cripple Creek Ballroom

PO14

**Phase transition of jammed suspensions of soft particles glasses in steady and oscillatory shear flows**Fardin Khabaz<sup>1</sup>, Tianfei Liu<sup>1</sup>, Michel Cloitre<sup>2</sup>, and Roger T. Bonnecaze<sup>1</sup><sup>1</sup>*McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78705, United States;* <sup>2</sup>*Laboratoire Matière Molle et Chimie, ESPCI ParisTech, Paris, Paris 75005, France*

We perform particle-dynamics simulation of jammed suspensions of soft particles glasses (SPG) in order to demonstrate SPGs can form different microstructures in steady and oscillatory shear flows. The flow and elastic energy curves of the suspensions with different volume fractions and polydispersity indices are determined in shear flow. Simulations indicate that monodisperse SPGs undergo a transition from a face-centered cubic (FCC) to a hexagonal close-pack (HCP), and polydisperse SPGs transfer from a glassy structure into a layered phase at high shear rates, regardless of the suspension volume fraction. The layers of particles are formed parallel to the flow-vorticity plane after an induction period prior to the structural rearrangement. The induction strain length decreases with the shear rate that implies this process is a shear activated event. The formation of these phases in both monodisperse and polydisperse suspensions is reversible. In addition we show that a single parameter, which is the ratio of the imposed shear rate to the particle elasticity, is sufficient to determine the dynamic state behavior for SPGs of varying polydispersity index and volume fraction. The same phenomenon is also observed in the oscillatory shear simulations. SPGs with a low and high degree of polydispersity transform into HCP and layered phases, respectively, at high shear rates, which is defined as the product of the frequency and maximum strain.

Wednesday 6:30 Cripple Creek Ballroom

PO15

**Uncertainty quantification in computations of a sedimenting sphere in Carbopol**Jaekwang Kim, Piyush K. Singh, Jonathan B. Freund, and Randy H. Ewoldt*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We elucidate how uncertainties in simulation propagate through a Generalized Newtonian Fluid (GNF) drag prediction for a sedimenting sphere. We use a Carreau model and a regularized Bingham model to compare to experiments of millimetric spheres settling under gravity in aqueous suspensions of Carbopol 940 microgel particles. Computations use a finite element method with adaptive mesh refinement (using the deal.II Finite Element Library) to solve for the highly localized flow. We analyze uncertainties in model-predicted drag force combining model parameter uncertainty with measurement uncertainties from the experiment. For a given sphere velocity we compute drag, and find that its expectation value is larger than the nominal value, owing to the nonlinearity of the governing equations. Yet, even this higher expectation value, with quantified prediction uncertainty, cannot predict the observed experimental drag force, which is larger than predicted by the GNF model. Though this analysis does not replace existing judgement that the GNF model may be insufficient for a sphere settling in Carbopol, we emphasize that the validation process for any rheological model should quantitatively include model-parameter uncertainties in model prediction.

Wednesday 6:30 Cripple Creek Ballroom

PO16

**Mesoscale modeling of transiently networked fluids**Lin Zhou<sup>1</sup> and L.Pamela Cook<sup>2</sup><sup>1</sup>*Mathematics, New York City College of Technology, CUNY, Brooklyn, NY 11201, United States;* <sup>2</sup>*Department of Mathematica Sciences, University of Delaware, Newark, DE, United States*

Modeling of transiently network fluids, such as wormlike micellar solutions has been carried out both at the macroscopic and at the mesoscopic level. Advantages of modeling at the mesoscopic level include avoiding closure approximations, and of relating macroscopic quantities to local properties of the worms such as the stretch, orientation and concentration. In this poster, we present a stochastic dumbbell model of wormlike micellar solutions in which chains of dumbbells can break and reform continuously. The topology of the strands is tracked in time. Flow curves resulting from distinct breakage and reforming energy functions will be presented and discussed. Both linear (Hookean) and nonlinear springs are considered in the simulation.

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PO17

**Multi-chain slip-spring simulation for entangled symmetric star polymer melts**Ankita Pandey and Yuichi Masubuchi*Materials Physics, Graduate School of Engineering, Nagoya University, Nagoya, Japan*

Modeling and simulation of the entangled polymeric system are one of the most challenging research areas in polymer physics. In spite of the notable successes of the tube based theories, there are demands for calculations of a variety of complex and the heterogeneous system. Although bead-spring simulations are a powerful tool for analyzing the dynamics, it is still not feasible to perform simulations of highly entangled polymer systems, due to their long equilibration and relaxation times. Hence there is a need for efficient computer simulation techniques for theoretical development. There is a class of coarse grained description in which the entanglement effect is mimicked by the slip-springs. These approaches successfully reproduced the entangled linear polymeric behavior. However, till now there is no attempt of such modeling and simulation for entangled branch polymeric system. In the present work, we propose a coarse grained approach to simulate entangled branched polymer melt, specifically entangled symmetric star polymer melt. In the slip-springs model, Rouse chains are temporally connected via slip-springs which mimic entanglement. These slip springs slip along the chain and destruct when they slip off from the chain end with a chosen probability. To mimic the arm retraction in entangled symmetric star polymer, we modified this model. When slip spring encounters the branch point of the star polymer, it returns back towards the arm end. The simulated dynamics of star polymer is consistent with that obtained via conventional bead-

spring simulations. We also explored the effect of different functionalities (arm number = 3,4,5) on the dynamics of the entangled symmetric star polymer melt.

Wednesday 6:30 Cripple Creek Ballroom

PO18

### **Modelling and visualizing the flow of standard reference materials for the calibration of rheometers used in the cement and concrete industries**

Nicos S. Martys, William L. George, Steven G. Satterfield, and Chiara F. Ferraris  
*National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

Concrete is the most widely used building material and plays a crucial role in our infrastructure. Because concrete may be pumped, poured and spread, understanding its rheological properties is crucial for its on-site placement. Measuring the rheological properties of cement based materials like mortar and concrete represent a challenge because the presence of solid inclusions (sand or rocks) can lead to flow artifacts that influence measurements. Examples of flow artifacts include shear induced migration, sedimentation, jamming, and slippage due to a weak coupling between the impeller and the material of interest. We have developed standard reference materials (SRMs), with properties similar to that of a fresh mortar and concrete, to help calibrate rheometers. The rheological properties of these SRMs were determined by a combination of experiment and computer simulation. This poster will describe a multi-scale approach used to develop the SRMs. Results will be presented that illustrate some of the typical flow artifacts that developed when simulating the flow of an SRM in an industrial rheometer. How these flow artifacts influence measurements will be shown.

Wednesday 6:30 Cripple Creek Ballroom

PO19

### **Structural analysis of aggregate breakup process under uniaxial extensional flow**

Seung Hui Kim and Kyung Hyun Ahn  
*Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea*

Colloidal aggregates breakage is deeply relevant to comprehend the meaning of heterogeneity with colloidal solution. When colloidal aggregates experience uniaxial elongational flow, the aggregates can split into small fragments with various sizes and configurations. Due to the randomness of fragments, it is necessary to define the breakage efficiency for analyzing or discussing breakage process. In this work, I used Brownian dynamic simulation with DLVO potential as interparticle interaction. An aggregate library containing clusters with size of 300 to 400 and fractal dimensions of 2.25 to 2.48 was used. As structural analysis for this simulation, I used Fourier transform to analyze space frequency of fragments as time goes. Because the main space frequency increases exponentially as time goes, I define the exponent of the exponential curve as the breakage efficiency. While each value of space frequency includes the information of fragment sizes, the breakage efficiency which refers to how the gaps between fragments are getting wider is irrelevant to the sizes of aggregates. The breakage efficiency with flow rate was investigated. Also, the breakage efficiency with respect to interparticle interaction was analyzed.

Wednesday 6:30 Cripple Creek Ballroom

PO20

### **Bayesian information criterion (BIC) for model selection with thixotropic yield stress fluids**

Anthony S. Margotta and Randy H. Ewoldt  
*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We study the use of the Bayesian Information Criterion (BIC), an algebraic approximation of the full Bayesian Inference technique [1], for selecting the most credible constitutive models for given sets of thixotropic yield stress fluid shear rheology data. The technique uses an Occam factor to penalize overparameterized models. We use two case studies, one with steady shear data and another including step down shear rate transient data [2]. In both cases, the BIC quantitatively identifies overparameterized models that fit the data exceedingly well, but are not credible. Surprisingly, it provides evidence that some highly parameterized models can still be credible. For example, with the thixotropy dataset our results based on the BIC suggest that the Wei-Solomon-Larson Stretched Exponential model [3] has more credibility than simpler models, despite having twice as many free parameters (10 versus 5). We discuss limitations of the BIC, as it only approximates the full Bayesian evidence calculation and omits any 'prior' information on expected model parameter values, which is part of the Occam factor weighting in the full Bayesian analysis [1].

[1] Freund, J. B., R. H. Ewoldt, "Quantitative rheological model selection: good fits versus credible models using Bayesian inference," *J. Rheol.* **59**(3), 667-701 (2015). [2] Armstrong, M. J., Beris, A. N., Rogers, S. A., Wagner, N. J., "Dynamic shear rheology of a thixotropic suspension: Comparison of an improved structure-based model with large amplitude oscillatory shear experiments," *J. Rheol.* **60**(3), 433-450 (2016). [3] Wei Y., Solomon M. J., Larson R. G., "Quantitative nonlinear thixotropic model with stretched exponential response in transient shear flows," *J. Rheol.* **60**(6), 1301-1315 (2016).

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PO21

**Study 3-dimensional giant molecules for dynamics beyond 1-D Polymers**Gengxin Liu<sup>1</sup>, Xueyan Feng<sup>1</sup>, Kening Lang<sup>1</sup>, Ruimeng Zhang<sup>1</sup>, Dong Guo<sup>1</sup>, Shuguang Yang<sup>2</sup>, and Stephen Cheng<sup>1</sup><sup>1</sup>*Department of Polymer Science, University of Akron, Akron, OH 44325, United States;* <sup>2</sup>*Center for Advanced Low-Dimension Materials, Donghua University, Shanghai 201620, China*

Other than point-like molecules, or chain-like polymers, we now have 3-dimensional giant molecules which are clusters of molecular nanoparticles. Unlike polymer chains that can always reptate regardless of chain length, there ought to be an upper critical diameter for giant molecules. Above it, giant molecules in bulk would be immobile. We hypothesize this critical diameter is also the critical length scale of the cooperative rearranging region. Then as a platform to study glassy dynamics, 3D structural clusters are more convenient to measure and quantify comparing to the dynamical clusters.

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PO22

**Numerical simulations of thixotropic fluid flows: Some preliminary results**Marleson Ferreira, Giovanni F. Furtado, and Sergio Frey*Mechanical Engineering, UFRGS, Porto Alegre, RS 90070-150, Brazil*

This work performs numerical investigations of thixotropic fluid flows. The thixotropic equation modifies the viscoelastic Oldroyd-B model in order to allow that both viscosity and relaxation time is dependent on the microstructure level. Such an equation is coupled with the usual mass and momentum conservation equations for incompressible materials, and a further evolution equation that takes into account the change rate of the microstructure level. This set of governing equations are approximated by a four-field Galerkin least-squares-like method in term of the structure level parameter, extra-stress, velocity and pressure. Two geometries are herein analyzed, namely a planar channel submitted to a four-to-one abrupt contraction, and a lid-driven cavity. Focusing on the influence of thixotropy, elasticity and yield-stress on flow pattern, the adimensional governing parameters are investigated in wide and relevant ranges. Taking the advantage of the good convergence features of the numerical scheme, all computations make use of an equal-order combination of bi-linear Lagrangian interpolations. Results indicate a strong interlace between elasticity and thixotropy on the position and shape of unyielded regions.

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PO23

**Imbalanced outflows, recirculation and vortex breakdown at a microfluidic T-junction**San To Chan, Simon J. Haward, Kazumi Toda-Peters, and Amy Q. Shen*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

We experimentally and numerically investigate the effects of imbalanced outflows in a dividing microfluidic T-junction, which contains one inlet and two symmetrical outlets. A glass microfluidic T-junction device with width  $w =$  height  $h = 0.4$  mm was produced within a glass block by a novel microfabrication technique called Selective Laser-induced Etching (SLE) [1]. Unlike traditional PMMA or PDMS devices, the use of a geometrically well-defined and structurally rigid glass device allows us to directly look into the channel while performing visualizations in various planes. Here we limit our studies to a Newtonian fluid (water) but the results can be extended to viscoelastic fluids. First we perform micro-Particle Image Velocimetry ( $\mu$ PIV) to directly visualize the formation of a pair of counter-rotating vortices, and show that its mechanism is qualitatively similar to the Dean instability in curved channels. Next we visualize the streamlines generated with balanced and imbalanced outflows for a fixed inlet Reynolds number  $Re = Uw/\nu \sim 133$  (where  $U =$  averaged inlet flow velocity and  $\nu =$  kinematic viscosity), which is below the value previously reported for the vortex breakdown regime ( $Re \sim 320$ ) [2][3], and relate them to numerically predicted pressure distributions along the vortex core. For imbalanced outflows, recirculation zones that resemble several features of vortex breakdown emerge, which we relate to the adverse pressure gradient developed within the vortices. Finally, we demonstrate that indeed vortex breakdown occurs with intermediate imbalance between outflows. Our study implies that one can engineer the position and dynamics of recirculation within an "impacting" T-junction simply by varying the imbalance between outflows, and highlights the risk of microfluidic design failure due to vortex breakdown.

[1] Hnatovsky C, et al. (2006) *Appl Phys A* 84: 47. [2] Chen K K, et al. (2015) *Phys Fluids* 27: 034107 [3] Chen K K, et al. (2017) *J Fluid Mech* 815: 257

Wednesday 6:30 Cripple Creek Ballroom

PO24

**The  $\mu$ -rheometer: An effective microfluidic platform to measure the relaxation time of weakly viscoelastic polymer solutions**Francesco Del Giudice<sup>1</sup>, Gaetano D'Avino<sup>2</sup>, Ilaria De Santo<sup>2</sup>, Vincenzo Calcagno<sup>2</sup>, Valeria Esposito Taliento<sup>2</sup>, Simon J. Haward<sup>1</sup>, Francesco Greco<sup>3</sup>, Paolo A. Netti<sup>4</sup>, Pier Luca Maffettone<sup>2</sup>, and Amy Q. Shen<sup>1</sup><sup>1</sup>*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan;* <sup>2</sup>*Dipartimento di Ingegneria Chimica, dei Materiali e della P, Università degli Studi di Napoli Federico II, Napoli, Italy;* <sup>3</sup>*Istituto di Ricerche sulla Combustione, IRC-CNR, Napoli, Italy;* <sup>4</sup>*Center for Advanced Biomaterials for Health Care CRIB, Istituto Italiano di Tecnologia, Napoli, Italy*

Measuring the longest relaxation time  $\lambda$  of a viscoelastic liquid is an important step in its rheological characterization. For very dilute macromolecular solutions, such measurement becomes challenging through conventional techniques, e.g. frequency response in linear viscoelasticity or first normal stress difference measurements. Here, we present a novel microfluidic platform, the  $\mu$ -rheometer, to estimate the relaxation time of various viscoelastic fluids, down to  $\mu$ -seconds. The working principle is based on the viscoelastic alignment of solid particles

in a straight microchannel. In this poster, we summarize our recent findings on the measurements of  $\lambda$  for several classes of polymer solutions: i) Dilute polymer solutions of neutral polymers in near-theta and good solvents. We compare these results between the  $\mu$ -rheometer and those obtained from an extensional flow based microfluidic platform relying on the onset of flow-induced birefringence, called OSCER. Good agreement between experimental measurements from the two platforms is found. ii) Dilute aqueous polyelectrolyte solutions, namely hyaluronic acid and chitosan, in salt-free and salty conditions. For the hyaluronic acid, good agreement is found between  $\lambda$  derived by using our  $\mu$ -rheometer and that evaluated by fitting the viscosity curves (obtained from conventional shear rheometry) through the Bird-Carreau model. For Chitosan solutions, comparison with other techniques is not possible due to small values of  $\lambda \sim 60$ s detected. Experimental measurements again agree well with theory. iii) Hydroxyethyl cellulose solutions in a semidilute regime.  $\lambda$  values derived from our  $\mu$ -rheometer with those obtained through bulk and micro-rheological techniques are in quantitative agreement.

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PO25

### **Viscoelastic flow around microfluidic cylinders with high aspect ratios and low blockage ratios**

Simon J. Haward, Kazumi Toda-Peters, and Amy Q. Shen

*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

We employ a state-of-the-art microfabrication technique (selective laser-induced etching, SLE [1]) to produce microfluidic cylinder geometries that explore new geometrical regimes. Using SLE, various microchannels are fabricated in monolithic fused silica substrate with heights  $h = 2$  mm and widths  $w = 0.4$  mm (aspect ratio  $AR = h/w = 4$ ). The channels enclose single cylinders, of height  $h$  and with radii in the range  $0.01 < r < 0.05$  mm, centered on the flow axis,  $w/2$ . The cylinders thus have very high aspect ratios  $20 < a = h/2r < 100$ , and provide blockage ratios  $0.05 < \beta = 2r/w < 0.25$ . Compared with cylinder geometries fabricated by soft lithography (which typically have  $AR \ll 1$  and  $\beta = 0.5$  [2]), these rigid glass devices provide a quasi-2D flow along the direction of the cylinder axis and also more clearly reveal the effects of the strong extensional wake at the trailing stagnation point. We use our novel geometries to study the flow of well-characterized viscoelastic polymer solutions with kinematic viscosities  $\eta \sim 0.001$  m<sup>2</sup>/s, and a range of relaxation times  $13 < \tau < 120$  ms. The small cylinder radii result in very high elasticity numbers  $520 < El = \eta U/r^2 < 120000$ , and we observe interesting purely-elastic flow asymmetries and time-dependent instabilities in the cylinder wakes as we vary the Weissenberg number of the flow,  $Wi = \eta U/r$ , where  $U$  is the average flow velocity. We characterize and study these instabilities by employing spatially and temporally-resolved flow velocimetry and birefringence imaging techniques. The results are presented in the form of stability diagrams in dimensionless state space and are analyzed in terms of the scaling suggested by the well-known Pakdel-McKinley criterion [3].

[1] Meineke et al (2016) Lab Chip **16**: 820. [2] Zhao et al (2016) Soft Matter **12**: 8666. [3] McKinley et al (1996) J. Non-Newton Fluid **67**: 19.

Wednesday 6:30 Cripple Creek Ballroom

PO26

### **Effect of surfactant and salt on oil displacement through microfluidic porous network**

Syed Ehsanur Rahman, Indranil Sinha, and Gordon F. Christopher

*Mechanical Engineering, Texas Tech University, Lubbock, TX 79401, United States*

Due to the increasing energy demands, it has become increasingly important to recover greater amounts of trapped oil from drilled reservoir more efficiently, leading to a range of secondary and tertiary enhanced oil recovery methods, including. One such technique is to use surfactant laden solutions to drive our trapped oil from the porous reservoir after primary pumping.

In this study, a microfluidic platform has been used to test the performance of cationic and non-ionic surfactant solutions on oil displacement. It has been shown that surfactant solutions increase recovery performance due to the reduction of interfacial tension in the literature. In this study, the role of salt concentration on surfactant solution displacement is studied to characterize how ionic strength affects performance. We find increasing cationic and non-ionic surfactant up to CMC value increases the effectiveness of oil recovery for both systems. Adding salt further decreases the interfacial tension of the surfactant solution, which in turn increased the effectiveness of oil recovery. This effect was seen for both non-ionic and cationic surfactants, despite the effect of salt on non-ionic solutions surface tension being relatively minor. This effect may be due to other changes in the interface behavior not captured by surface tension alone, which we are still investigating.

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PO27

### **Three-dimensional visualization of oil displacement by flexible microcapsules suspensions in porous media**

Jose R. Vimieiro, Debora F. Nascimento, and Marcio S. Carvalho

*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Brazil*

In a globalized world, the demand for energy is always growing. Since the oil and gas industry is responsible for delivering most of this demand, this makes hydrocarbon components increasingly important in the worldwide economy. However, such resources are finite, so a conscious exploration always seeking the maximum performance is required. As oil reservoirs after the application of primary and secondary recovery techniques usually still have about 65% of the original oil volume contained in their pores, methods that aim its reduction are gaining an increasingly important role in the energy industry. In this context, this work presents a three-dimensional micromodel representative of a porous medium that is used for pore-scale flow analysis. Confocal microscopy is used to visualize the microscale phenomena, leading to specific information about ganglia dynamics, related to its formation, mobilization and entrapment. The residual oil saturation, an important value to measure the amount of oil produced in a given reservoir is determined for different flow conditions. The results show that the suspensions composed by flexible microcapsules could be used as a mobility control agent, since it modifies the fluid distribution in the porous media, improving the pore-scale displacement efficiency, and consequently reducing the residual oil saturation.

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PO28

**Combining rheometry, microscopy, and modulated temperature differential scanning calorimetry to assess wax crystallization in crude oils**Felipe Paiva<sup>1</sup>, Veronica Calado<sup>1</sup>, and Flavio H. Marchesini<sup>2</sup><sup>1</sup>*School of Chemistry, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil;* <sup>2</sup>*Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453 900, Brazil*

It has long been known that wax crystallization during crude oil production and transportation can cause flow assurance issues that give rise to nonproductive times and increase in costs. In the present work, measurements of the Wax Precipitation Temperature (WPT) of waxy crude oil samples by a type of Modulated Temperature Differential Scanning Calorimetry (SSDSC), are reported and further compared to rheometric and microscopy results. When appropriate parameters are used, two exothermic peaks can be detected on the non-reversing component and one peak on the reversing component (RC) of SSDSC thermograms. Additionally, by further adjusting SSDSC experimental parameters, because SSDSC is not based on a sinusoidal temperature modulation, reproduction of SSDSC cooling programs by rheometry and Polarized Light Microscopy (PLM) was possible. It was found that the different values used for the SSDSC cooling parameters, when reproduced on the rheometer, do not impact the oil's rheological behavior significantly at the applied shear rate, although a greater viscosity increase during isothermal time segments is favored by higher temperature steps in the cooling procedure. As shown by Microscopy calculations, this likely results from a greater degree of wax crystal nucleation, which is associated in turn with supersaturation of the medium. Furthermore, there is good agreement between the onset of the peak detected on the RC portion of SSDSC thermograms and a significant increase in wax crystal number during the cooling procedure, which occurs at a temperature much lower than the actual start of wax crystallization (WPT). Therefore, the peak on RC arises from an increase in crystallization rate and it is then only after this increase is detected that the gelation temperature is identified for these oil samples. This supports the need for a saturated medium of precipitating, interacting crystals for identification of the gelation temperature of waxy crude oils and clearly distinguishes it from measurements of the WPT.

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PO29

**Aging oil-water interfaces with asphaltene adsorption: Interface rheology and heterogeneity**

Chih-Cheng Chang, Nowbahar Arash, Mansard Vincent, and Squires Todd

*Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

Water is often used in the production and processing of oil, but the water and oil must ultimately be separated. Such separations can be very challenging, because various surface-active materials naturally exist in crude oil that stabilize water-oil interfaces. Polycyclic aromatic hydrocarbons called asphaltenes are a broad class of surface-active compounds that adsorb at water-oil interfaces and stabilize such emulsions. We use ferromagnetic microbuttons as interfacial rheological probes to probe the evolution of oil/water interfaces as asphaltenes adsorb, and the effect of chemical additives like ethylcellulose (EC) on the evolution of the mechanical properties of the interface. Oil/water interfaces progressively stiffen as asphaltenes adsorb; this process, however, can be prevented or reversed with the addition of EC. To probe the mechanism behind these observations, we visualize the deformation (strain) field of the oil/water interface in response to the stresses imposed by the microbutton. Asphaltene-adsorbed oil/water interfaces show significant mechanical heterogeneity, with pronounced stiff and weak regions. EC affects these heterogeneous regions differently, suggesting various hypotheses for its action on asphaltene-stabilized interfaces. Our study reveals the rich properties of water/asphaltene/oil interfaces, and highlights new tools to probe mechanically heterogeneous interfaces as they evolve in response to their local chemical environments.

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PO30

**Simple method for determining stress and strain constants for non-standard measuring systems on a rotational rheometer**John Casola<sup>1</sup>, Keith Yang<sup>2</sup>, John Duffy<sup>3</sup>, Adrian Hill<sup>3</sup>, and Shona Murphy<sup>3</sup><sup>1</sup>*Malvern Instruments, Westborough, MA 01581, United States;* <sup>2</sup>*Malvern Instruments, Beijing, China;* <sup>3</sup>*Malvern Instruments, Malvern, United Kingdom*

There is often a necessity to measure, or at least estimate, true viscosity values using non-standard measuring systems on a rotational rheometer. This may be to replicate a mixing or manufacturing process on a lab scale, to keep a sample dispersed and uniform during a measurement or to measure some rheological property that would be difficult or impossible with a standard configuration. Such measurements can be made easily enough, but without a process for converting torque to shear stress and angular velocity to shear rate only these raw data variables can be reported. In this poster a simple and novel empirical method for determining strain/strain rate (C1) and stress (C2) constants for non-standard measuring systems on a rotational rheometer is presented. This method uses relative torque measurements made with a Newtonian and non-Newtonian material and their corresponding power law fitting parameters to determine C1 and C2 using a non-linear regression analysis. Equilibrium flow curves generated for two non-Newtonian fluids using two non-standard mixing geometries show very good agreement with data generated using a standard cone and plate configuration, therefore, validating the approach.

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PO31

### **Characterizing the modulus of a sealant using outdoor exposure**

Christopher C. White, Emmitt O'Brien, Kar Tean Tan, and Donald Hunston  
*Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States*

Sealant is critical to the systems that separates indoor from outdoor. It is used to bridge gaps between two dissimilar components of the building envelope. As these components (ex: glass and steel) are warmed and cooled as part of the daily cycle, the gap between them grows and shrinks. These changes impose strain on the sealant bridging the gap. This presentation focuses on the tools, methods, standards and instruments designed to accurately mimic this natural phenomenon. The ability to impose strain like the in-service environment allows for more accurate accelerated testing of sealants. The use of these devices reveal some interesting observations. Using the thermally induced strain and monitored stress, the modulus of sealant can be determined. The development and application of the tools, methods, standards and instruments for imposing strain using outdoor environments will be presented.

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PO32

### **Precise control over position and orientation of anisotropic colloidal particles using a Stokes trap**

Dinesh Kumar<sup>1</sup>, Anish Shenoy<sup>2</sup>, and Charles M. Schroeder<sup>1</sup>

<sup>1</sup>*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Suspensions of anisotropic colloidal particles are commonly encountered in a wide array of applications, including smart materials for targeted drug delivery and injectable materials for therapeutic applications. A grand challenge in the field of directed assembly is to precisely assemble chemically and structurally distinct anisotropic particles into functional hierarchical structures. Such complex assembly schemes will require precise control over both the position and orientation of individual rods. Despite recent progress, it remains challenging to control both the center-of-mass position and orientation of single and multiple rod-like Brownian colloidal particles for these applications. In this work, we demonstrate simultaneous control over the 2D center-of-mass position and orientation of anisotropic Brownian colloidal particles (polystyrene rod-like particles) using a Stokes trap. In this way, the orientation and position of single rod-like particles is controlled using the sole action of fluid flow. In particular, we use a 4-channel Stokes trap with a model-predictive control scheme as a feedback controller to solve a constrained optimization problem in real time. Using this approach, a flow pattern is generated that translates and rotates rod-like particles from their initial state to a final desired position and orientation. Unlike alternative techniques that exploit intrinsic material properties of rod-like particles (e.g. index of refraction, magnetic properties, surface charge) to control position and orientation, our method imposes no restrictions on the physical or chemical properties of the particles, and hence, can be used for rods of any material and size, assuming they can be imaged or detected. Moving forward, this approach could be further engineered to achieve fluidic-directed assembly of asymmetric objects on a meso- to micro-scale level.

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PO33

### **New approaches to asphalt testing**

Gregory W. Kamykowski

*US West, TA Instruments, Wood Dale, IL 60191, United States*

Many tests have been devised to correlate asphalt properties with road performance. There are standard tests that have been accepted by the industry and by state departments of transportation, but new methods are always being explored to characterize asphalt on rotational rheometers that will help predict road performance. Some of the methods that will be shown on this poster are the following: Testing with 4-mm diameter plates at low temperatures; flexural testing at low temperatures in both oscillation and transient modes; Binding Energy Yield Testing.

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PO34

### **Accurate measurement of low viscosity liquid at low shear-rate range by Rheology Spectrometer**

Yoshikazu Yamakawa<sup>1</sup>, Yoji Okada<sup>1</sup>, and Keiji Sakai<sup>2</sup>

<sup>1</sup>*Triple Eye Co. Ltd., Kyoto, Japan;* <sup>2</sup>*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, Japan*

Recently, we developed a new type of viscometer based on the Electro-Magnetically Spinning (EMS) method. Here, we give a brief account of the measurement system. A probe rotor is a thin metal disk, which is placed in the sample. A rotating magnetic field is generated by a couple of magnets attached to a motor, and is applied to the disk probe. Temporal modulation of the direction of the magnetic field induces a current in the disk and the Lorentz interaction between the current and the applied magnetic field induces a torque to the disk. By observing the rotational speed of the probe disk, we can determine the viscosity of the sample. A remarkable feature of the system is that we can apply a torque remotely to the disk. We can, therefore, easily measure the viscosity in extraordinary environments, such as high/low temperatures and pressures. The system is also effective for the use of bio-hazardous materials. Just recently, we developed a new auto-balancing type rotor to improve the accuracy of the measurement especially in lowly viscous region. The probe rotor can stand perpendicularly in the sample with the aid of the buoyancy and surface tension. A tip at the center of the disk is in contact with the sample bottom, which corroborates the accurate thickness of the sample. The accuracy of the measurement is better than 2 % for the measurement of 1 mPa·s at the shear deformation rate of 10 s<sup>-1</sup>. To demonstrate the performance of the system in detecting low viscosity, we carried out the viscosity measurement of various ethanol solutions including beers, wines, whiskies and of course Japanese Sake. As is well known, viscosity of aqueous solution of ethanol shows characteristic dependence on the concentration; a peak appears at around 30 % of ethanol. We examined the behavior of viscosity of these drinkable liquids and in the presentation, we would discuss the difference between the rheological properties of these intoxicating beverages and pure aqueous solution of ethanol.

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PO35

### **On-line viscosity monitoring in a mixing tank with non-Newtonian fluids**

Hae Jin Jo and Wook Ryol Hwang

*Gyeongsang National University, Jinju, Republic of Korea*

In this study, in-situ measurement of the viscosity of non-Newtonian fluid in a mixing system with an anchor impeller has been investigated, which is commonly employed in blending highly viscous fluids, particularly for viscoplastic fluids with yield stress. The effective shear rate constant  $K_s$  and the energy dissipation rate constant  $K_p$  according to the geometry of an anchor impeller system are measured in experimental and numerical investigations using the Metzner-Otto correlation based on the energy dissipation rate. Viscosity behavior of a shear thinning fluid can be easily measured by measuring the torque inside the fluid with the predetermined flow number  $K_s$  and  $K_p$  once and for all, in which the viscosity estimation can be done simultaneous with torque measurement. Aqueous carbopol 940 solution, which is a viscoplastic fluid, and xanthan gum solution, which has elasticity and shear thinning behavior are employed as the model fluid. Measurements of viscosity with both fluids show good agreement.

This work is supported by Korea Agency for Infrastructure Technology Advancement grant funded by Ministry of Land, Infrastructure and Transport (17IFIP-B133614-01, The Industrial Strategic Technology Development Program).

Wednesday 6:30 Cripple Creek Ballroom

PO36

### **Frequency sweeps: Can time be eliminated?**

Montgomery T. Shaw

*Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States*

Perhaps the most widely used characterization of the linear viscoelastic properties of a material is the frequency sweep. This experiment is easy to execute and, if the frequency range runs down to say 0.1 rad/s, it is quick. Of course, much of the valuable viscoelastic information is available only at much lower frequencies, say from 0.1 to 0.001 rad/s or even lower. The experimentalist is then spending hours or even days to gather the data, and time effects begin to creep in. Depending on the test materials, geometry and instrument, these effects might be gelation, chemical degradation, sedimentation, agglomeration, solvent loss (or gain), transducer drift, etc. Described in the literature are methods for approaching this problem, but all require more time and effort. Introduced in this poster is a work-around that does not take additional time. The method calls for running the selected frequencies in random order. Such automatically converts time trends to random error, which can be handled effectively. This is illustrated with models and selected materials of current interest.

Wednesday 6:30 Cripple Creek Ballroom

PO37

### **Rheological analysis tools for complex materials**

David Moonay

*AMETEK Brookfield, Middleboro, MA 02346, United States*

This poster presents information concerning some tools useful for rheologically analyzing different materials in various applications. Many products are modified with biopolymers or other macromolecules and, as a result, exhibit complex rheological behavior. Many also are heterogeneous, having suspended particles of varying degrees of solidity and ranges of sizes. Traditional geometries such as disk or cylindrical spindles immersed in various containers, coaxial cylinder and cone-and-plate, provide useful information when measuring viscosities. However, other geometries may be required to better define the behavior of a material as a whole. A serrated spindle within cylindrical cup successfully provides data with fine suspensions comprising components prone to slip. Vane spindles may provide more realistic data with for samples with larger suspended particles. T-shaped spindles driven through helical paths provide meaningful QC data for soft solids that irreversibly deform and/or structurally break down, as well. Data for various products, using different rheometers, viscometers and geometries, are presented.

Wednesday 6:30 Cripple Creek Ballroom

PO38

### **Extensional rheometry with a handheld mobile device**

Kristin A. Marshall, Aleesha M. Liedtke, and Travis W. Walker

*CBEE, Oregon State University, Corvallis, OR 97331, United States*

The on-site characterization of complex fluids is important for a number of academic and industrial applications. Consequently, a need exists to develop portable rheometers that can provide in-the-field diagnostics and serve as tools for rapid quality assurance. With the advancement of smartphone technology and the widespread global ownership of smart devices, mobile applications are attractive as platforms for rheological characterization. The present work investigates the use of a smartphone device for the extensional characterization of a series of Boger fluids composed of glycerol/water and poly(ethylene oxide), taking advantage of the increasing high-speed video capabilities (currently up to 240 Hz capture rate at 720p) of smartphone cameras. We report a noticeable difference in the characterization of samples with slight variations in polymer concentration and discuss current device limitations. Potential benefits of a handheld extensional rheometer include its use as a point-of-care diagnostic tool, especially in developing communities, as well as a simple and inexpensive tool for assessing product quality in industry.

Wednesday 6:30 Cripple Creek Ballroom

PO39

**Physical interpretation of oscillatory shear flow: Application of Sequence of Physical Process (SPP) analysis to Soft Glassy Rheology (SGR) model**Jun Dong Park and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

The rheological behaviors of Soft Glassy Materials (SGM) under oscillatory shear flow are explored with Sequence of Physical Process (SPP) analysis. The complex rheological behavior under oscillatory flow, especially under Large Amplitude Oscillatory Shear (LAOS), has been one of the main concerns in rheology. Reflecting the great interest, various analysis approaches have been suggested and attempted. However, current methods are inadequate to provide physical interpretation between bulk rheology and microscopic length scale physics, such as microstructural change. Recently, as an alternative, the SPP analysis has been developed to enable comprehensive physical interpretation of stress responses to transient deformations. In this work, the SPP analysis is applied to Soft Glassy Rheology (SGR) model which is well defined and effective model to describe the SGM, for example, colloidal glasses and dense emulsions. The SPP approach quantifies intra-cycle transient rheological behaviors of SGR model by two differential parameters,  $G'_i(t)$  and  $G''_i(t)$ , that indicate elastic and viscous characteristics, respectively. The change in  $G'_i(t)$  and  $G''_i(t)$  is related to the physics of mesoscopic elements that compose SGM. The elastic strain distribution of mesoscopic elements and yielding rate, which are the microscopic level origins of elastic and viscous properties, provide a consistent physical explanation on the change in  $G'_i(t)$  and  $G''_i(t)$  during an oscillatory cycle. The successful application of SPP analysis to SGR model connotes significant potential for various materials and flow conditions.

Wednesday 6:30 Cripple Creek Ballroom

PO40

**Sequencing the transient rheology of soft solids**Ching-Wei Lee and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We show how the results to large amplitude oscillatory shear (LAOS) of two soft solids is best described as resulting from a sequence of physical processes. This approach was first proposed in a phenomenological manner in 2011 [1]. We revisit those original results and apply a newly-published [2] quantitative analysis scheme, which views response to LAOS as trajectories in deformation space. Time-dependent storage and loss moduli are obtained, along with a moving equilibrium strain. While the original colloidal glass work [1] physically divided the response into several stages within an oscillation and provided a qualitative way to rationalize the response in terms of physical concepts, here we employ a fully quantitative analysis with associated physical interpretations. A notable observation is that of a nearly constant elasticity ( $G'$ ) across a wide range of strain amplitudes at instants close to strain extrema, which is reminiscent of the cage modulus [1]. However, unlike the determination of the cage modulus, in which the stress response is considered purely elastic, the current enhanced analysis suggests that viscous contribution still exists during cage deformation.

[1] S. A. Rogers, B. M. Erwin, D. Vlassopoulos, and M. Cloitre. A sequence of physical processes determined and quantified in LAOS: Application to a yield stress fluid. *Journal of Rheology*, 55(2):435-458, 2011. [2] S. A. Rogers. In search of physical meaning: defining transient parameters for nonlinear viscoelasticity. *Rheologica Acta*, 56(5):501-525, 2017.

Wednesday 6:30 Cripple Creek Ballroom

PO41

**Using LAOS and transient data to “fingerprint” human blood rheological data**Tyler Helton*Chemistry and Life Science, United States Military Academy, West Point, NY, United States*

Complex, viscoelastic materials exhibit a change in viscosity depending on the extent of shearing forces placed upon them. Among these types of materials is blood, a well documented viscoelastic material. An underdeveloped area of study in this field analyzing these mechanical measurements of blood for use in clinical diagnoses. Rheologists have long studied a unique condition of shear flow called large amplitude oscillatory shear (LAOS). The challenge of this condition is its nonlinearity, stemming from the difficulty of modeling the unique internal structure of each material. There is a possibility that blood could be classified using its own unique LAOS signature, and with the addition of large quantities of data for comparison, could be used as a method of diagnoses. Blood is a great example of a non-Newtonian fluid. It is a suspension red blood cells (RBCs), white blood cells, proteins, hormones, platelets, and other ionic solutes in the blood plasma. This internal microstructure affects the dynamic viscosity of blood when forced into flow conditions. The interactions of the microstructure play a major role in determining the viscosity of blood. RBC aggregation, deformability, and membrane rigidity all contribute to the blood's viscosity. Plasma proteins, most notably fibrinogen, contribute to the interactions among RBCs as well as platelets.

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PO42

**Comparison of simple rheological models in fitting and predicting steady state and transient blood rheology**Michael Deegan and Matthew J. Armstrong*Chemistry and Life Science, United States Military Academy, West Point, NY, United States*

Many complex materials have thixotropic behaviors, displaying time dependent viscous and elastic properties that are a function of microstructure. Some examples of thixotropic materials are aqueous nuclear waste, crude oil, and paints. Another example is blood. Modeling the behavior of these materials allows us to better understand how they can be used effectively in their respective industry. We have characterized human blood

using published steady state data and different models from literature. First, we looked at data from previous rheological experiments (Moreno and Sousa) done on blood and modeled them using nine different simple models. Using the best model, we predicted small amplitude oscillatory shear (SAOS) with our own parameter determination technique and used two published transient models to predict large amplitude oscillatory shear (LAOS) and SAOS. We characterize blood to develop better models, and evolve strategies to give way to better understanding of blood to facilitate benchmarking blood's "normal" rheological fingerprint, with a view toward a methodology to diagnose pathologies based on rheological deviations from blood's baseline mechanical properties. Based on the biochemistry of blood, its fluid mechanics, and rheological properties, pathological blood will have different rheological properties than healthy blood. By modeling healthy blood, we can establish a baseline that will then allow us to characterize and diagnose pathological blood based on its flow behavior, as was seen in the Moreno paper with high cholesterol.

Wednesday 6:30 Cripple Creek Ballroom

PO43

### **Shear thickening behavior of suspensions of acetylated cassava starch in glycerol**

Osman F. Silva and Veronica Calado

*School of Chemistry, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil*

In the last decades, with the technological advances applied to the production of low cost materials, resistant and with high capacity of molding, the use of polymers derived from petroleum has increased considerably and becoming one of the main reasons of concern in the environmental area. As a result, there has been a growing interest in the development of biodegradable materials that may substitute petroleum products, especially those produced from renewable resources.

Among the polysaccharides available in nature, cassava starch is one of the most interesting options given its easy production with a high purity and low cost. Its industrial production system moves significant amounts of roots to the starch production, generating liquid and solid residues with high starch content. The use of native non-gelatinized starch is still restricted to some applications as a vehicle for pharmaceutical and cosmetic formulations and as a desiccant and non-stick latex glove. However, among its most interesting and yet poorly exploited properties is its ability to generate semi-fluid aqueous suspensions with dilatant properties at high volume fractions.

The objective of the present work is to obtain potentially biodegradable fluids with improved dilatant characteristics, basically composed of glycerol and acetylated cassava starch.

The rheological behavior of suspensions of native cassava starch or its low GS acetylated derivative on glycerol was studied with and without the addition of organophilic clay. The influence of the suspension volumetric fraction and the time were analyzed. A shear thickening behavior of the suspensions was noticed, showing that the suspensions prepared with the acetylated cassava starch presented significant advantages over those ones prepared with the native starch. The addition of organophilic clay in specific amounts improved the strength of the suspensions at high temperatures; also, significant gains in absolute values of maximum apparent viscosity were achieved.

Wednesday 6:30 Cripple Creek Ballroom

PO44

### **Experimental study on reversible formation of 2D flocs from plate-like particles dispersed in Newtonian fluid under torsional flow**

Hyunseop Lee and Chongyup Kim

*Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea*

In this study the reversible aggregation and breakage of flocs are investigated experimentally in a suspension under a torsional flow between two parallel plates. The suspension was prepared by dispersing platelike particles in a Newtonian fluid. The Newtonian fluid has a viscosity of 1.27 Pa.s and the average dimension of the particle face is approximately 1 $\mu$ m with a thickness of 250nm. Peclet number of the particle is over 100 and the aggregation is orthokinetic. The microstructure was examined under an optical microscope without disturbing the flow or particle motions. The result shows that two dimensional (2D) flocs of non-circular and fractal types are formed by the aggregation of platelike particles and the face of the planar floc is oriented in the same direction of the velocity gradient. The most probable aspect ratio of the floc face is 1.75 approximately. The 2D flocs have size dependent fractal dimensions. While remaining in the shear plane, the 2D flocs are oriented along the vorticity or flow direction depending on shear rate. The orientation is found to be closely related with the breakage and the breakage occurs mostly at the middle of the floc after being aligned along the flow direction. Erosion does not appear to be important in the breakage of 2D flocs. It was found that the rate of viscosity of the suspension increase is not monotonic in shear rate and is related with the kinetics of aggregation as well as the size of the floc.

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Wednesday 6:30 Cripple Creek Ballroom

PO45

### **Superposition rheology and anisotropy in rheological properties of sheared colloidal gels**

Gabriele Colombo<sup>1</sup> and Jan Vermant<sup>2</sup>

<sup>1</sup>*Department of Materials, ETH Zürich, Zürich, Zürich 8093, Switzerland;* <sup>2</sup>*ETH Zurich, Zurich, Switzerland*

Gelling colloidal suspensions represent an important class of soft materials. Their mechanical response is characterized by a solid-to-liquid transition at a given shear stress level. Moreover, they often exhibit a complex time-dependent rheological behavior known as thixotropy. The viscosity changes find their origin in the microstructure, which depends on flow history. Yet, the structural response to flow of colloidal gels differs fundamentally from most complex fluids, where flow induces orientation. Upon yielding, low to intermediate volume fraction gels break

down in a spatially anisotropic way. Bonds in the velocity-velocity gradient plane are broken, whereas microstructural features in other planes are less affected. The subsequent flow-induced microstructural anisotropy is characterized by typical butterfly scattering patterns. However, as yet there was no evidence for the pertinence of this anisotropy for the rheological properties of these systems. In the present work, orthogonal superposition rheometry was used to first evaluate how the flow-induced microstructure affects the viscoelastic properties. It was shown to retain significant elasticity in the velocity-vorticity plane, even when the structure liquefied. Further, the shear-induced mechanical anisotropy was measured using two-dimensional small amplitude oscillatory shear, exploiting the fact that for suitable thixotropic samples the recovery after arresting the flow is relatively slow. It was hence possible to measure the anisotropy of the moduli upon cessation of flow. The mechanical anisotropy was shown to be spectacular, with the storage moduli in perpendicular directions differing by as much as two orders of magnitude.

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PO46

### **Using thermal processing to control structure and rheology in thermoresponsive colloidal gels**

Tuan Nguyen, Juntae Kim, and Matthew E. Helgeson

*Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106, United States*

Thermoresponsive (TR) colloidal systems form the basis of colloidal gels for use in consumer products, 3D printing inks and mesostructured materials. Engineering these gels requires control of the kinetic process of gelation, which can occur by mechanisms including homogeneous percolation, attractive glass formation and arrested phase separation. The material outcomes are sensitive to the thermal history (i.e. "quench") of interparticle interactions leading to the arrested state. However, there have yet to be any systematic experimental studies of how the details of the quench toward these non-equilibrium states influences the rheological properties of the arrested gel, or its aging over time. To fill this gap, here we study the effects of varying thermal quench depth and rate on a model TR colloidal gel system controlled by TR polymer bridging attractions. First, we experimentally establish an equilibrium colloidal phase diagram to identify the temperature-dependent interaction potential and its resulting phase behavior. The phase diagram is used to study the outcome of gelation upon isochoric quenches of varying colloid volume fraction into the gelled state. In doing so, we identify how the mechanism and kinetics of gel formation are controlled by the details of the thermal quench, and how these characteristics determine various features of the rheological properties including linear modulus, yield strain, and aging rate. For example, we find that quenches into the equilibrium spinodal boundary exhibit a complex, and in some cases non-monotonic, dependence of the gelation kinetics with increasing quench depth and rate due to competing time scales of gelation, phase separation, and thermal quenching. For quenches into the attractive glass state, we observe similar dependence of the gelation kinetics, but with markedly different outcomes for the viscoelasticity and aging of the final gel. Overall, these results elucidate new design considerations for using thermal processing to control the properties of TR gels.

Wednesday 6:30 Cripple Creek Ballroom

PO47

### **Characterizing caking behavior in cohesive bulk solids using a rotational rheometer**

Julia-Grace Polich, Abhishek Shetty, and Gina Paroline

*Anton Paar USA, Inc., Ashland, VA, United States*

Powder handling is a common feature found in several industrial unit operations like mixing, storage, feeding, fluidization, compaction, blending etc. These operations encounter challenges related to powder flow. It is important to understand the flow of powders, because often it is the powder's flowability which dictates quality and efficiency in a powder process. Powders can generally be classified as cohesive or free-flowing. Bulk of the powders found in nature are of the cohesive type. Cohesive powder particles can stick together due to inter-particle forces and form large agglomerations, referred to as caking. This caking behavior is a non-desired effect, because it reduces the flowability of a powder. In this work, a repeatable and robust method for characterizing caking in cohesive powders is introduced. Various Geldart C powders were characterized using a Warren Springs geometry on a rotational rheometer fitted with a powder cell accessory. This work is based on the pioneering work of Geldart and co-workers who used a torsional device called the Warren Springs Bradford cohesion tester\*. Warren Springs cohesion is used as parameter to characterize the caking behavior seen in the different Geldart C powders studied.

\* Geldart D., E.C. Abdullah & A. Verlinden, "Characterization of dry powders". Powder Technology, 190(1):70-74, 2009.

Wednesday 6:30 Cripple Creek Ballroom

PO48

### **Hyper time-resolution rheology measurement by airborne liquid droplet analysis**

Keiji Sakai<sup>1</sup>, Syujiro Mitani<sup>1</sup>, and Yoshikazu Yamakawa<sup>2</sup>

<sup>1</sup>*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, Japan;* <sup>2</sup>*Triple Eye Co. Ltd., Kyoto, Japan*

Accurate measurement of mechanical liquid properties including viscosity and surface tension are requisite for the design of micro-liquid processes, such as the inkjet and micro-fluidics, however, rapid measurement of viscosity and surface tension has been quite difficult. We recently developed a new method to measure the surface tension with a time resolution better than 0.01 ms by using the technique of emission and manipulation of pico-liter liquid droplets. In the experiment, a series of liquid droplets with diameter of 10 micron is generated by applying ultrasonic modulation to the constant pressure to emit a liquid jet from a nozzle, and the rapid flying behavior of the droplets are observed by the stroboscopic method. Liquid droplets are continuously emitted from the nozzle at the rate higher than 50 kHz and fly in the air, where a couple of electrodes are placed to apply a local electric field to the flying droplets. Sphere liquid droplets going through the gap of electrodes feel the dielectric force and their shape is deformed to the ellipsoid. The droplets shape then begins to oscillate, where the surface tension works as a restoring force, therefore, we can determine the surface tension by measuring the oscillation frequency. The position of the electrodes is swept along the trajectory of the droplets to observe the temporal change of the surface tension; the surface soon after the emission is fresh and get old as the droplets fly, during which the surface tension decreases due to the molecular adsorption. We could successfully observe the decrease in the

surface tension of the aqueous solution of 10 mM sodium dodecyl sulfate in the time region from 0.01 ms to 10 ms. We could also determine the temporal change of the viscosity, since the decay constant of the particle oscillation is inversely proportional to the viscosity. In the presentation, we introduce microscopic and slow motion movies showing the emission, flight and oscillation of the macro liquid droplets.

Wednesday 6:30 Cripple Creek Ballroom

PO49

### **Linear viscoelasticity of a dilute emulsion of drops containing soluble surfactant**

Rajarshi Sengupta, Lynn M. Walker, and Aditya S. Khair

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

The linear viscoelasticity of a dilute emulsion of drops containing soluble surfactant is calculated under a small-amplitude oscillatory shear deformation. It is assumed that the drops remain spherical. At small values of the strain rate, the contribution of surfactant transport by convection in the bulk is small, i.e., the bulk Peclet number ( $Pe$ ) is small, and the surfactant distribution is linearly coupled to the flow field at  $O(Pe)$ . Using regular perturbation expansions about  $Pe$ , we calculate the complex viscosity of the emulsion upto  $O(Pe\phi\mu_0)$ , where  $\phi$  is the small volume fraction of the dispersed phase, and  $\mu_0$  is the viscosity of the suspending fluid. When soluble surfactants are present in the dispersed phase, their adsorption to the interface may cause a significant decrease in the bulk concentration, a phenomenon that is known as depletion. The impact of depletion is characterized by two parameters:  $h$ , which is the ratio of the minimum bulk concentration required to saturate the interface to the initial bulk concentration, and  $k$ , which is the ratio of the desorption time scale to the adsorption time scale. From the Fourier inversion of the complex viscosity we calculate the relaxation modulus of the emulsion at different limits of these two parameters, and identify the appropriate time scales for stress relaxation. We show that the relaxation spectrum can be used to extract information about the dynamics of surfactant adsorption and diffusion at fluid-fluid interfaces.

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PO50

### **Free surface flows and extensional rheology of polymer solutions**

Jelena Dinic, Leidy N. Jimenez, Madeleine Biagioli, Alexandro Estrada, and Vivek Sharma

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

Free-surface flows -- jetting, spraying, atomization during fuel injection, roller-coating, gravure printing, several microfluidic drop/particle formation techniques, and screen-printing -- all involve the formation of axisymmetric fluid elements that spontaneously break into droplets by a surface-tension-driven instability. The growth of the capillary-driven instability and pinch-off dynamics are dictated by a complex interplay of inertial, viscous and capillary stresses for simple fluids. Additional contributions by elasticity, extensibility and extensional viscosity play a role for complex fluids. We show that visualization and analysis of capillary-driven thinning and pinch-off dynamics of the columnar neck in an asymmetric liquid bridge created by dripping-onto-substrate (DoS) can be used for characterizing the extensional rheology of complex fluids. Using a wide variety of complex fluids, we show the measurement of the extensional relaxation time, extensional viscosity, power-law index and shear viscosity. Lastly, we elucidate how polymer composition, flexibility, and molecular weight determine the thinning and pinch-off dynamics of polymeric complex fluids.

Wednesday 6:30 Cripple Creek Ballroom

PO51

### **Influence of interfacial elasticity on drainage in foam films using Dynamic Fluid-film Interferometry**

John M. Frostad<sup>1</sup>, Gigi L. Lin<sup>2</sup>, and Gerald G. Fuller<sup>2</sup>

<sup>1</sup>*Chemical Engineering and Food Science, University of British Columbia, Vancouver, Canada;* <sup>2</sup>*Chemical Engineering, Stanford University, Stanford, CA 94305, United States*

Foams are found in a diverse range systems such as the head on a glass of beer, the froth used for separation of minerals, or in specialized fire-fighting foams. In each case, bulk properties such as the density and stability of the foam should be carefully tuned for the requirements of the respective applications. In prior work, we established that the foam density is directly correlated to measurements of film drainage dynamics on individual bubbles using a technique called Dynamic Fluid-film Interferometry. We take advantage of this correlative behavior to gain insight into the influence of interfacial elasticity on drainage dynamics and by extension, the density of foams.

Many authors have studied the influence of interfacial elasticity on film drainage dynamics, but in the literature one can find predictions that cover the entire spectrum of possible dependencies. Namely, some predict that increasing interfacial elasticity will slow down drainage, some predict that it will speed up drainage, and some predict no significant impact. In this experimental study we attempt to shed some light on these discrepancies. To do this we systematically varied the interfacial shear elasticity in protein solutions and employed Dynamic Fluid-film Interferometry to observe the resulting influence on drainage dynamics.

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PO52

### **Viscoelastic properties of ultrathin atactic poly(methyl methacrylate) films dewetting on a liquid substrate**

Chunhua Lou and Gregory B. McKenna

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

Dewetting on a liquid substrate is a special measurement of viscoelastic properties of ultrathin polymer films. In this present work, we investigated the viscoelastic properties of atactic poly(methyl methacrylate) (a-PMMA) with molecular weight of 120 kg/mol dewetting on a ionic liquid (1-Butyl-3-methyl imidazolium tetrafluoroborate). The apparent rubbery plateau compliance is found to increase with increasing initial film thickness.

Glass transition temperature ( $T_g$ ) reduction was observed as a-PMMA film thickness decreased. The  $T_g(h)$  behavior was similar to that obtained by Roth for freely-standing a-PMMA films with a linear decrease with decreasing film thickness.

Wednesday 6:30 Cripple Creek Ballroom

PO53

### **Effect of viscoelasticity on liquid curtain breakup**

Marisa S. Bazzi and Marcio S. Carvalho

*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Brazil*

Thin liquid sheets appear in a wide range of practical applications such as atomization, paper manufacturing, and curtain coating. In curtain coating, a thin liquid sheet is formed and falls under the influence of gravity over a considerable height before it impinges onto a moving substrate. Liquid curtain breaks below a critical flow rate, which is a function of the liquid properties. The breakup is a result of a very fast sequence of events: a small perturbation on the liquid interface grows and pinches-off the curtain, creating a small hole. Capillary forces expand the hole causing the curtain disintegration. Most of the available studies of film breakup consider the fluid as a Newtonian liquid. However, most coating liquids have more complex rheological behavior. Experimental studies have shown that viscoelastic forces may delay curtain breakup. The mechanisms responsible for this delay are still not fully understood. This work investigates how viscoelasticity affects curtain stability in two different ways: first delaying the liquid curtain rupture and then by reducing the speed by which a hole grows and breaks the curtain. The mathematical model is based on mass and momentum conservation equations modified by the long-wave theory. In order to include the viscoelastic effects, two different approaches have been explored: Generalized Newtonian model with an extensional viscosity that varies with extension rate and Oldroyd-B model. The nonlinear-coupled system was solved by Finite Difference method. The results show the stabilizing effect of viscoelastic stresses on both the evolution of a small perturbation in a liquid sheet and on the capillary-driven hole growth. The results show how liquid rheology may be optimized in order to achieve thinner coated films using curtain coating process.

Wednesday 6:30 Cripple Creek Ballroom

PO54

### **Rheo-NMR of transient and steady state shear-banding in wormlike micelles**

Rehab N. Al-kaby<sup>1</sup>, Sarah L. Codd<sup>1</sup>, Joseph D. Seymour<sup>2</sup>, Timothy I. Brox<sup>3</sup>, and Jennifer R. Brown<sup>2</sup>

<sup>1</sup>*Mechanical & Industrial Engineering Department, Montana State University, Bozeman, MT 59715, United States;* <sup>2</sup>*Chemical and Biological Engineering Department, Montana State University, Bozeman, MT 59717, United States;* <sup>3</sup>*MacDiarmid Institute for Advanced Materials & Nanotechnology, Victoria University of Wellington, Wellington 6140, New Zealand*

In this study, the shear banding of a wormlike micelle (WLMs) solution was investigated under steady state and time dependent conditions. The system was a solution of 6 wt. % cetylpyridinium chloride (CPCI) and sodium salicylate (NaSal) in 0.5 M NaCl brine in a concentric cylinder Rheo-NMR shear cell. 1D velocity profiles across the 1 mm fluid gap were recorded every 0.8 s after shear start-up using Rheo-NMR velocimetry and used to evaluate shear rates in the low and high shear band as well as interface position. Transient and steady state shear banding was demonstrated and discussed for a range of shear rates across the stress plateau and results compared for flow protocols with and without pre-shear. The evolution of the shear rate and interface position with time after start-up was used to evaluate changes in the kinetics of shear band formation as a function of shear rate and flow protocol.

Wednesday 6:30 Cripple Creek Ballroom

PO55

### **Shear induced de-mixing in a shear banding wormlike micellar solution**

Alireza Dalili and Hadi Mohammadigoushki

*Department of Chemical and Biomedical Engineering, Florida A&M University - Florida State University, Tallahassee, FL, United States*

We report experiments on a simple shear flow of a model shear banding wormlike micellar solutions with a custom-built Taylor-Couette (TC) cell. The wormlike micellar solution contains cetyl trimethyl ammonium tosylate (CTAT), sodium dodecyl benzene sulfonate (SDBS) and sodium tosylate (NaTos). Rheological measurements indicate formation of a shear stress plateau for  $0.87 < \dot{\gamma} < 30.2$  (1/s). Local velocity profiles in the  $r$ - $\theta$  plane of the TC cell confirmed formation of a shear banded velocity profile with no wall-slip at the moving boundary and the proportion of the high shear band compares well with the lever rule. However, flow visualizations in the  $r$ - $z$  plane revealed transition from a stable to an unstable flow for shear rates close to the onset of shear banding plateau. This transition is characterized by formation of a chaotic pattern akin to shear induced de-mixing or shear induced phase separation. This pattern prevails for shear rates that lie within the shear banding plateau. However, for shear rates higher than the shear banding plateau, travelling waves are reported. All these transitions are characterized by extremely high elasticity numbers ( $El = Wi/Re \gg 10$ ), thus confirming the elastic nature of the instability.

Wednesday 6:30 Cripple Creek Ballroom

PO56

### **Design of patchy nanoparticles via the self-assembly of triblock terpolymers in selective solvents**

Nicolas Moreno and Eliot Fried

*Mathematics, Mechanics, and Materials Unit, Okinawa Institute of Science and Technology, Onna, Japan*

The hierarchical self-assembly of triblock terpolymers in solution is a successful bottom-up methodology for constructing functional patchy nanoparticles with prescribed topology and shape. Currently, the design of such nanoparticles requires an iterative process to identify the proper experimental phase parameters to produce any target pattern. The broad use of this technology is therefore cumbersome and limited by an incomplete understanding of the mechanisms underlying patch transition with variations of the ambient conditions. An understanding of the critical

balance between thermodynamics and kinetics governing the topology of the assemblies is also still elusive. Here, we present a set of rules for programming desired shapes of the nanoparticles and predict the pathways by which they assemble. We investigate systematically the interplay between entropic and enthalpic parameters governing the self-assembly of ABC triblock copolymers in a selective solvent for the C block. We use computational modeling at the mesoscale and thereby encompass the length and time scales associated with the motion and assembly of the polymer coils, while accurately approximating the chemically driven interactions. The phase diagram predicted by our computational model is consistent with the characteristic micellar shapes that have been experimentally identified. We find that the effective volume fraction of the soluble block determines the size of the micelles and the distribution of the patches via steric interactions. Moreover, we find that the relative fraction of the patch-forming block and its affinity with the core of the nanoparticles dictates the amount and shape of the patches. As a major outcome, we construct a morphologically-based library of micelles. That library can be used to hierarchically design mesoscale aggregates with prescribed shape. Our results provide novel insights regarding the intriguing mechanisms that determine the morphology of nanometer scale objects in synthetic and naturally occurring systems.

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PO57

**The synergistic effects of polymer nanocomposites based on chemically stitched CNT/graphene hybrids: Rheological and electrical properties**

Mohammad Heydarnejad Moghadam, Fatemeh Goharpey, and Hosein Nazockdast

*Department of Polymer Engineering and Color Science, Amirkabir university of technology, Tehran, Tehran, Iran*

Graphene Nanosheets and Multi Walled Carbon nanotubes were first surface modified with ODA (octadecylamine) to prevent the aggregation of Nanoparticles themselves and also improve the compatibility between the Nanoparticles and hydrophobic SEBS (styrene-b-(ethylene-co-butylene)-b-styrene) matrix. then Chemical hybrid of nanoparticles was synthesized by Stitching Graphene and CNT and further modification by ODA. Nanocomposites were prepared by solution mixing method. FE-SEM images of nanocomposites showed a well dispersed morphology of nanoparticles in SEBS matrix. Rheological and Electrical measurements demonstrate synergistic transport effect due to Graphene-CNT chemically interconnected network structure formed throughout the matrix. Also, it has been shown that Chemical Hybrid of nanoparticles has relatively high critical component in Percolation theory for both rheological and electrical properties that result in more complex Nano structures in stitched CNT/Graphene Hybrid. Finally, it should be noted that the values for critical component in rheological measurements are lower than electrical measurements, due to microphase separated network structure of PS domains in SEBS matrix.

Wednesday 6:30 Cripple Creek Ballroom

PO58

**Linear viscoelasticity of epoxy monomer/TiO<sub>2</sub> nanoparticle mixtures under curing**

Keroles B. Riad and Paula Wood-Adams

*Mechanical, Industrial, Aerospace Engineering, Concordia University, Montreal, Quebec H3G 1M8, Canada*

The sensitivity of current initiators for the photocuring of epoxy to UVA radiation in solar light makes the products unstable. This creates the need for initiators that can only be triggered by wavelengths outside the spectrum of solar light. Using semiconducting nanoparticles as photo initiators may address this issue as their bandgaps can be engineered via the quantized effect. We study the effect of using TiO<sub>2</sub> particles to photocure epoxy. We confirm the occurrence of an epoxy polymerization reaction by ex situ FTIR, LVE, and Tg measurements at constant degrees of cure. FTIR confirms the presence of an oxidation reaction that consumes epoxide groups. The titania-epoxy composite exhibits LVE behavior common to colloidal suspensions, with yield like behavior at low frequencies followed by a steep decrease in complex viscosity at higher frequencies. The behavior varies with time after mixture preparation due to particle agglomeration complicating the study of its LVE. As epoxy polymerization advances, the complex viscosity increases significantly although the shape of the complex viscosity curves are similar. This work will provide important understanding for the processing and photocuring of epoxy using TiO<sub>2</sub> nanoparticles as initiators.

Wednesday 6:30 Cripple Creek Ballroom

PO59

**Mechanical property and glass transition temperature measurements on freestanding ultrathin films of unblended rigid polyvinyl chloride (RPVC) and their deviation from bulk behavior using the nanobubble inflation technique**

Aric A. Denton, Heedong Yoon, and Gregory B. McKenna

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

The nanobubble inflation technique uses an atomic force microscope (AFM) to measure the mechanical behavior of nanoconfined and bulk freestanding films over time. Using the nanobubble inflation method, the biaxial creep compliance of 120,000 g/mol molecular weight unblended rigid polyvinyl chloride (RPVC) was established with data taken both in the bending regime and in the membrane limit. An energy balance approach was used to calculate the compliance for the bending regime data. The membrane limit was treated as described in [P. A. O'Connell and G. B. McKenna, *Science* 307, 1760-1763 (2005)]. The glass transition temperature (T<sub>g</sub>) was determined for various film thicknesses by changing the temperatures within the glassy and rubbery regimes for each thickness. A conventional differential scanning calorimeter (DSC) was also used to collect the bulk T<sub>g</sub> values which were then compared to the apparent T<sub>g</sub> at each thickness. The dynamic fragility and the rubbery stiffening index were determined for the RPVC and compared to previous correlations for other materials shown by [Li, X., & McKenna, G. B. (2015). *Ultrathin Polymer Films: Rubbery Stiffening, Fragility, and T<sub>g</sub> Reduction*. *Macromolecules*, 48(17), 6329-6336].

The authors gratefully acknowledge the National Science Foundation under grant number DMR-1610495 and the John R. Bradford Endowment at Texas Tech, each for partial support of this work. The Office of Naval Research through the DURIP program Grant No. N00014-12-1-0876, is also thanked for instrumental support.

Wednesday 6:30 Cripple Creek Ballroom

PO60

### **Global strain-field mapping of a carbon nanotube-laden interface using digital image correlation**

Shing-Yun Chang, Sahil Vora, Huseini Patanwala, Brice Bogner, Michelle Si Wan Li, and Anson Ma

*University of Connecticut, Storrs, CT, United States*

Identifying the correct stress-strain relationship experimentally is important to understanding the mechanical response of an interface and provides the basis for the theoretical development and experimental validation of any constitutive models. Langmuir-Pockels (LP) trough is one of the most commonly used tools for studying an interface. In a typical LP trough experiment, as the interface is compressed by a pair of barriers, a Wilhelmy microbalance is used to measure the corresponding "surface pressure". Despite the relatively simple experimental setup, a mixed deformation field is created, further complicating the interpretation of the experimental results. Most, if not all, existing studies assume a 1D uniaxial compression during a LP-trough compression experiment. To examine this assumption, we custom-built a glass-bottomed LP trough equipped with a camera to capture a series of optical images as an interface is compressed. Carbon nanotubes (CNTs) were chosen as the model system as they formed a "speckle pattern" when spread onto an air-water interface. Based on the change in this speckle pattern, the displacement and strain fields were calculated using digital image correlation (DIC) analysis. Our experimental findings clearly show, for the first time, the development of a non-uniform and complex 2D strain field during compression. Although the compressive strain averaged over the whole trough area closely resembles the 1D uniaxial compression strain, the 1D compression assumption underestimates the local strain at the center of the trough by about 36% (for a compression area of 25 cm<sup>2</sup>). This DIC-based method may be applicable to other systems with similar optical texture, allowing the correct identification of stress-strain relationship of an interface.

This work is supported by NSF CAREER (#1253613), GE fellowship, and Anton Paar fellowship.

Wednesday 6:30 Cripple Creek Ballroom

PO61

### **Linear dynamic mechanics and creep flow of matrix-free polymer grafted nanocomposites**

Eileen N. Buening<sup>1</sup>, Daniele Parisi<sup>2</sup>, Brian Benicewicz<sup>3</sup>, Dimitris Vlassopoulos<sup>2</sup>, and Sanat K. Kumar<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Columbia University, New York, NY, United States*; <sup>2</sup>*FORTH-IESL, HERAKLION, Greece*; <sup>3</sup>*Chemistry and Biochemistry, University of South Carolina, Columbia, NY, United States*

Recent works have exhibited enhanced molecular transport for membranes comprised solely of polymer grafted nanoparticles compared to that of bulk polymer or un-grafted, "traditional" mixed composites. Additionally, for a fixed grafting density, these enhancements appear non-monotonic as a function of grafted chain length. We postulate chemically grafting polymers to the surface of nanoparticles restricts the ability of the chains to sufficiently pack the spaces between the particle cores. In this regime, there exist locations which are essentially "starved" of polymer at the edges of the brush. To support these claims and investigate the origin of the non-monotonic behavior in diffusion we use both linear small amplitude oscillatory shear and creep flow studies to probe the chain dynamics. Interestingly, the most significant enhancement in the transport is found to occur at a molecular weight where the long-time flow behavior of the material transitions from being polymer chain dominated to core nanoparticle dominated. The understanding of the dynamic behavior of these complex colloids may lead to better rational design of novel materials.

Wednesday 6:30 Cripple Creek Ballroom

PO62

### **Viscoelastic characterization of CNT-grafted fiber reinforced epoxy composite**

Ajay Krishnamurthy<sup>1</sup>, Ran Tao<sup>1</sup>, Sagar Doshi<sup>2</sup>, Erik Thostenson<sup>2</sup>, and Aaron M. Forster<sup>1</sup>

<sup>1</sup>*Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, United States*;

<sup>2</sup>*Department of Mechanical Engineering, University of Delaware, Newark, DE, United States*

Carbon nanotubes (CNT) have been shown to provide multifunctional capabilities to fiber reinforced composites. CNTs improve out of plane mechanical properties and act as electrically conductive pathways. CNTs grafted onto fiber surfaces have been shown to directly improve the stress transfer at the fiber-polymer interface. An important aspect of these hierarchical composites is the effect of the CNTs on the viscoelastic properties. Dynamic mechanical thermal analysis was conducted on unidirectional glass fiber reinforced composites containing 1.35 mass % of multiwall CNTs. Master curves were generated on the composites with and without CNTs using time-temperature superposition. The incorporation of CNTs slightly reinforces the glassy shear modulus of the fiber composite, while decreasing the rubbery shear modulus. The glass transition temperature (T<sub>g</sub>) remains nearly unchanged compared to the fiber composite. The temperature dependence of the horizontal shift factors above T<sub>g</sub> can be described by the Williams-Landel-Ferry (WLF) equation, and the data below T<sub>g</sub> are fitted to Arrhenius equation. The effect of CNT on the polymer-fiber interface is discussed.

Wednesday 6:30 Cripple Creek Ballroom

PO63

**Effect of CNT synthesis conditions on nonlinear rheological response of CNT/PVDF nanocomposites**Milad Kamkar, Soheil Sadeghi, Mohammad Arjmand, and Uttandaraman Sundararaj*Department of Chemical and Petroleum Engineering, University of Calgary, Calgary T2N 1N4, Canada*

Employing chemical vapor deposition technique, multi-walled carbon nanotubes (CNTs) were synthesized over Fe catalyst at a broad range of temperatures, i.e. 550°C to 950°C. Synthesized CNTs were melt-mixed into a poly(vinylidene fluoride) (PVDF) matrix at various loadings. Characterization of nanofillers and nanocomposites revealed that synthesis temperature has a huge impact on the morphology of synthesized CNTs and the nanocomposites thereof. It was realized that CNT650 (CNT synthesized at 650°C), by far, featured the highest carbon purity and CNT quality among the synthesized CNTs. CNT550 had the lowest carbon purity and a considerable amount of amorphous carbon, while CNT850 and CNT950 comprised a significant amount of thermally resistant carbonaceous fillers covering the surface of sintered catalyst. Optical microscopy and transmission electron microscopy of nanocomposites showed significantly better micro- and nano-dispersion for CNT650. The understanding rheological behavior of polymer nanocomposites is crucial to get fundamental insight about the microstructure. Accordingly, we carried out oscillatory amplitude sweep test on CNT/PVDF nanocomposites. All nanocomposite samples, except for CNT650/PVDF, showed a multi-step transition into a nonlinear regime as  $G'$  dropped to an intermediate plateau and then decreased significantly. These results reveal a significant difference in the microstructure of CNT650/PVDF and other nanocomposites. Moreover, the non-linear viscoelasticity of nanocomposites has been studied by large amplitude oscillatory shear (LAOS) experiments. Results of the nonlinear response of nanocomposites are mainly presented using qualitative stress-strain or stress-strain rate Lissajous-Bowditch plots, and physical interpretations based on intra- and inter-cycle nonlinearity parameters.

Wednesday 6:30 Cripple Creek Ballroom

PO64

**The synergistic effects of polymer nanocomposites based on chemically stitched CNT/graphene hybrids:****Rheological, electrical and mechanical properties**Mohammad Heydarnejad Moghadam, Fatemeh Goharpey, and Nazockdast Hosein*Department of Polymer Engineering and Color Science, Amirkabir university of technology, Tehran, Tehran, Iran*

Graphene Nanosheets and Multi Walled Carbon nanotubes (MWCNT) were modified by ODA (octadecylamine) to prevent the aggregation of Nanoparticles and also improve the compatibility between the Nanoparticles and hydrophobic SEBS (styrene-*b*-(ethylene-co-butylene)-*b*-styrene) matrix. Chemical hybrid of nanoparticles was synthesized by Stitching Graphene and CNT and further modification by ODA. Nanocomposites were prepared by solution mixing method. FE-SEM images of nanocomposites showed well dispersed nanoparticles in SEBS matrix. Rheological, Electrical and Mechanical measurements demonstrate synergistic transport effect due to Graphene-CNT chemically interconnected network structure formed throughout the matrix. Also, it has been shown that Chemically Hybrid of nanoparticles has relatively high critical component in Percolation theory for both rheological and electrical properties that is caused by more complex Nano structures in stitched CNT/Graphene Hybrid. Finally, it should be noted that the values for critical component in rheological measurements is lower than electrical measurements, due to network structure of PS microphase separated domains in SEBS matrix.

Wednesday 6:30 Cripple Creek Ballroom

PO65

**Nano-rheology of entangled polymer melts**Ting Ge<sup>1</sup>, Gary S. Grest<sup>2</sup>, and Michael Rubinstein<sup>1</sup>*<sup>1</sup>Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, United States; <sup>2</sup>Sandia National Laboratories, Albuquerque, NM 87185, United States*

We probe local viscoelasticity of an entangled polymer melt at the nanoscale by studying the motion of embedded non-sticky nanoparticles (NPs). As in conventional microrheology, the generalized Stokes-Einstein relation is employed to extract an effective stress relaxation function  $G_{GSE}(t)$  from the mean square displacement of NPs.  $G_{GSE}(t)$  for different NP diameters  $d$  are compared with the stress relaxation function  $G(t)$  of a pure polymer melt. For linear polymers, a plateau in  $G_{GSE}$  emerges as  $d$  exceeds the entanglement mesh size  $a$  and approaches the entanglement plateau in  $G(t)$  for a pure melt with increasing  $d$ . The deviation of  $G_{GSE}$  from  $G(t)$  for  $a < d < 3a$  reflects the incomplete coupling between NPs and the long-time modes of the melt. For ring polymers, as  $d$  increases towards the spanning size  $R$  of ring polymers,  $G_{GSE}$  approaches  $G(t)$  of ring melt with no entanglement plateau.

Wednesday 6:30 Cripple Creek Ballroom

PO66

**Complicated issues in paint making: Order of addition and so on**Hao Sun*PPG Industries, Inc., Allison Park, PA 15101, United States*

It is known that the preparation of paints is a complex process and the properties of paints depend on the ingredient compositions, order of mixing, and many other processing parameters. In this study, we picked up a few key components from an automotive coating and demonstrated the importance of the order of addition. We found certain components play a vital role in determining the rheological properties of the mixture. We will show how to design the order of addition experiments by statistical tool and how to understand the data. We will also provide scientific vision and mechanisms behind the experiments.

Wednesday 6:30 Cripple Creek Ballroom

PO67

**Microrheology of a drying paint**Selwin Varghese<sup>1</sup>, Reza M. Rock<sup>2</sup>, James F. Gilchrist<sup>3</sup>, and Christopher L. Wirth<sup>1</sup><sup>1</sup>Chemical and Biomedical Engineering, Cleveland State University, Cleveland, OH 44115, United States; <sup>2</sup>PPG Industries, Allison Park, PA 15101, United States; <sup>3</sup>Lehigh University, Bethlehem, PA, United States

Controlling the rheological behavior of a coating is crucial to improving coating aesthetics and performance. Unfortunately, the transient rheological properties of a coating during the flash and cure process are often difficult to measure and, consequently, not well understood. Microrheology, a technique that uses nano- to micrometer scale probe particles for a rheological measurement, is one potential non-invasive technique for probing the transient material properties of a drying paint. We used microrheology to probe the rheological properties of paints at both steady (i.e. non-drying) and unsteady (i.e. drying) conditions in 3-dimensions. By doing so, we determined how various parameters such as coating thickness and fluid evaporation rate affected the viscoelastic properties of the thin film.

Wednesday 6:30 Cripple Creek Ballroom

PO68

**Linear and non-linear rheology of PBT/PTHF segmented copolymers**André De Almeida<sup>1</sup>, Guilhem P. Baeza<sup>1</sup>, and Dimitris Vlassopoulos<sup>2</sup><sup>1</sup>INSA Lyon, villeurbanne, France; <sup>2</sup>FORTH-IESL, HERAKLION, Greece

Thermoplastic elastomers represent an important class of materials for the energy and the transport industries. While their molecular structure is reasonably well understood [1], a formidable challenge from the engineering point of view is the molecular understanding of their processing performance. In this work, we study the linear and non-linear rheology of segmented copolymer melts made of successive incompatible units of crystallizable polybutylene terephthalate (pBT) and poly-tetrahydrofuran (pTHF) [2] with varying pBT content (from 30 to 60% in weight). In particular, we examine the crystallization kinetics at different temperatures below their melting point by observing the time evolution of  $G'$  and  $G''$  (as well as DSC thermograms) following quenching. Interestingly, while the general trend resembles the familiar Avrami S-shape, two steps of moduli growth are evidenced during the crystallization process, reflecting a change in the mechanism of crystal growth. By following the same quenching protocol during start-up experiments at different shear rates (performed by means of a cone-partioned-plate "CPP" setup), we observe an unusual strain hardening after a long period of steady stress. The latter scales roughly with strain and is attributed to induced structure of the pBT phase. Similar tests at different times (4min, 8min, 20min and 55min) during the crystallization process support this scenario of structure formation.

References: [1] Gaymans, R.J., Segmented copolymers with monodisperse crystallizable hard segments: Novel semi-crystalline materials. Progress in Polymer Science, 2011. 36(6): p. 713-748. [2] Gabriëlse, W., M. Soliman, and K. Dijkstra, Microstructure and Phase Behavior of Block Copoly(ether ester) Thermoplastic Elastomers. Macromolecules, 2001. 34(6): p. 1685-1693.

Wednesday 6:30 Cripple Creek Ballroom

PO69

**Linear rheological responses of second-generation dendronized wedge-type polymer**Zhiyuan Qian<sup>1</sup>, Alice B. Chang<sup>2</sup>, Tzu-Pin Lin<sup>2</sup>, Pablo E. Guzman<sup>3</sup>, Robert H. Grubbs<sup>2</sup>, and Gregory B. McKenna<sup>1</sup><sup>1</sup>Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; <sup>2</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States; <sup>3</sup>Energetics Technology Branch, U.S. Army Research Laboratory, APG, MD 21005, United States

The linear rheological responses of second-generation dendronized wedge-type polymer synthesized by ring-opening metathesis polymerization have been measured. By applying time-temperature superposition (TTS) principle, the master curve was constructed over the temperature ranging from terminal regime to glassy regime. An extremely low glassy modulus of 100 MPa is observed which may due to the bulky side group in the structure. The apparent extremely low rubbery plateau of approximately 16 kPa in the dynamic response and Van Gurp-Palmen plot is found to be a false plateau after further investigating the retardation spectrum.

The authors are thankful to the J. R. Bradford Endowment at Texas Tech University for partial support for this work.

Wednesday 6:30 Cripple Creek Ballroom

PO70

**A transient study of the gelation of aqueous solutions of pluronic F-127 using SAOS**

Cameron C. Hopkins and John R. de Bruyn

Department of Physics and Astronomy, The University of Western Ontario, London, Ontario N6A3K7, Canada

The rheology of aqueous solutions of Pluronic F-127 with concentrations 16, 18, and 20 wt.%, was studied as a function of temperature and time using SAOS. Pluronic F-127 is a linear ABA triblock copolymer with chemical structure Polyethylene Oxide-Polypropylene Oxide-Polyethylene Oxide (PEO-PPO-PEO). At low temperature, the fluid is a solution of noninteracting unimers and exhibits Newtonian behaviour [1]. As the temperature is increased the solubility of PPO decreases and spherical micelles form consisting of PPO cores with PEO shells. At sufficiently high concentration, the micelles pack into a cubic lattice and form a stiff gel [2]. At higher temperature, the PEO shells dehydrate and the gel structure collapses [2]. Using both discrete and continuous temperature ramps, the two transitions were studied by measuring the storage and loss moduli at a fixed frequency and amplitude as a function of time. While heating the solution, transient measurements at the gel transition temperature show that the gelation process has a long relaxation time, on the order of several hours. The dissolution of the gel structure at higher temperature is a two-step process, where the material first weakens before the complete breakup of the gel occurs at further higher temperature. Cooling the solution

back down reveals a hysteresis at both the high temperature and room temperature transitions. This study demonstrates that the formation and break up of the micellar gel structure are complicated dynamic phenomena. Due to the long relaxation time near the transitions, the material is not in a steady state, and so waiting times in typical experiments are insufficient to achieve rheological equilibrium.

[1] - Jalaal, M., Cottrell, G., Balmforth N., and Stoeber., B., "On the rheology of Pluronic F127 aqueous solutions," *Journal of Rheology* 61 139-146 (2017) [2] - Prud'homme, R. K., Wu, G., and Schneider, D. K., "Structure and rheology studies of poly (oxyethylene-oxypropylene-oxyethylene) aqueous solution," *Langmuir* 12, 4651-4659 (1996)

Wednesday 6:30 Cripple Creek Ballroom

PO71

### **Wide angle X-ray scattering study of nematic interactions in a bi-disperse polystyrene melt**

Anine Borger<sup>1</sup>, Kell Mortensen<sup>1</sup>, Qian Huang<sup>2</sup>, Ole Hassager<sup>2</sup>, Jacob Kirkensgaard<sup>1</sup>, and Kristoffer Almdal<sup>3</sup>

<sup>1</sup>Niels Bohr Institute, University of Copenhagen, Copenhagen 2100 Kbh O, Denmark; <sup>2</sup>Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kongens Lyngby, Denmark; <sup>3</sup>Department of Micro- and Nanotechnology, Technical University of Denmark, Kgs. Lyngby 2800, Denmark

Commercial polymer materials are polydisperse. This study investigates the effects of such dispersity by probing how the presence of longer chains affects the response to deformation of a short-chain model system, i.e. a bi-disperse melt of well-defined long and short chains compared to a monodisperse model system of short chains. The experiment is carried out in two steps: The first step is to stretch the sample and allow it to relax while measuring its response using a Filament Stretch Rheometer, which both makes the deformation and measures the rheological parameters. After the response measurement, the sample is quenched below its glass-transition temperature, with the aim to preserve the molecular conformation for the further studies. The second step is to measure the molecular alignment of the polymer molecules in the quenched samples using Small-Angle Neutron Scattering (SANS) for the overall coil conformation, and Wide-Angle X-ray Scattering (WAXS) to probe the structure shorter length scales. The previous SANS study showed that in the presence of the long chains, the short chains are stretched ~50 % more at the same strain and strain rate due to the nematic field from the long chains. The current Wide Angle X-ray (WAXS) study shows that the correlations on the scale of the packing length are strongly enhanced in the bidisperse melt, which supports the conclusion of a nematic field from the long chains.

Wednesday 6:30 Cripple Creek Ballroom

PO72

### **Flow-induced crystallization in isotactic polypropylene via simultaneous measures of modulus, helicity and morphology**

Kalman Migler and Anthony P. Kotula

*Materials Science and Engineering, NIST, Gaithersburg, MD 20899, United States*

It is well known that application of flow fields can enhance the nucleation rate in polymers by orders of magnitude. The mechanism is still under debate, a recent concept posits that specific work hypothesis determines the onset and extent of the phenomena. Here we use the rheo-Raman microscope to carry out critical tests of this hypothesis. This instrument provides the ability to simultaneously measure the growth of shear moduli, along with the helicity of the chains (via Raman), and the growth of spherulites (via optical microscopy); further, in a plate-plate geometry the latter two can be measured as a function of radial position. This capability provides us with the ability to modify the applied specific work by approximately five orders of magnitude. We report the scaling of the crystallization half-time as a function of both specific work and dimensionless shear rate.

Wednesday 6:30 Cripple Creek Ballroom

PO73

### **Shear alignment and relaxation behavior of pluronic/water/p-xylene mesophases**

Sahar Qavi and Reza Foudazi

*Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

Amphiphilic molecules self-assemble at water/oil interface and form mesomorphic structures, known as mesophases. Mesophases have received well-deserved attentions due to their broad range of applications in separation and adsorption processes, biotechnology, nanotechnology, and energy storage. Mesophases are subjected to flow filed in various applications, thus, the effect of flow on their alignment should be investigated. While shear deformation is a known method for orientating block copolymers in bulk, its effect on the self-assembled block copolymers in the presence of two solvents is less addressed. In this work, a flow protocol consisting of stress growth at different shear rates has been done on mesophases of Pluronic/water/p-xylene, to shed light on their alignment under shear and subsequent relaxation behavior.

Wednesday 6:30 Cripple Creek Ballroom

PO75

### **Rheological properties of corn stover slurries during fermentation to ethanol**

Sanchari Ghosh, Brenden Epps, and Lee Lynd

*Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, United States*

In typical processes that convert cellulosic biomass into ethanol fuel, fermentation is carried out by saccharolytic enzymes; however, these enzymes require an expensive pretreatment step to make the biomass accessible before they can initiate fermentation. We have proposed a potentially-less-expensive approach using the bacterium *Clostridium thermocellum*, which can initiate fermentation without pretreatment. Moreover, we have proposed a process called "cotreatment", in which fermentation and mechanical milling occur alternately so as to achieve the highest ethanol yield

for the least milling energy input. In order to inform the energetic requirements of cotreatment, we experimentally characterized the rheological properties of corn stover slurries at various stages of the fermentation process. Results show that a corn stover slurry is a yield stress fluid, with shear thinning behavior well described by a power law model (over the range of strain rates considered). Viscosity decreases dramatically upon fermentation, controlling for variables such as solids concentration and particle size distribution. To the author's knowledge, this is the first study to characterize the changes in the physical properties of biomass during fermentation by a thermophilic bacterium.

Wednesday 6:30 Cripple Creek Ballroom

PO76

### **Rheological properties and interparticle interactions of fuel cell catalyst dispersions**

Scott A. Mauger<sup>1</sup>, Sunilkumar Khandavalli<sup>1</sup>, Jonathan J. Sticke<sup>2</sup>, Katherine Hurst<sup>1</sup>, K.C. Neyerlin<sup>1</sup>, and Michael Ulsh<sup>1</sup>

<sup>1</sup>*Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, CO 80401, United States;* <sup>2</sup>*National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401, United States*

The rheological properties of colloidal dispersions, like the inks used to coat fuel cell catalyst layers, are dependent on many factors including concentration of the dispersed particles and polymers, particle porosity, and aggregation. There is a significant body of research examining the rheological properties of both Nafion and carbon black dispersions. However, there has been almost no published research examining the rheological properties of fuel cell catalyst inks containing Nafion and carbon-black-supported catalysts. This may stem from the fact that the inks often used for lab-scale fabrication of fuel cell electrodes tend to be dilute, and thus the rheological properties are dominated by the dispersion medium. However, for roll-to-roll production of electrodes, the inks are an order of magnitude more concentrated, and the properties of the dispersed materials become more important. In this work we used steady-shear and oscillatory rheometry to quantify the influences of carbon type, presence of catalyst particles, and ionomer-to-carbon ratio on the rheological properties of catalyst inks. We found that, for neat carbon black dispersions the rheological properties were non-Newtonian and highly dependent on the pore volume of the particles. The addition of Pt to the particles or Nafion to the dispersion decreased the viscosity. The decrease in viscosity with the addition of Nafion was due to Nafion acting as a surfactant and stabilizing the carbon black particles, consistent with previous studies of aggregation kinetics. Interestingly, we found that when Nafion was added to Pt-on-carbon dispersions, the change in rheological properties was dependent on carbon type: we observed an increase in viscosity for high-surface area carbon but a decrease for the more graphitic Vulcan XC-72. This suggests a difference in interparticle interactions that is dependent on carbon type.

Wednesday 6:30 Cripple Creek Ballroom

PO77

### **The conformation and dynamics of polyelectrolytes in ionic liquids with high salt concentrations**

Atsushi Matsumoto and Amy Q. Shen

*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

Polyelectrolytes are polymers possessing dissociable ions with repeating unit. It has been reported that, in polyelectrolyte solutions with low salt contents, polymer chains are stretched out due to the strong Coulombic repulsion between the repeating units, thus the specific shear viscosity of the polyelectrolyte solutions decreases with increasing concentrations of additive salts due to the screening of Coulombic interaction. In this work, we measured specific shear viscosity of a polyelectrolyte solution (0.00025 M of poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide)) mixed with an ionic liquid (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide)) with varying concentrations. The ionic liquid acts as an additive salt. We observed that the specific viscosity decreased with increasing ionic liquid concentrations, similar to the behavior of the ordinary polyelectrolyte solutions. However, a non-monotonic trend was observed in our polyelectrolyte-ionic liquid mixture. The specific viscosity started to increase when the ionic liquid concentration became greater than 100 M. Based on the conjectures on electrostatic screening by Dobrynin et al.[1], our results suggest that the electrostatic screening length of polyion charge can exceed the size of the electrostatic blob at sufficiently high ionic liquid concentration, including the extension of polymer chains, hence increase the specific viscosity of our polyelectrolyte-ionic liquid mixtures.

[1] Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *Macromolecules* 1995, 28, 1859-1871

Wednesday 6:30 Cripple Creek Ballroom

PO78

### **Filament dynamics in a salt-free viscoelastic surfactant solutions**

Rose Omidvar<sup>1</sup> and Hadi Mohammadigoushki<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Florida State University, Tallahassee, FL 32310, United States;* <sup>2</sup>*Florida State University, Tallahassee, FL 32310, United States*

In this work, we study the dynamics of a model wormlike micellar solutions via CaBER, shear rheology and TEM imaging. Wormlike micellar solutions contain cetyltrimethylammonium tosylate (CTAT) in deionized water. At low concentrations (0.7 wt% < c < 1.1 wt%), solutions exhibit shear thickening and elongational flow shows formation of elastic filaments possibly due to formation of elongation induced structures. In this range of concentrations, the extensional relaxation time is fairly constant around 0.03 s. At higher concentrations 1.1 wt% < c < 2-3 wt%, a significant increase in shear relaxation time is observed. However, beyond 2 wt%, the shear relaxation time decreases and the zero shear viscosity approaches an asymptotic value. TEM images confirm no sign of branched networks beyond the concentration of 2 wt%. It is shown that the maximum Trouton ratio measured from transient rheology experiments decreases as concentration increases and finally reaches a constant value around  $Tr \sim 3$  for  $c > 2$  wt%.

Wednesday 6:30 Cripple Creek Ballroom

PO79

### **Thermalized formulation of soft glassy rheology**

Robert S. Hoy

*Physics, University of South Florida, Tampa, FL 33620, United States*

We develop a continuous formulation of soft glassy rheology (SGR) theory that corresponds to the infinite-system-size limit and includes thermalized strain degrees of freedom. The continuous formulation provides multiple novel results that cannot be straightforwardly obtained via the standard, discrete-zone formulation. In particular, it allows for quantitative analysis of systems' heterogeneous yielding dynamics and nonequilibrium deformation thermodynamics. As a demonstration of the method, we illustrate the very different characters of fully-thermal and nearly-athermal plasticity by comparing results for thermalized vs. nonthermalized strain degrees of freedom and plastic flow rules.

Wednesday 6:30 Cripple Creek Ballroom

PO80

### **Glass former colloids dynamics in isochoric conditions**

Davide Pierleoni<sup>1</sup>, Ferruccio Doghieri<sup>2</sup>, and Gregory B. McKenna<sup>3</sup>

<sup>1</sup>*University of Bologna, Urbino, Pesaro e Urbino 61029, Italy;* <sup>2</sup>*Dept. of civil, chemical, environmental and materials eng., University of Bologna, Bologna, Italy;* <sup>3</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Glass former colloids had a huge increase on research interest in the last decade as model materials for glass dynamics analysis, due to analogies found with macromolecular glasses and highly tunable chemical synthesis. However, the similar behavior between such different materials is still an open question. Instead of undergo to the glass transition as a reduction of chain mobility, in soft colloids like poly(N-isopropylacrylamide) the structure change is attributed to a volume increment of particles under specific conditions, as example below a characteristic temperature, causing an increase of the volume fraction of colloid; this volume change is attributed to a massive increase of dispersant solubility. In the framework of molecular glass dynamics, Colucci et al demonstrated the existence of a glass transition under isochoric conditions, also underlining differences with the isobaric transition. Afterwards Merzlyakov et al developed a novel experimental method for the characterization of thermal stress of epoxy resins in isochoric conditions. This was possible through the development of a novel experimental method, consisting on pressure measurements inside a constraining thick-walled tube filled with sample, at controlled temperature. This work consists on the development of a novel experimental apparatus based on the thick-walled tube equipment, in order to characterize the isochoric behavior of glass forming colloids. A new design was carried out to allow a fine control of temperature, and to increase the experimental possibilities offered by the apparatus. Possible detection of a pressure increase associated to the transition could represent a great innovation on the colloid research field: as a matter of facts, perfect volume additivity is commonly accepted, relying on the idea of particle expansion for dispersant penetration. A purposely made design of experiments will also outline the glassy colloid behavior at isochoric conditions; the latter will then compared with the macromolecular glass behavior.

Wednesday 6:30 Cripple Creek Ballroom

PO81

### **Linear rheology of a nematic liquid crystal in the presence of a magnetic field**

Jacob Britton and Eric P. Choate

*Department of Mathematics and Statistics, Radford University, Radford, VA 24142, United States*

We explore how the linear response of a nematic liquid crystal to small amplitude oscillatory shear is affected by the presence of a static magnetic field. The magnetic field forces an equilibrium alignment of the liquid crystal of our choosing, and the flow causes the orientation to oscillate around this equilibrium. We use Leslie-Erikson theory to model the oscillations in the orientation and predict the storage and loss moduli. This model allows us to observe the effect of the orientation and strength of the magnetic field on the moduli. For liquid crystals that are flow aligning in response to steady shear, aligning the field in the flow alignment direction makes the nematic effectively a viscous fluid. A field that aligns the nematic orthogonal to the plates maximizes the storage modulus. For a fixed field orientation, there is a critical field strength that maximizes the storage modulus with both very weak and very strong fields resulting in viscous-like responses, but the effective viscosity increases to a plateau with increasing field strength.

Wednesday 6:30 Cripple Creek Ballroom

PO82

### **Chitosan as a yield stress fluid: Concentration dependent rheology and microdynamics**

Nina M. Gasbarro and Michael J. Solomon

*Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI 48105, United States*

Chitosan and its derivatives are of interest due to their versatility and potential both as a biomaterial and additive for rheological control. For chitosan concentrations ranging from the dilute to concentrated regime, we report two regions of shear thinning at high and low shear rates. The shear thinning at low shear rates, although reported for chitosan derivatives, has not been investigated in aqueous chitosan and is consistent with the existence of an apparent yield-stress. We probe the physicochemical and microdynamical origins of this behavior by the addition of urea - a hydrogen bond and hydrophobic interaction disrupter - and by dynamic light scattering (DLS). Our findings suggest that urea is not able to fully disrupt chitosan associations and only marginally lowers the yield stress parameter and viscosity. The microstructure of highly concentrated chitosan solutions, as revealed by DLS, is dominated by extremely slow microdynamics, suggesting a network of large, associating aggregates. At the highest concentration analyzed by DLS, the dynamics are consistent with weak gel behavior.

Wednesday 6:30 Cripple Creek Ballroom

PO83

**Observation of dynamically correlated region in colloidal glasses by small-angle neutron scattering**Zhe Wang<sup>1</sup>, Takuya Iwashita<sup>2</sup>, Lionel Porcar<sup>3</sup>, Yangyang Wang<sup>4</sup>, Yun Liu<sup>5</sup>, Luis Sanchez-Diaz<sup>1</sup>, Bin Wu<sup>1</sup>, Takeshi Egami<sup>6</sup>, and Wei-Ren Chen<sup>1</sup>*<sup>1</sup>Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States; <sup>2</sup>Department of Electrical and Electronic Engineering, Oita University, Oita, Japan; <sup>3</sup>Institut Laue-Langevin, Grenoble, France; <sup>4</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States; <sup>5</sup>Center for Neutron Research, National Institute of Standard and Technology, Gaithersburg, MD, United States; <sup>6</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, United States*

The microscopic deformation mechanism of charged colloidal glasses with long-range interactions under shear is investigated by in-situ small-angle neutron scattering, and a dynamically correlated region (DCR) is identified. This short-lived region provides the resistance to the configurational rearrangement imposed by the external deformation, as evidenced by the evolution of the size of DCR in the shear thinning regime and the quantitative agreement between the local stress sustained by DCR and the macroscopic stress from rheological measurements. This finding suggests that DCR is an important quantity for microscopically addressing the flow and deformation behavior of strongly interacting colloids.

Wednesday 6:30 Cripple Creek Ballroom

PO84

**Feel the burn: Incorporating tribological techniques to characterize fabric wear**James P. Eickhoff and Dalton Echard*Rheology, Anton Paar USA, Ashland, VA 23005, United States*

Comfort is very important for a long distance runner. This comfort stems from past experience in which every runner has gone through of "runner's rash" or chafing. Chafing occurs from the wear behaviour between the contact between skin and the fabric worn. The wearing response can from a small wear to very painful blisters, making it difficult to run. This wearing behaviour is influenced by the type of fabric worn as well as the environmental conditions (temperature, humidity, etc.). In recent years various types of fabric technologies have been developed to help minimize the wear. In this study, a series of fabrics were measured with a rotational rheometer combined with a tribological attachment to study this wear influence under varying temperature and humidity conditions a runner would experience.

Wednesday 6:30 Cripple Creek Ballroom

PO85

**Rheology investigation of architectural paints**Yu Wang*Architectural, PPG, allison park, PA 15101, United States*

Application performance is very important to customer perception of architectural paints. Unfortunately, the conventional viscosity profile of paint often fails to explain the application properties. Here we developed a rheology test method that mimic the roller application process. The data derived from this new test method shows strong correlation with application data, such as applied hiding, appearance, application feel and paint transfer. The knowledge learned from the rheology study has helped us improve the formula and the performance of architectural paints, and potentially will help the customer satisfaction rate.

Wednesday 6:30 Cripple Creek Ballroom

PO86

**Design criteria for thixotropic yield-stress fluids for hose flow and surface coating**Brendan C. Blackwell, Alex Wu, and Randy H. Ewoldt*Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Yield-stress fluids can stick and accumulate after spray impact, motivating several applications including manufacturing processes and fire suppression, wherein this phenomena is useful both in extinguishing a flame and in preventing re-ignition. Here we theoretically develop formulation-agnostic rheological design criteria for thixotropic yield-stress fluids to satisfy the competing requirements of minimum flowrate, maximum pressure drop, and minimum resulting coating thickness. This involves the yield stress, high shear viscosity, and thixotropic restructuring timescale. Experimentally, we study several yield-stress fluids (model materials and commercially formulated products), examining the steady-flow rheology and transient thixotropic restructuring times from rheometer tests, as well as flowrates and pressure drops from full-scale firefighting hose-flow experiments. We use the new design criteria to execute a downselection process based on rheological measurements alone, demonstrating how to identify candidate materials for the application.

Wednesday 6:30 Cripple Creek Ballroom

PO87

**Effect of rising motion of spherical bodies on structured fluids with yield stress**Shadi Mirzaagha<sup>1</sup>, Rossana Pasquino<sup>1</sup>, Vincenzo Guida<sup>2</sup>, Fabio Zonfrilli<sup>2</sup>, and Nino Grizzuti<sup>1</sup>*<sup>1</sup>Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Naples 80125, Italy; <sup>2</sup>Brussels Innovation Center, Procter&Gamble, Brussels, Belgium*

In this work, the analysis of the physical stability of a structured detergent containing air bubbles has been performed on a simplified model fluid used for washing machines. The system is a suspension of hydrogenated castor oil colloidal fibers in a surfactant micellar solution. The fiber

network confers to the fluid a viscoelastic behavior, with a well-defined yield stress, which increases with increasing fiber concentration. Basically, the main responsible of this instability is the action of an external force, i.e. the load applied by air bubbles which sometimes are found into finished structured detergents due to processing conditions. As a result, the network can be subjected to a clear phase separation, with the matrix without fibers standing on the bottom of the fluid volume, whereas a more concentrated system is forming towards the free surface. We studied various samples, which differ from each other for aeration level and fiber concentration (hence, resulting fluid yield stress). The rheological behavior and the microstructure of these fluids have been rheologically characterized. To try to model the real system, we also replaced the air bubbles with hollow glass microspheres. The motion of a spherical single body (air bubble or hollow glass microsphere) as well as the cooperative effect of the particle ensembles have been analyzed by a home-made time lapse photography technique in a way to study the dynamics of the spherical bodies and to verify the possibility of a microstructure collapse in the presence of many spheres. The experiments last as long as several weeks. The rising motion of the single sphere and the edge split during phase separation have been monitored by changing various parameters such as temperature, aeration content and fluid yield stress. The results are novel for the peculiarity of the system and for the wide range of aspects used to study the phenomenon. The results could have important implications in the fabric and personal care detergency, a technological area where many fluids have composition and show rheological properties similar to those considered in the current work.

Wednesday 6:30 Cripple Creek Ballroom

PO88

**Big effects of small sticky nanoparticles on the glass transition, fragility, and viscoelastic properties of polymer nanocomposites**

Shiwang Cheng<sup>1</sup>, Shi-Jie Xie<sup>2</sup>, Jan-Michael Carrillo<sup>3</sup>, Robert Carroll<sup>4</sup>, Halle Martin<sup>4</sup>, Mark Dadmun<sup>4</sup>, Bobby Sumpter<sup>3</sup>, Ken S. Schweizer<sup>2</sup>, and Alexei Sokolov<sup>3</sup>

<sup>1</sup>*Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, United States;*

<sup>2</sup>*Dept. Materials Science, University of Illinois at Urbana-Champaign, Urbana, IL, United States;* <sup>3</sup>*Oak Ridge National Laboratory, Oak Ridge, TN, United States;* <sup>4</sup>*University of Tennessee, Knoxville, TN, United States*

Polymer nanocomposites with small nanoparticles, such as fullerene, polyhedral oligomeric silsesquioxane, and their derivatives, typically end up in a reduction in the glass transition and viscosity at low nanoparticle loadings and a gelation at high loadings of nanoparticles. Consequently, the usage of small nanoparticles is largely eliminated, and the role of small nanoparticles is not well understood. Here, we demonstrate that well-dispersed, small (diameter ~1.8 nm) nanoparticles with attractive interactions lead to unexpectedly large and qualitatively new changes in PNC structural dynamics in comparison to conventional composites based on particles of diameter ~10-50 nm. At the same time, the zero-shear viscosity at high temperatures remains comparable to that of the neat polymer, thereby retaining good processibility and resolving a major challenge in PNC applications. Our results suggest that the nanoparticle mobility and relatively short lifetimes of nanoparticle-polymer associations open qualitatively new horizons in tunability of macroscopic properties in nanocomposites with high potential for the development of new functional materials.



# Gallery of Rheology

## Symposium GR Gallery of Rheology Contest

Organizers: Anne M. Grillet, Randy H. Ewoldt and Faith A. Morrison

Wednesday 6:30 Cripple Creek Foyer GR1

### **Cells dynamically engineer the rheology of their microenvironment**

Kelly M. Schultz and Maryam Daviran

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

The phase change cells induce by enzymatic degradation is instrumental in the ability for them to move. These images show human mesenchymal stem cell remodeling of synthetic hydrogel scaffolds during motility. Brightfield images taken over approximately an hour are averaged showing the cell and probe particle movement. Probe particles are embedded into the material to enable microrheological measurements.

Wednesday 6:30 Cripple Creek Foyer GR2

### **Microstructural deformation in active matter**

Eric W. Burkholder and John F. Brady

*Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

Active materials exhibit rich dynamic and rheological behaviors that defy conventional intuition regarding colloidal fluids: e.g. a lower critical solution temperature phase transition and negative shear stresses. Underpinning these fascinating macroscopic behaviors is a complex microscopic structure, which may be described by the same statistical-mechanical framework as passive colloidal suspensions by recognizing the role of the swim force — an internal body force that drives active particle motion. We study the microstructural deformation in a suspension of active Brownian particles due to the motion of a colloidal probe particle subject to an external force (i.e. microrheology). Specifically, we compute and visualize the spatial variations in concentration, polar order, and nematic order as a result of the probe's motion. These captivating structures yield not only microscopic information regarding the effects of active particle distributions, but are directly linked to the macroscopic properties of the material, thus giving insight into how particle activity affects, for example, biological processes.

Wednesday 6:30 Cripple Creek Foyer GR3

### **Recreating the starry night via shear rheometry**

Gaurav Chaudhary, Gabriel Juarez, and Randy H. Ewoldt

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

Dinoflagellate are the most common source of bioluminescence in the sea; Puerto Rico, Jamaica, and Bali being the most famous habitats. These cells respond to mechanical disturbances in their surroundings by flashing visible light almost instantaneously. A few studies have utilized this response for flow visualization and studying turbulence in waves. We studied this response under a controlled flow and found that a threshold stress of 0.1 Pa is required for the bioluminescent response with each individual flash lasting for around 0.5s.

Wednesday 6:30 Cripple Creek Foyer GR4

### **The Möbius dance: Hydrodynamic interactions of non-orientable objects moving in a fluid**

Nicolas Moreno, David Vazquez-Cortes, and Eliot Fried

*Mathematics, Mechanics, and Materials Unit, Okinawa Institute of Science and Technology, Onna, Japan*

The rheological behavior of colloidal dispersions is controlled by the balance between thermodynamic and hydrodynamic interactions. Whereas the thermodynamic interactions are governed by the chemical nature of the species in the system, the hydrodynamic interactions are dominated by the geometry of the colloid. In this work, we explore how the geometry of non-orientable shapes or Möbius bands (circular bands with half pi twist) influence the hydrodynamic behavior of a moving object and the surrounding fluid. As a prototype model, we investigate the sedimentation of rigid polystyrene bands in water. Different aspect ratios and flow regimes allow us to identify the dominant modes of the motion of these objects. We find that these geometries follow helicoidal paths and may exhibit tumbling, rotational, and translational motions. Controlling the dimensions of the bands allows us fine tune the characteristic frequency of their dominant modes and to prescribe the amplitude of the path. The direction of the twist in the band defines its spinning direction. The hydrodynamic properties of these objects offer an interesting number of applications, including chiral-tracing, mixing, and separation in medical or microfluidics applications, and as prototypes for passive swimmers.

Wednesday 6:30 Cripple Creek Foyer GR5

### High speed confocal imaging of sheared colloidal gels

Gabriele Colombo<sup>1</sup> and Jan Vermant<sup>2</sup>

<sup>1</sup>*Department of Materials, ETH Zürich, Zürich, Zürich 8093, Switzerland;* <sup>2</sup>*ETH Zurich, Zurich, Switzerland*

Colloidal gels are an important class of soft materials with a wide range of technological applications, exploiting the combination of solid-like rest structure and liquefaction under mechanical stress of these thixotropic materials. Even though such complex flow behavior is widespread in a number of consumer products and industrially relevant systems, the changes in microstructure underlying thixotropy remain poorly understood. Our experimental approach relies on the quantitative study of the gel microstructure using high-speed confocal microscopy. Microscopic studies under flow are performed using a stress controlled rheometer with a home-made shear cell for counter-rotation of the lower plate, allowing single particles to be located and tracked for long times at the stagnation plane. The confocal images of the disordered structures of colloidal gels not only contain valuable microstructural information: they are also visually striking examples of network structures that dominate the macroscopic behavior of such yield stress, thixotropic materials.

Wednesday 6:30 Cripple Creek Foyer GR6

### Spreading of oil-in-water emulsions on water surface

Neda Sanatkar<sup>1</sup>, Alexander Y. Malkin<sup>2</sup>, and Reza Foudazi<sup>1</sup>

<sup>1</sup>*Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States;* <sup>2</sup>*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 119991, Russia*

Marangoni spreading is a common phenomenon in colloid-related technologies, where a surface tension gradient between the colloidal system and the substrate surface is the driving force of spreading. Emulsions as complex colloidal systems could experience Marangoni spreading in various processes of coating, agricultural, and pharmaceutical industries. Our study of water-in-oil emulsions spreading at water surface shows that the emulsion spreading goes through different stages, depending on the volume fraction and droplet size of the oil phase. A bursting-like spreading upon collision, followed by rapid propagation of emulsion thin film, is observed for all the samples. As the volume fraction of oil phase in the emulsion increases above a threshold that is dependent on the droplet size, a second bursting is observed. The results indicate while the Marangoni stresses initiate the spreading, but osmotic pressure and coalescence of oil droplets play an important role in the spreading mechanism and second bursting of the emulsions. The images show different steps of spreading of the emulsions with double bursting behavior.

Wednesday 6:30 Cripple Creek Foyer GR7

### Bead formation on a viscoelastic drop's tail

Haonan Xu and Robert J. Poole

*School of Engineering, University of Liverpool, Liverpool L69 3GH, United Kingdom*

As a viscoelastic droplet moves on an inclined superhydrophobic surface an intriguing "beads-on-a-tail" structure emerges. The interaction of the surface features and the viscoelasticity of the drop results in a significant slowing of the drop - in comparison with an equivalent-viscosity Newtonian drop - and an instability on this fluid tail gives rise to the bead-like structure.

Wednesday 6:30 Cripple Creek Foyer GR8

### From liquid to solid in a splash

Michela Geri, Bavand Keshavarz, and Gareth H. McKinley

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

The impact of a droplet with a bath of an immiscible liquid is an interesting and complex phenomenon even for simple Newtonian liquids. Different morphologies can emerge depending on the Weber number of the impacting droplet and the corresponding density difference with the bath liquid. In this work, we focus on the case where the droplet is a hot solution of paraffin in mineral oil, impacting on a cold bath of water. Due to the high degree of sub-cooling, solidification of the paraffin happens upon impact while the droplet is still deforming. Using high-speed imaging we show that the final shape of the impacting droplet depends on its Weber number, leading to unique patterns of solidified wax that change from a simple cup to floral shapes, with an increasing number of petals which grow in size with increasing impact velocity. Thermorheological changes in the wax mixture coupled with the involved hydrodynamic instabilities due to the impact govern the formation of these elegant patterns.

Wednesday 6:30 Cripple Creek Foyer GR9

### High-speed imaging of fracture in polymer liquids under extensional flow

Qian Huang<sup>1</sup>, Nicolas J. Alvarez<sup>2</sup>, Aamir Shabbir<sup>1</sup>, and Ole Hassager<sup>1</sup>

<sup>1</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby 2800, Denmark;* <sup>2</sup>*Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States*

We show images of crack propagation in polymer liquids under uniaxial extensional flow. The total time of the fracture process is about 10ms, and the pictures are taken by a high-speed camera with 10,000 frames per second. The images show that elastic rupture in polymer liquids occurs via an edge fracture; and simultaneous propagation of multiple cracks is also observed. The crack profiles reveal the mechanism of energy dissipation during crack propagation.

Wednesday 6:30 Cripple Creek Foyer GR10

### **Yield-stress fluids can be highly extensible**

Arif Z. Nelson and Randy H. Ewoldt

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

Yield-stress fluids are capable of surviving much larger extensional strains than would be indicated by the behavior of common "model" materials. This high extensibility may affect performance requirements in applications. These images demonstrate the need for better model materials and beg for constitutive models that can capture this important behavior.

Wednesday 6:30 Cripple Creek Foyer GR11

### **Silly putty tetrapus**

Anja Vananroye<sup>1</sup>, Peter Van Puyvelde<sup>2</sup>, and Christian Clasen<sup>1</sup>

<sup>1</sup>*KU Leuven, Heverlee, Belgium*; <sup>2</sup>*KU Leuven, Leuven, Belgium*

When silly putty is forced to undergo a shearing deformation in a plate-plate geometry, it develops a peculiar instability that leads to a sample loss in form of four curled 'arms' that stretch out and rotate around the geometry, forming the silly putty tetrapus.

Wednesday 6:30 Cripple Creek Foyer GR12

### **Direct observation of single polymer dynamics in large-amplitude oscillatory extension (LAOE)**

Yuecheng Zhou<sup>1</sup> and Charles M. Schroeder<sup>2</sup>

<sup>1</sup>*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*; <sup>2</sup>*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We directly probe single polymer dynamics in large amplitude oscillatory extensional flow (LAOE) using precisely controlled microfluidics (Stokes trap). Using this method, we generate both small amplitude and large amplitude sinusoidal oscillatory extensional flow in a cross-slot microfluidic device while imaging the non-equilibrium conformational dynamics of single DNA polymers in flow. Using this experimental technique, we study the single chain dynamics of single polymers as a function of the Weissenberg number ( $Wi$ , flow strength) and Deborah number ( $De$ , probing frequency). In LAOE, polymer chains undergo repeated cycles of compression, rotation, and stretching between extensional and compressional axes in a highly dynamic and transient manner. Using this approach, we characterize transient chain dynamics by constructing molecular Lissajous curves (polymer stretch-strain rate curves), which are defined based on single chain conformation and reveal a strikingly rich set of shapes defined by dynamic chain conformations in Pipkin space. In all cases, single polymer experiments are complemented by Brownian dynamics (BD) simulations. To our knowledge, this work is the first demonstration of a molecular rheology experiment utilizing time-dependent control over the entire two-dimensional flow plane.

Wednesday 6:30 Cripple Creek Foyer GR13

### **Microfluidic comet tails**

Simon J. Haward and Amy Q. Shen

*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

In this poster we showcase some striking images of birefringent signals recorded for flows of dilute polymer solutions past microfluidic cylinders. We have fabricated glass microfluidic cylinder devices with high aspect ratios  $23.5 < h/r < 100$  and low blockage ratios  $0.1 < 2r/w < 0.43$ , where  $h = 2$  mm is the channel height,  $w = 0.4$  mm is the channel width and  $20 < r < 85$   $\mu$ m is the cylinder radius. Using full-field birefringence imaging in these devices, we are able to clearly observe the effect of the extensional wake downstream of the trailing stagnation point as we vary the Weissenberg number  $Wi$  of the flow. The birefringence slowly decays with downstream distance from cylinder, giving the resulting images the appearance of 'comet tails', which for high  $Wi$  and small  $r$  reach at least 250 cylinder radii in length.

Wednesday 6:30 Cripple Creek Foyer GR14

### **Chevron-like waves of a submerged viscoelastic jet**

Bavand Keshavarz, Michela Geri, and Gareth H. McKinley

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

A novel experimental setup, equipped with strobe imaging, is used to study the instability patterns of a submerged liquid jet. Visualizations for the Newtonian liquids show that the jet is unstable to the linear perturbations. At low wave-numbers, unstable varicose waves pile up into a continuously growing sinuous mode due to the difference in the corresponding wave speeds. This leads to some unique concertina or chevron-like patterns. Using the strobe technique, we can record the evolution of these complex axisymmetric waves at high spatial and temporal resolutions. For viscoelastic jets, the growth of the inertial waves is substantially inhibited by the streamline tension due to the added elasticity.

Wednesday 6:30 Cripple Creek Foyer

GR15

**Flexible sheet oscillation due to elastic instabilities in a flow of wormlike micelle solution**

Anita A. Dey, Yahya Modarres-Sadeghi, and Jonathan Rothstein

*Mechanical Engineering, University of Massachusetts Amherst, Amherst, MA 01002, United States*

When an elastic structure like a rectangular flexible sheet is placed in the flow of a viscoelastic fluid such as a wormlike micelle solution, the flexible sheet gets deformed and stretched due to the growing stresses developed in its wake. The flow-induced birefringence (FIB) visualizations below show a birefringent tail growing in size and length in the wake of a stretched flexible sheet. Unlike Newtonian fluids, the flow of viscoelastic fluids can become unstable at infinitesimal Reynolds numbers due to an elastic instability. Because of this instability, the wormlike micelle solution can no longer withstand the stretched flexible sheet, instead, it ruptures and releases the flexible sheet causing it to recoil rapidly. The last image shows a contracted birefringent region in the wake of the recoiled flexible sheet. This sequence of FIB images demonstrates a single oscillation cycle of a viscoelastic-fluid structure interaction.

Wednesday 6:30 Cripple Creek Foyer

GR16

**Yield-stress fluid fingering instability**

Arif Z. Nelson and Randy H. Ewoldt

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

The fingering instability arises when one fluid displaces another. When a yield-stress fluid is displaced, the highly branched pattern is held in place. This instability is relevant to understanding the behavior of adhesives on surfaces.

Wednesday 6:30 Cripple Creek Foyer

GR17

**Calming a storm: Controlling formation and intensity of a “micro-typhoon”**

Noa Burshtein, Amy Q. Shen, and Simon J. Haward

*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

The dramatic effect of minor changes in fluid elasticity on the onset and development of a spiral vortex instability, a "micro-typhoon", in the cross-slot channel is shown. Flow visualization is performed using quantitative micro-particle image velocimetry, from which vorticity fields in the cross-section of the spiral vortex are computed. We find that the addition of high molecular weight poly(ethylene oxide) (PEO) in very low concentrations (1-10ppm) results in a significant reduction of vortex intensity. Furthermore, we discover that the polymer additive has a destabilizing effect on the flow, causing a reduction in the critical conditions needed for the onset of the spiral vortex. Our experiments provide new insight into the effects of drag-reducing concentrations of polymer on vortex formation and dynamics.

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## Plenary Lectures and Award Presentation

<b>Monday, October 9</b> 8:30 AM Cripple Creek Ballroom	<b>Energy, entropy and structure of soft particle glasses</b> <u>Roger T. Bonnecaze</u> <i>Chemical Engineering, The University of Texas at Austin</i>
<b>Tuesday, October 10</b> Bingham Lecture, 8:30 AM Cripple Creek Ballroom	<b>Flow, structure and function</b> <u>Julie A. Kornfield</u> <i>Chemical Engineering, California Institute of Technology</i>
<b>Wednesday, October 11</b> 8:30 AM Cripple Creek Ballroom	<b>Understanding and probing the dynamics of cell-material interactions in four dimensions</b> <u>Kristi Anseth</u> <i>Chemical and Biological Engineering, University of Colorado Boulder</i>
<b>Thursday, October 12</b> Metzner Award Presentation 8:00 AM, Crystal Ballroom C	<b>Drift redux</b> <u>Aditya S. Khair</u> <i>Chemical Engineering, Carnegie Mellon University</i>

## Social Program and Special Events

<b>Sunday, October 8</b>	<b>Student-Industry Forum</b> 4:00 PM – 6:00 PM      Crystal Ballroom C <i>Sponsored by American Institute of Physics and DowDuPont</i>
	<b>Welcoming Reception</b> 6:30 PM – 8:30 PM      Cripple Creek Ballroom
<b>Monday, October 9</b>	<b>Gallery of Rheology Preview</b> 1:30 PM – 5:00 PM      Cripple Creek Foyer
	<b>Monday Evening Reception</b> 6:30 PM – 9:30 PM      Colorado History Museum <i>Reception hosted by TA Instruments</i>
<b>Tuesday, October 10</b>	<b>Gallery of Rheology Preview</b> 8:30 AM – 4:00 PM      Cripple Creek Foyer
	<b>Society Business Meeting</b> 11:55 AM – 1:30 PM      Crystal Ballroom C
	<b>Awards Reception</b> 7:00 PM – 8:00 PM      Cripple Creek & Silverton Foyers
	<b>Awards Banquet</b> 8:00 PM      Cripple Creek Ballroom
<b>Wednesday, October 11</b>	<b>Gallery of Rheology Preview</b> 8:30 AM – 4:00 PM      Cripple Creek Foyer
	<b>Poster Session and Reception</b> 6:30 PM – 8:30 PM      Cripple Creek Ballroom <i>Sponsored by Anton-Paar USA</i>
	<b>Gallery of Rheology Contest</b> 6:30 PM – 8:30 PM      Cripple Creek Foyer Online voting 10 AM – 8 PM

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Anton-Paar USA, Malvern Instruments, TA Instruments,  
American Institute of Physics, and DowDuPont.*