



# THE SOCIETY OF RHEOLOGY

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

Hyatt Regency Baltimore Inner Harbor  
Baltimore, Maryland  
October 11 - 15, 2015

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# Meeting Schedule

## Monday, October 12, 2015

	CC	CD	CE	CF	BA	FC
8:30			J. Vermant (PL1) - CDF			
9:20			Coffee Break			
10:00	SC1	SM1	IR1	BM1	SG1	NF1
10:25	SC2	SM2	IR2	BM2	SG2	NF2
10:50	SC3	SM3	IR3	BM3	SG3	NF3
11:15	SC4	SM4	IR4	BM4	SG4	NF4
11:40	SC5	SM5	IR5	BM5	SG5	NF5
12:05			Lunch Break			
1:30	SC6	SM6	IR6	BM6	SG6	NF6
1:55	SC7	SM7	IR7	BM7	SG7	NF7
2:20	SC8	SM8	IR8	BM8	SG8	NF8
2:45	SC9	SM9	IR9	BM9	SG9	NF9
3:10	SC10	SM10	IR10		SG10	NF10
3:35			Coffee Break			
4:00	SC11	SM11	IR11	BM11		NF11
4:25	SC12	SM12	IR12	BM12	SG12	NF12
4:50	SC13	SM13	IR13	BM13	SG13	NF13
5:15	SC14	SM14	IR14	BM14	SG14	NF14
5:40	SC15	SM15	IR15	BM15	SG15	NF15
6:05			End			
7:00			Baltimore Aquarium Reception 7:00-9:30			

## Tuesday, October 13, 2015

	CC	CD	CE	CF	BA	FC
8:30			H. Watanabe (PL2) - CDF			
9:20			Coffee Break			
10:00	SC16	SM16	SA1	BM16	SG16	NF16
10:25	SC17	SM17	SA2	BM17	SG17	NF17
10:50	SC18	SM18	SA3	BM18	SG18	NF18
11:15	SC19	SM19	SA4	BM19	SG19	NF19
11:40	SC20	SM20	SA5	BM20	SG20	NF20
12:05			Lunch Break / Society Business Meeting - CC			
1:30	SC21	SM21	SA6	BM21	SG21	NF21
1:55	SC22	SM22	SA7	BM22	SG22	NF22
2:20	SC23	SM23	SA8	BM23	SG23	NF23
2:45	SC24	SM24	SA9	BM24	SG24	NF24
3:10	SC25	SM25	SA10	BM25	SG25	
3:35			Coffee Break			
4:00		SM26	SA11		SG26	
4:25	SC27	SM27	SA12		SG27	NF26
4:50	SC28	SM28	SA13		SG28	NF27
5:15	SC29	SM29	SA14			NF28
5:40	SC30	SM30	SA15			NF29
6:05			End			
7:00			Awards Reception - FA			
8:00			Awards Banquet - CDF			

## Wednesday, October 14, 2015

	CC	CD	CE	CF	BA	FC
8:30			M. O. Robbins (PL3) - CDF			
9:20			Coffee Break			
10:00	SC31	SM31	SA16	CR1	PM1	MN1
10:25	SC32	SM32	SA17	CR2	PM2	MN2
10:50	SC33	SM33	SA18	CR3	PM3	MN3
11:15	SC34	SM34	SA19	CR4	PM4	MN4
11:40	SC35	SM35	SA20	CR5	PM5	MN5
12:05			Lunch Break			
1:30	SC36	SM36	SA21	CR6	PM6	MN6
1:55	SC37	SM37	SA22	CR7	PM7	MN7
2:20	SC38	SM38	SA23	CR8	PM8	MN8
2:45	SC39	SM39	SA24	CR9	PM9	MN9
3:10	SC40	SM40	SA25	CR10		MN10
3:35			Coffee Break			
4:00	SC41	SM41	SA26	CR11		MN11
4:25	SC42	SM42	SA27	CR12		MN12
4:50	SC43	SM43	SA28	CR13		
5:15	SC44	SM44	SA29	CR14		
5:40	SC45	SM45	SA30	CR15		
6:05			End			
6:05			Poster Session & Reception - AH / 6:05-8:00			

## Thursday, October 15, 2015

	CC	CD	CE	CF
8:00			A. Ma (AP1) - CA	
8:40	SC46	SM46	SA31	CR16
9:05	SC47	SM47	SA32	CR17
9:30	SC48	SM48	SA33	CR18
9:55			Coffee Break	
10:25	SC49	SM49	SA34	CR19
10:50		SM50	SA35	CR20
11:15		SM51		
11:40		SM52		
12:05			End	

## Session and Room Codes

AP = Award Presentations  
 BM = Biological Macromolecules:  
 Proteins, Cellulosic Biomass  
 and other Biomaterials  
 CR = Computational Rheology  
 IR = Interfacial Rheology  
 MN = Micro and Nanofluidics  
 NF = Non-Newtonian Fluid Mechanics  
 PL = Plenary Lectures  
 PM = Probe Microrheology  
 SA = Self-assembled Systems and Gels

SC = Suspensions and Colloids  
 SG = Solids, Glasses, and Composites  
 SM = Polymer Solutions and Melts

AH = Atrium/Harborview  
 BA = Baltimore/Annapolis  
 CA = Constellation A  
 CC = Constellation C  
 CD = Constellation D  
 CDF = Constellation D-F  
 CE = Constellation E  
 CF = Constellation F  
 FA = Foyer/Atrium  
 FC = Frederick/Columbia

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## Monday Morning

### Symposium PL Plenary Lectures

Monday 8:30 Constellation D-F

PL1

#### **Rheological excursions in flatland: From monolayers to bilayers**

Jan Vermant

*Materials Science, ETH Zürich, Zürich 8093, Switzerland*

Complex fluid-fluid interfaces (quite literally) surround us. When surfactants, phospholipids, proteins or particles accumulate at an interface, they may form a structured "soft matter interface", whose response to flow and deformation must be interrogated [1]. Applications of interfacial rheology can be found in materials of technological interest, including emulsions or foams, but there are also diverse biological applications such as lung surfactants or cell membranes. Despite the ubiquitous nature of such soft matter interfaces, a complete rheological description of interfaces remains difficult. Unlike bulk fluids, interfaces can dilate/compress, which leads to additional material functions. And unlike Abbott's flatland [2], the interfaces are intimately linked to the bulk fluids that surround them. This requires that we characterize the transfer of both mass and momentum to the surrounding phases, and the interfacial rheological constitutive equation appears in the stress boundary condition.

To determine constitutive relations, we need rheometers that apply well-defined kinematic conditions, to get material functions in shear or dilation. Classical devices, such as the Langmuir trough, lead to mixed deformation fields and microrheological methods cannot be used without some caveats. In this talk I will review the progress in measuring the interfacial rheological properties for selected applications and the efforts to separate thermodynamic, kinetic and rheological effects. However, probably the most important area of application lies in the understanding of bilayers, which so far have only been studied by indirect or micro-rheological methods. With the production of large area suspended bilayers we may be a step closer to unlocking this area.

[1] Fuller, G., and J. Vermant. *Ann Rev Chem Biom Eng.* 3 (2012): 519. [2] Abbott, Edwin A. *Flatland: A Romance in Many Dimensions* (1884).

### Symposium SC Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Monday 10:00 Constellation C

SC1

#### **A simple paradigm for strongly nonlinear large-amplitude oscillatory shear (LAOS) rheology**

Aditya S. Khair

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

We quantify the dynamics of a dilute dispersion of nearly spherical particles that undergo Brownian rotations in an oscillatory shear flow, as a paradigm for large-amplitude oscillatory shear (LAOS) rheology. Our focus is on *strongly nonlinear* LAOS:  $\beta \gg 1$  and  $\beta/\alpha \gg 1$ , where  $\beta$  is a dimensionless shear-rate amplitude (or Weissenberg number) and  $\alpha$  is a dimensionless oscillation frequency (or Deborah number). We derive an asymptotic solution for the long-time periodic orientation probability density function of the particles. Our analysis reveals that the orientation dynamics consists of periods of rapid oscillation (on the time-scale of the inverse shear-rate amplitude) separated by comparatively short "turning points" of slow evolution when the imposed flow vanishes. Uniformly valid approximations to the shear stress and normal stress differences (NSDs) of the dispersion are then constructed: the particle contribution to the shear stress, first NSD, and second NSD, decays as  $\beta^{-3/2}$ ,  $\beta^{-1}$ , and  $\beta^{-1/2}$ , respectively. These stress scalings originate from the orientation dynamics at the turning points; thus, it is the times when the flow vanishes that dominate the LAOS rheology of this paradigmatic complex fluid, surprisingly.

Monday 10:25 Constellation C

SC2

#### **Unsteady shear flows of colloidal suspensions: Simulation by Accelerated Stokesian Dynamics**

Stephanie Marenne and Jeffrey F. Morris

*Levich Institute and Chemical Engineering Department, City College of New York, New York, NY 10040, United States*

Transient microstructural development and the associated rheological response are considered for monodisperse colloidal suspensions, using Accelerated Stokesian Dynamics to simulate the flow behavior. These suspensions are described for steady shear flow by two parameters: the volume fraction and the Peclet number. The volume fraction used in most simulations is 40%. The Peclet number represents the ratio of hydrodynamic to Brownian forces:  $Pe = 6 \pi \eta \dot{\gamma} a^3 / k T$ , where  $\eta$  is the fluid viscosity,  $\dot{\gamma}$  is the shear rate,  $a$  is the particle radius,  $k$  is the Boltzmann constant and  $T$  the absolute temperature. The simulations are performed with  $0.1 < Pe < 1000$ . The case of suspensions of hard spheres is compared to that of soft particles. The start-up and cessation of shear flow demonstrate different time dependence for the shear stress, the first and the second normal stress differences. These time dependences can be related to the evolution of the structure. The suspension behavior under

Medium Amplitude Oscillatory Shear and Large Amplitude Oscillatory Shear, which introduce an additional parameter which we take as the characteristic strain in an oscillation (the alternative is a dimensionless frequency of oscillation) shows strong nonlinear effects. The correlation between the evolution of the microstructure and the normal stress differences during oscillatory shear is of particular interest, allowing the basis for stress overshoot on startup to be determined, as an example. The findings are compared to available experimental results.

Monday 10:50 Constellation C

SC3

### **Athermal analogue of sheared dense Brownian suspensions**

Martin Trulsson<sup>1</sup>, Mehdi Bouzid<sup>2</sup>, Jorge Kurchan<sup>1</sup>, Eric Clément<sup>1</sup>, Philippe Claudin<sup>1</sup>, and Bruno Andreotti<sup>1</sup>

<sup>1</sup>*Physique et Mécanique des Milieux Hétérogènes, ESPCI, Paris 75005, France;* <sup>2</sup>*Department of Physics, Georgetown University, Washington DC, DC 20057, United States*

The rheology of dense Brownian suspensions of hard spheres is investigated numerically beyond the low shear rate Newtonian regime.

We analyze an athermal analogue of these suspensions, with an effective logarithmic repulsive potential representing the vibrational entropic forces. We show that both systems present the same rheology without adjustable parameters. Moreover, all rheological responses display similar Herschel-Bulkley relations once the shear stress and the shear rate are respectively rescaled by a characteristic stress scale and by a microscopic reorganization time-scale, both related to the normal confining pressure.

This pressure-controlled approach, originally developed for granular flows, reveals a striking physical analogy between the colloidal glass transition and granular jamming.

Monday 11:15 Constellation C

SC4

### **Silica particles dispersion in the ionic liquid [C<sub>4</sub>mim][BF<sub>4</sub>]**

Jingsi Gao and Norman J. Wagner

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

Shear thickening dispersions of colloidal particles in ionic liquids are being developed for use to improve the ballistic, puncture and abrasion resistance of space suits and micrometeorite and orbital debris (MMOD) shielding for spacecraft. Ionic liquids are proposed as the solvent phase of STF's formulation for space application because of their stability over the broad range of temperatures and low volatility. However, this can be challenging because the high ionic strength of ionic liquids screens the electrostatic stabilizing forces. In our previous research (Gao et al. ACS Nano 2015), we created stable nanoparticle dispersion in the ionic liquid [C<sub>4</sub>mim][BF<sub>4</sub>] by inducing solvation layering, where 5 nm solvation layers form around the particle due to hydrogen bonding between anion [BF<sub>4</sub>]<sup>-</sup> and the fluorinated alcohol functionalized particle surface. However, the surface fluorinated alcohol functionalized silica particle dispersion did not exhibit strong shear thickening behavior due to the thick solvation layers preventing the formation of hydroclusters. To achieve stronger shear thickening, commercial silica particles with an organic functionalized particle surface were dispersed in the ionic liquid [C<sub>4</sub>mim][BF<sub>4</sub>]. It is expected that the organic coating will have weaker hydrogen bonds with anion [BF<sub>4</sub>]<sup>-</sup> leading to a thinner solvation layer that is still sufficient for dispersion, but would enable hydrocluster formation at high shear rates. Dynamic light scattering (DLS), small angle neutron scattering (SANS) and rheology were employed to determine the solvation layer thickness and microstructure of dispersions. Analysis of SANS spectra across a broad range of particle concentrations was used to develop a quantitative model for the inter-particle interactions including the thickness of the solvation layer. The effects of temperature and impurities (i.e. water) on microstructure and rheology are reported.

Monday 11:40 Constellation C

SC5

### **The role of hydrodynamic interactions in shear-induced clustering in polymer-colloid suspensions**

Juntae Kim and Matthew E. Helgeson

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

The appearance of shear-induced particle clusters is common to many polymer-colloid mixtures including solutions and melts. Due to the apparent alignment of these clusters along the vorticity direction when observed in the flow-vorticity plane, cluster formation has been hypothesized to arise from the influence of polymer normal stresses on particle-particle interactions. To test this hypothesis, we have performed 3D microstructural measurements under shear flow in non-aggregating polymer-colloid mixtures using flow-small angle neutron scattering in the flow-vorticity and flow-gradient planes. As a model system, we use oil-in-water nanoemulsions in the presence of polyethylene glycol, which form non-aggregating viscoelastic networks. These fluids exhibit significant flow-induced anisotropy in the droplet microstructure consistent with cluster formation, which develops during strong shear thinning of the fluid. Specifically, butterfly scattering appears in the flow-vorticity plane at shear rates corresponding to the shear thinning, with projected orientation in the vorticity direction, in agreement with previous studies. However, significant anisotropy also develops in the flow-gradient plane, with orientation along the compressional axis of shear, which is inconsistent with previous hypothesized mechanism of shear-induced clustering through polymer normal stresses. These results suggest vorticity-aligned aggregates possess anisotropic cross section, and that hydrodynamic interactions in the flow plane, in addition to polymer normal stresses, play an important role in the formation of shear-induced clusters. To demonstrate this, we show that collapse of the flow-induced alignment and shear thinning responses over a number of different viscoelastic parameters through a modified Peclet number for the suspended colloids. Overall, this structural information provides a basis to control the rheology and suspension microstructure of non-aggregating polymer-colloid mixtures.

## Symposium SM Polymer Solutions and Melts

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Monday 10:00 Constellation D SM1

### **Force-level theory of multiscale transient localization and emergent elasticity in polymer solutions and melts**

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

<sup>1</sup>*Department of Physics, University of Illinois, Urbana, IL, United States;* <sup>2</sup>*Materials Science, University of Illinois, Urbana, IL, United States*

The fundamental understanding of tagged polymer dynamics in concentrated liquids from the segmental to macromolecular scale is an open problem due to the complex interplay between the *intra*-molecular and *inter*-molecular forces and chain connectivity. This interplay is crucial for determining the dynamic and mechanical properties of polymer glasses and gels, as well as entangled rubbery polymers. To theoretically treat these systems we propose a statistical mechanical theory that explicitly accounts for *intra*- (via Rouse-like springs) and *inter*-molecular forces at the Kuhn segment level. The theory is self-consistently closed at the dynamical second moment level (matrix of mean square displacements) and predictions are made for the conditions required for isotropic transient localization. Two regimes of localized behavior are broadly found: (i) in semidilute solutions, weak localization emerges on a mesoscopic length scale intermediate between segment and chain scales, and (ii) in dense melts, strong localization is predicted on a scale smaller than the segment size. In regime (i), power law scaling of the localization length with packing length is found, which is consistent with extent ideas for when isotropic Rouse motion breaks down due to emergent entanglement constraints. In regime (ii), we recover the predictions of recent theories for glassy localization that a priori ignored chain connectivity. Connections to the intermediate time, dynamic plateau shear modulus are made, and the predicted scaling with polymer density and order of magnitudes are consistent with rubbery and glassy elasticity for regimes (i) and (ii), respectively. To our knowledge, this is the first force-level theory that captures entanglement and glassy transient localization and elasticity in a unified, force-level framework. Generalizations to treat physical bond formation in gel-forming polymer materials, and chemically cross-linked networks, are also possible.

Monday 10:25 Constellation D SM2

### **Tubes and entanglements in polymer melts**

Alexei E. Likhtman

*School of Mathematical and Physical Science, University of Reading, Reading, Berkshire RG6 6AX, United Kingdom*

A system of concatenated rings is an ideal ground to define entanglements. Indeed, for long enough chains their local properties are indistinguishable from those of linear chains. At the same time, entanglements are permanent in such system, and therefore analysis of very long trajectories is possible. In this work, I report a novel definition of tube axis as a curve average of chain trajectory over time. Unlike the old procedure of averaging positions of individual monomers, curve average provides results of remarkable clarity. In the system of rings, individual entanglements are easily identified either as close contacts between tube axis of different chains, or as curvature peaks in the tube axis. The results of this analysis are then compared with the contact map analysis, identifying similarities and differences of two definitions.

Monday 10:50 Constellation D SM3

### **Single chain dynamics of entangled linear polyethylene liquids under homogenous shear and planer elongational flows using nonequilibrium molecular dynamics simulations**

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

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

Nonequilibrium molecular dynamics (NEMD) simulations of an entangled C<sub>700</sub>H<sub>1402</sub> linear polyethylene melt were performed to investigate the chain dynamics over a wide range of Weissenberg numbers (Wi) under steady shearing flow. Similar to the unentangled (C<sub>78</sub>H<sub>158</sub>) and moderately entangled (C<sub>400</sub>H<sub>802</sub>) melts examined in prior studies, the distribution of the chain end-to-end distance,  $|\mathbf{R}_{ete}|$ , at high Wi was bimodal with a peak at low  $|\mathbf{R}_{ete}|$  which is associated with the dynamical rotation/retraction cycles experienced by individual chains, and a peak at high  $|\mathbf{R}_{ete}|$  which corresponds to the highly stretched and oriented chains. To understand the underlying physics, the relevant system time scales including the entanglement time, Rouse time, and disengagement time were determined using segmental mean square displacement analysis of the chains. The longest ( $\tau_d$ ) and rotational ( $\tau_{rot}$ ) relaxation times at high Wi were extracted by fitting a functional form of  $A \exp(-t/\tau_d) \cos(2\pi t/\tau_{rot})$  to the end-to-end vector autocorrelation data. The number of entanglements and other topological features were also computed as functions of Wi.

NEMD simulations of polyethylene melts with different chain lengths (C<sub>400</sub>H<sub>802</sub>, C<sub>700</sub>H<sub>1402</sub>, and C<sub>1000</sub>H<sub>2002</sub>) were also performed in planer extensional flow and rheological and topological behavior of entangled systems were studied in nonlinear regime. Specifically, we studied the behavior of extensional viscosity as a function of strain rate to examine the thinning exponents and determine if there are any signs of an upturn in viscosity for extensional rates on the order of the inverse Rouse time, as predicted by standard theories. The effects of the chain stretch, entanglement density, and chain disentangling on the system behavior will also be discussed.

Monday 11:15 Constellation D

SM4

**Viscoelastic relaxation of Rouse chains undergoing head-to-head association and dissociation. 1. Simple modeling of motional coupling through chemical equilibrium**Hiroshi Watanabe and Yumi Matsumiya*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

For non-entangled Rouse chains undergoing the head-to-head association and dissociation, the normalized viscoelastic relaxation functions  $g_1(t)$  and  $g_2(t)$  was formulated analytically for a case that a dissociated unimer rapidly re-associates with its original partner. The relaxation of the unimer and dimer was essentially determined by ratios  $r_a$  and  $r_d$  of the association and dissociation times to the Rouse relaxation time in the absence of reaction. For small  $r_a$  and  $r_d$ , the reaction was slow so that the unimer and dimer relaxed through respective pure Rouse modes, as naturally expected. However, for most cases in wide ranges of  $r_a$  and  $r_d$ , the dimer relaxation was accelerated with increasing  $r_d$  ( $> 1$ ) and  $g_2$  of the dimer was indistinguishable from the pure Rouse relaxation function of the unimer,  $g_{1,Rouse}$ . For those cases,  $g_1$  of the unimer also coincided with  $g_{1,Rouse}$ . These results demonstrate that the motional coupling between the unimer and dimer, occurring through the association/dissociation reaction, strongly affects the relaxation. The Rouse modes of the unimer and dimer split in two series due to this coupling, and new relaxation modes due to the coupling emerged as well.  $g_1$  and  $g_2$  were largely contributed from those new modes, thereby superficially agreeing with  $g_{1,Rouse}$  for the cases of  $r_a, r_d > 1$ .

Monday 11:40 Constellation D

SM5

**Viscoelastic relaxation of Rouse chains undergoing head-to-head association and dissociation. 2. Experimental test**Yumi Matsumiya and Hiroshi Watanabe*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

In the previous talk, a model was formulated for the viscoelastic relaxation functions of the Rouse unimer and dimer undergoing the head-to-head association/dissociation, with an assumption that a dissociated unimer rapidly re-associates with its original partner. This model was tested for polyisoprene ( $M = 30k$ ) having a carboxyl group at the chain end and being diluted to 10% in an oligomeric butadiene (oB). The carboxyl group, introduced through reaction of living PI anion precursor with carbon dioxide, is known to exhibit the dimerization/dissociation equilibrium in a nonpolar medium. Thus, the dilute solution of end-carboxyl polyisoprene (PI-COOH) allowed us to test the model. The modulus data of the 10 % PI-COOH/oB solution was compared with the data of "reference solutions" of unfunctionalized unimer and dimer having the same concentration. (The unfunctionalized unimer and dimer, respectively, were separately prepared through termination of the PI anion precursor with methanol and through bimolecular coupling with xylylene dichloride.) The reference solutions exhibited Rouse-like relaxation, and the data of the PI-COOH/oB solution at low temperatures ( $T$ ) agreed with a weighed average of the data of the reference solutions (because the Rouse relaxation was much faster than the association/dissociation at low  $T$ ). The equilibrium population ratio [unimer]/[dimer], equivalent to this averaging weight, was utilized to estimate the dissociation energy of dimer of PI-COOH. The modulus of the PI-COOH/oB solution, calculated from this dissociation energy and the Rouse time data of the reference solutions, was close to the data of the PI-COOH/oB solution, lending support to the model assumption of a rapid re-association of dissociated unimer with the original partner.

## Symposium IR Interfacial Rheology

Organizers: Gordon Christopher and Sachin Velankar

Monday 10:00 Constellation E

IR1

**Modelling of complex interfaces for pendant drop experiments**Caroline Balemans, Martien A. Hulsen, and Patrick D. Anderson*Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands*

For most applications where interfaces of fluid-fluid systems are important, surfactants are adsorbed onto the interface. Interfaces containing proteins, particles or insoluble species forming Langmuir monolayers appear to act like viscoelastic solids. In this work, an axisymmetric finite element model is designed to study the behavior of these interfaces in pendant drop experiments. The bulk material is a Newtonian fluid following the Navier-Stokes balance equations. A 2D Kelvin-Voigt constitutive model suitable for large strains, as proposed by Verwijlen et al.[1], is used to characterize the viscoelastic interface with dominating elasticity. In this relation, five model parameters are defined: the surface tension, surface dilatational viscosity, surface shear viscosity, surface dilatational elasticity and surface shear elasticity. The model has been extensively validated where for an interface with constant surface tension our results are compared with existing literature. From a parameter study, in which the system is subjected to a constant inflow, relaxation and a free outflow, we observe that an equilibrium between the elasticity and surface tension is reached during the outflow regime for higher values of the dilatational elasticity. For the used parameter range, the influence of both the shear viscosity and shear elasticity on the apex length is negligible.

Reference: [1] T. Verwijlen, L. Imperiali and J. Vermant, *Separating viscoelastic and compressibility contributions in pressure-area isotherm measurements*, Advances in Colloid and Interface Science, 2014, Volume 206, 428-436.

Monday 10:25 Constellation E

IR2

**An oscillating pendant drop method to study the interfacial viscoelasticity of monolayers**Mathias Nagel, Martina Pepicelli, and Jan Vermant*Materials Science, ETH Zürich, Zürich 8093, Switzerland*

The adsorption of surface-active substances to a liquid interface influences not only the surface tension but adds also a viscous or viscoelastic character to the interface. Two established methods are commonly used to characterize these complex interfaces, the Langmuir trough and the pendant drop method. Where the Langmuir trough offers well-controlled conditions, it uses relatively large amounts of surface-active material and the compressions rates are lower compared to the oscillating pendant drop. The traditional pendant drop method evaluates the surface tension by fitting a drop shape of constant surface tension that is obtained from Laplace's law. In previous studies by various researchers the elasticity has been quantified through the error between the best fit and the actual drop shape, the elasticity causing the drop shape to deviate from the ideal shape. In order to quantify the viscoelastic contributions more precisely than by error estimation we compare measurements from a pendant drop subject to an oscillating pressure, to numerical simulations. In a first step the necessary material parameters for the simulation have been obtained by measurement on a Langmuir trough. Our first studies focus on emblematic systems of high elasticity or incompressibility of the interface. The future goal is to identify material properties of unknown systems by a pendant drop method with a richer parameter space than just surface tension.

Monday 10:50 Constellation E

IR3

**Shear thinning behavior of surface viscosity for surfactant monolayer at low shear rate**Taichi Hirano and Keiji Sakai*Fundamental Engineering, Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, Japan*

We introduce a measurement system of liquid surface viscosity using the Electro-Magnetically Spinning (EMS) technique, and report rheological properties of surfactant monolayers expanded on the surface of distilled water at low surface-shear rate in the order of  $10^{-1} \text{ s}^{-1}$ .

In the EMS technique, a rotating magnetic field induces the eddy currents in a metal rotor, and the Lorentz interaction between the induced currents and the magnetic field gives a driving torque to the rotor. The rotational speed of the rotor is determined from the balance between the driving torque and the resistant torque due to the viscosity of surrounding fluids, and therefore the viscosity is obtained by measuring the rotor speed under the control of the rotational speed of the magnetic field. Our newly developed system employs a thin disk rotor floating on the surface of sample fluids as the viscosity probe, and enables more accurate measurement by the reduction of the mechanical friction. It is noteworthy that the accuracy for measuring the viscosity of water (around  $1 \text{ mPa}\cdot\text{s}$ ) is better than 0.5%.

In this presentation, we demonstrate the high sensitivity of the disk-type EMS system for the surface and interfacial rheology. We successfully measured the surface viscosity of surfactant monolayers on distilled water, and investigated the relations between the surface viscosity and the surface density of the adsorbed amphiphilic molecules. We also obtained shear thinning behavior at low surface-shear rate especially in semi-dilute region of the monolayer.

Monday 11:15 Constellation E

IR4

**Relative importance of capillarity and microstructure on interfacial viscoelasticity of particle laden interfaces**Sourav Barman and Gordon F. Christopher*Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Characterization of particle laden interfaces' deformation response has increased significantly due to the ubiquitous use of Pickering Emulsions in many industrial sectors. Pickering emulsions' bulk properties are dependent on interfacial rheology, which is a function of deforming microstructure determined by system attributes. Using a modified double wall ring interfacial rheometer to simultaneously visualize an interface and measure interfacial viscoelasticity, we have studied the relative importance of the strength of adhesion between particles and the long range microstructure on interfacial viscoelasticity of particle laden.

We have characterized a particle laden interface composed of 3 micron polystyrene particles on an air/water interface. In order to control microstructure and capillary adhesion, subphase salt concentration and surface concentration are adjusted. Due to moderate particle hydrophobicity, high salt systems resulted in tightly bound clusters of particles, low salt systems created loosely bound clusters, and no salt systems create slightly disordered crystals arrays. Changing surface concentration takes interfaces from jammed to moderately packing. Using small amplitude oscillatory shear, the effect of both control parameters on microstructure and interfacial viscoelasticity are evaluated. We find that long range microstructure is primarily responsible for determining quantities such as yield strain,  $\tan(\delta)$ , and other global rheological behaviors. However, viscoelastic moduli magnitude is dictated primarily by the relative strength of the capillary adhesion to dipole repulsion. The local degree of caging provides a secondary effect on magnitude. These unique measurements should have significant impact on the design and understanding of particle laden interfaces.

Monday 11:40 Constellation E

IR5

**A 2D Stokesian dynamics simulation of microstructure deformation of particle laden interfaces**Nader Laal-Dehghani, Sourav Barman, and Gordon F. Christopher*Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The experimental study of the shear deformation of particle laden interfaces has increased significantly in recent years. However, modeling of particle laden interfaces has primarily focused on Monte-Carlo and other equilibrium simulations that predict equilibrium microstructure of particle

laden interfaces for a wide range of conditions. However, the interfacial viscoelasticity of particle laden interfaces is determined not by equilibrium conditions but by the interfacial microstructure's resistance to deformation. To model this behavior, we have developed a 2D Stokesian dynamics simulation for non-inertial particles on an interface using an implicit solvent. Viscous forces are balanced by inter-particle forces: capillarity due to contact line undulation and induced dipole repulsion. Using force and a torque balance, particle trajectories and orientations are obtained over a wide range of conditions.

Using this methodology, the behavior of highly repulsive particle systems in bounded and unbounded surface Couette flow has been analyzed. These systems have been observed experimentally to exhibit movement perpendicular to shear in order to maintain crystal structure at high surface concentrations and shear rates. In simulations, this behavior is replicated. We characterize the degree of rotation of the crystal structure, loci of rotation, and time-dependent behavior. We identify the mechanisms that create the onset of these flows which can be characterized by the relative magnitude of repulsive forces to viscous shear forces. We find the importance of the walls in delaying the onset of these rotations is significant. Finally, we outline a phase space at which rotation occurs based on a number of dimensionless parameters.

## Symposium BM

### Biological Macromolecules: Proteins, Cellulosic Biomass and other Biomaterials

Organizers: Jai A. Pathak and Patrick Underhill

Monday 10:00 Constellation F

BM1

#### How do distinct extracellular matrix polymers confer distinct mechanical properties on bacterial biofilms?

Kristin Kovach<sup>1</sup>, Megan Davis-Fields<sup>2</sup>, Shashvat Doorwar<sup>3</sup>, Kishore Mohanty<sup>3</sup>, and Vernita D. Gordon<sup>1</sup>

<sup>1</sup>Department of Physics and Center for Nonlinear Dynamics, The University of Texas at Austin, Austin, TX 78712, United States;

<sup>2</sup>Department of Molecular Biosciences, The University of Texas at Austin, Austin, TX 78712, United States; <sup>3</sup>Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, Austin, TX 78712, United States

Biofilms are aggregates of microorganisms embedded in a self-produced extracellular polymer matrix. The distinct polymer components of this matrix are known to provide chemical protection that helps biofilm infections resist the immune system and antibiotics, thereby increasing the toll biofilms take on public health. However, very little is known about the degree to which distinct matrix polymers may provide distinct mechanical protections. *Pseudomonas aeruginosa* is widely used as a model biofilm-forming bacterium because it is an opportunistic human pathogen common in hospital-acquired infections, chronic wounds, and cystic fibrosis lung disease. The distinct extracellular polysaccharides Pel, Psl, and alginate are found in multiple types of *P. aeruginosa*. Why this organism should make three matrix polymers instead of one is not known.

We use bulk rheology of biofilms grown using isogenic variants of one type of *P. aeruginosa* (the PAO1 lab strain) to show that these three polysaccharides each play a unique role in the mechanics of a biofilm. Alginate softens a biofilm. Psl increases the elastic storage modulus  $G'$  while Pel increases the yield strain of the biofilm, leaving  $G'$  unchanged. Increased expression of either Psl or Pel increases the yield stress. Increasing the concentration of polymer in a gel is well-known to increase the gel's stiffness, but this straightforward physical analysis is inadequate to explain the different mechanical effects produced by different biofilm matrix polymers. Identifying the mechanisms—such as cross-linking by proteins or electrostatic bundling—by which these polymers contribute to the mechanics of the biofilm could inspire new approaches to effective biofilm clearance, by revealing targets for disruption of the biofilm.

Monday 10:25 Constellation F

BM2

#### Evolution to change the matrix composition of clinical biofilm infections makes the biofilms stiffer, consistent with a mechanical fitness benefit

Vernita D. Gordon<sup>1</sup>, Megan Davis-Fields<sup>2</sup>, Kristin Kovach<sup>1</sup>, Shashvat Doorwar<sup>3</sup>, and Kishore Mohanty<sup>3</sup>

<sup>1</sup>Department of Physics and Center for Nonlinear Dynamics, The University of Texas at Austin, Austin, TX 78731, United States;

<sup>2</sup>Department of Molecular Biosciences, The University of Texas at Austin, Austin, TX 78712, United States; <sup>3</sup>Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, Austin, TX 78712, United States

Biofilms are aggregates of microorganisms embedded in a self-produced extracellular polymer matrix. The distinct polysaccharides Pel, Psl, and alginate are all components of the matrices of biofilms formed by *P. aeruginosa*, which is an opportunistic human pathogen common in hospital-acquired infections, chronic wounds, and cystic fibrosis (CF) lung disease. The polymer components of the biofilm matrix are known to provide chemical protection that helps biofilm infections resist the immune system and antibiotics, thereby increasing the toll biofilms take on public health.

*P. aeruginosa* biofilm infections in the lungs of CF patients can persist for decades, ample time for the infecting microbes to evolve. It has long been known that CF infections tend to evolve to increase production of alginate, and that increased alginate is associated with much worse outcomes for infected patients. Other researchers have recently found that CF lung infections also evolve to increase production of the matrix polymer Psl. Sets of chronological clinical isolates from four CF patients at discrete timepoints over decades of infection provide evolutionary snapshots of the infecting organism. We do bulk rheological measurements of biofilms grown from these sets of chronological isolates from cystic fibrosis patients. We find that biofilms with increased Psl have elastic moduli  $G'$  up to 13x greater ( $p=10^{-8}$  by a Student two-tailed t-test), and yield stresses that are up to 2.5x greater ( $p=0.006$ ), than the corresponding values for biofilm grown from clinical isolates that have evolved to increase alginate but not Psl. Biofilm elastic moduli are ~kPa, which is comparable to the stresses others have estimated to be exerted by phagocytosing

neutrophils. This suggests that increased Psl expression could confer a mechanical fitness benefit on *P. aeruginosa* biofilm infections that is distinct from and complementary to the advantages conferred by alginate.

Monday 10:50 Constellation F

BM3

### **Effect of particulate contaminants on the development and interfacial rheology of pellicle biofilms**

Zhenhuan Zhang and Gordon F. Christopher

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

Bacterial biofilms are a community of bacteria embedded in a self-secreted extracellular polymer matrix (EPS). The resultant material is a complex mixture of bacteria, proteins and polymers, which exhibit unique rheological behavior. Most research on biofilms has focused on those formed at liquid-solid interfaces. Pellicles, biofilms formed at air/water or oil/water interfaces, have not been as commonly studied despite their relevance to porous flow, water treatment, and oil processing. In these applications, pellicle interfacial rheology impacts both bulk viscoelasticity and transport through porous networks.

Typically, pellicle rheology has been examined for clean air/water interfaces using a single bacteria strain. However, pellicles coexist with other surface active materials in actual applications including surfactants, particles and other bacteria. In this study, we examine interfacial shear rheology and microstructure of pellicles composed of *E. Coli* UTI 189 at an air/water interface, and examine how the presence of small concentrations of interfacial particles disrupt pellicle formation. Particles are placed directly onto and interface prior to formation of the pellicle, and then the pellicle is allowed to grow on the interface over several days. The particles physically disrupt the formation of EPS directly at the air/water interface, which is the densest region of the EPS growth in pellicles. This disruption does not affect timescale of formation/adsorption, but does weaken pellicle elasticity. We examine how this physical disruption is affected by particle size, concentration, and surface chemistry by using both polymeric and silver colloids of varying sizes.

Monday 11:15 Constellation F

BM4

### ***Pseudomonas aeruginosa* biofilm rheology**

Uranbileg Daalkhajav and Travis W. Walker

*Chemical, Biological, Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States*

Bacterial biofilms are one of the most intractable problems facing industries ranging from petroleum to the healthcare industry. This matrix of EPS provides a diffusion barrier against antimicrobial agents and provides a protective microenvironment where bacterial cultures can thrive. *Pseudomonas aeruginosa* is an environmental bacteria that is known for its ability to produce alginate incased biofilm. It can cause major problems in the medical field as an opportunistic pathogen causing recurrent infections in cystic fibrosis patients and acute infections in burn victims. We find that *P. aeruginosa* (PAO1) biofilm is viscoelastic, showing predominantly gel-like behavior, which is likely responsible for *P. aeruginosa* biofilm robustness in the face of outside stresses. The inclusion of variety of salts and sugars into the medium affected the biofilm development and the rheological characteristics of the resulting biofilm. Our future objective is to find treatments to disrupt already developed biofilm so the weakened mechanical structure will result in increased effectiveness of traditional infection treatments like antibiotics.

Monday 11:40 Constellation F

BM5

### **Study of the linear rheology and structure of Casein gels at different concentrations**

Bavand Keshavarz<sup>1</sup>, Mathieu Leocmach<sup>2</sup>, Sébastien Manneville<sup>2</sup>, Thibaut Divoux<sup>3</sup>, and Gareth H. McKinley<sup>1</sup>

<sup>1</sup>*Hatsopoulos Microfluids Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, United States;*

<sup>2</sup>*Laboratoire de Physique, ENS Lyon, Lyon 69007, France;* <sup>3</sup>*Centre de Recherche Paul Pascal - CNRS, Pessac 33600, France*

The rheology of food gels is key to many industrial and biological applications. In this talk we present a rheological study for acid-induced casein gels made of sodium caseinate and acidified by glucono-delta-lactone (GDL) at different concentrations. Linear viscoelasticity measurements, including small amplitude oscillatory shear (SAOS), stress relaxation, and creep in the linear region, show robust power-law behavior holding over a span of four orders of magnitude change in time/frequency. This striking behavior is captured by a simple one-element fractional model similar to the one originally proposed by Scott-Blair (G. W. S. Blair, "Analytical and Integrative Aspects of the Stress-Strain-Time Problem," *J. Sci. Instrum.*, vol. 21, no. 5, pp. 80-84, May 1944). By using a modified damping function, the behavior of these gels can be modeled even at the onset of nonlinear deformations. A thorough rheological study of these gels combined with microscopy imaging of the physical network helps us to identify the physical origin of the power laws reported in these materials and to interpret the parameters used in the fractional model in terms of the fractal gel microstructure.

## Symposium SG Solids, Glasses, and Composites

Organizers: Lynden Archer and Anne Grillet

Monday 10:00 Baltimore/Annapolis SG1

### **Echoes in x-ray speckles track nanometer-scale plastic events in nanostructured soft disordered solids under shear**

Robert L. Leheny<sup>1</sup>, Michael C. Rogers<sup>2</sup>, Kui Chen<sup>1</sup>, Thomas G. Mason<sup>3</sup>, Suresh Narayanan<sup>4</sup>, Subramanian Ramakrishnan<sup>5</sup>, and James L. Harden<sup>2</sup>

<sup>1</sup>Johns Hopkins University, Baltimore, MD, United States; <sup>2</sup>University of Ottawa, Ottawa, Canada; <sup>3</sup>University of California, Los Angeles, Los Angeles, CA, United States; <sup>4</sup>Argonne National Laboratory, Argonne, IL, United States; <sup>5</sup>FAMU-FSU College of Engineering, Tallahassee, FL, United States

Any solid under applied stress possesses an elastic limit above which it yields. The microscopic signatures of yield are irreversible changes to the material's structure. We describe x-ray photon correlation spectroscopy experiments on a set of disordered soft solids -- including concentrated nanocolloidal gels, laponite clay suspensions, and nanoemulsions -- subject to in situ oscillatory shear strain that provide unique information about the spatial character of rearrangements above yielding at the nanometer scale. The oscillatory strain causes periodic echoes in the x-ray speckle pattern, creating peaks in the intensity autocorrelation function. The peak amplitudes are attenuated above a threshold strain, signaling the onset of irreversible particle rearrangements. The gels and nanoemulsions displays strain softening well below the threshold, indicating a range of strains at which deformations are nonlinear but reversible. In the gels, the peak amplitudes decay exponentially with the number of shear cycles above the threshold strain, demonstrating that all regions in the sample are equally susceptible to yielding and surprisingly that the probability of a region yielding is independent of previous shear history. The wave-vector dependence of the decay rate reveals a power-law distribution in the size of rearranging regions, suggesting a nonequilibrium critical transition at yielding.

Monday 10:25 Baltimore/Annapolis SG2

### **Theory of polymer dynamics in model nanocomposites**

Umi Yamamoto<sup>1</sup> and Kenneth S. Schweizer<sup>2</sup>

<sup>1</sup>Chemical Engineering, California Institute of Technology, Pasadena, CA, United States; <sup>2</sup>Materials Science, University of Illinois, Urbana, IL, United States

Slow dynamics in polymer nanocomposites remains poorly understood due the simultaneous presence of multiple length and time scales, anisotropic excluded volume forces, geometric confinement, and topological entanglements. The physics underlying this complexity is also relevant to polymer motion in quenched porous media and in biological contexts. We have developed force-level statistical mechanical theories for polymer liquids dissolved in non-adsorbing spherical particle matrices [1]. Polymer dynamics is deeply modified in a manner that depends on polymer-particle size ratio, degree of entanglement, and nanoparticle loading and mobility. For isotropic rod solutions in an array of immobile hard spheres, topological entanglements compete with two new forces associated with excluded volume constraints which modify in a distinct, but coupled manner, polymer motion parallel and orthogonal to its axis. The rich dependences of the transient transverse localization length (tube diameter) and diffusion constant tensor on system parameters have been established. Tube compression is predicted, and a universal master curve emerges based on a dimensionless particle volume fraction involving three distinct length scales. In a restricted window of parameter space, rods are found to diffuse via a "renormalized reptation" motion involving tube compression and partial blocking of longitudinal diffusivity. A literal dynamic localization transition is predicted beyond a system-dependent particle volume fraction. Complex diffusional behavior also occurs for unentangled rod solutions and in the tracer limit. Generalization of the theory to treat how nanoparticles modify the tube diameter in entangled flexible chain melts has been achieved based on a self-consistent primitive path mapping idea, and the results agree well with simulation.

[1] U.Yamamoto and K.S.Schweizer, ACS MacroLetters 2, 955 (2013); 4, 53 (2015).

Monday 10:50 Baltimore/Annapolis SG3

### **Entangled polymer-nanocomposites: Structure and dynamics**

Rahul Mangal<sup>1</sup>, Samanvaya Srivastava<sup>2</sup>, and Lynden A. Archer<sup>1</sup>

<sup>1</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States; <sup>2</sup>Institute for molecular engineering, The university of Chicago, Chicago, IL, United States

Nanoparticle-polymer composites, or polymer nanocomposites (PNCs), exhibit unusual mechanical and dynamical features when the particle size ( $D$ ) approaches the random coil dimensions of the host polymer. Here we report on creating *model PNCs* in which spherical nanoparticles (NPs) are uniformly dispersed in high molecular weight ( $M_w$ ) entangled polymers. Specifically, by harnessing favorable enthalpic interactions between particle-tethered and host polymers we show that particle-particle aggregation can be completely avoided. Investigation of the mechanical properties of these model PNCs reveal that nanoparticles have profound effects on their host polymer's dynamics on all timescales. On short timescales, nanoparticles slow-down the local dynamics of polymer segments and lower the glass transition temperature of the host. On intermediate timescales, where polymer chain motion is typically constrained by the surrounding chains in an entanglement tube, nanoparticles provide additional constraints leading to an earlier discovery of the tube than observed in entangled melts. On long timescales, nanoparticles lead to an early onset of terminal relaxation of the polymer chains. X-ray Photon Correlation Spectroscopy (XPCS) is employed as a sensitive probe

of nanoparticle relaxation dynamics to investigate the origins of these behaviors. Remarkably, we find that as the nanoparticle size  $D$ , is progressively increased above the tube diameter of the host polymer ( $a$ ), particles undergo a transition from normal diffusion to hyperdiffusive relaxation dynamics. In contrast, for unentangled hosts, diffusive particle relaxation are observed. Our experimental observations are discussed in terms of force dipole relaxation in filled systems and using a recently proposed scaling model for hopping of NPs in polymers.

Monday 11:15 Baltimore/Annapolis

SG4

### **Effective pairwise mobility determines the rheology of soft particle glasses**

Soumik Das<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, University of Texas at Austin, Austin, TX 78712, United States; <sup>2</sup>ESPCI ParisTech, Paris, France

An analytic effective medium theory is presented that predicts the rheology of concentrated suspensions of soft particles or soft particle glasses. The theory is founded on a conservation equation for the pair distribution function of the particles, which includes its flux represented by the product of the effective mobility of a soft particle in shear flow and the forces acting on a particle in the suspension. From an asymptotic expansion in the limit of shear flow with strong elastic forces, we obtain a universal pair distribution function that depends only on volume fraction and the effective mobility. It is found that the bulk rheology of soft particle glasses is determined by the effective pairwise mobility. The functional form of the effective mobility is determined from the velocity-force relationship of a particle pulled in a soft particle glass [Mohan et al. *J. Rheol.* **58**(5), 1465-1482 (2014)] and the parameters are extracted from the limits of low and high shear stresses of soft particle glasses [Seth et al. *Nature Materials* **10**, 838-843 (2011)]. With the effective pairwise mobility, the flow curve for shear stress is predicted accurately. Accurate prediction of the normal stresses provides additional validation of the effective medium theory and mobility. The theory is also used to predict the shear stress relaxation of soft particle glasses following cessation of flow. This new method provides an efficient method to predict the microstructure of soft particle glasses and understand the rheology and dynamics of these materials without time-intensive computational simulations.

Monday 11:40 Baltimore/Annapolis

SG5

### **Effect of attractions on the yielding behavior of glasses**

Mansi A. Kumar<sup>1</sup>, Randy H. Ewoldt<sup>2</sup>, and Charles F. Zukoski<sup>3</sup>

<sup>1</sup>Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, IL, United States; <sup>2</sup>University of Illinois at Urbana-Champaign, Urbana, IL, United States; <sup>3</sup>Chemical and Biological Engineering, University of Buffalo, Buffalo, NY, United States

Yielding is associated with the onset of irrecoverable deformation in solid materials. With the recognition that a solid-like response results from deforming a system faster than its characteristic diffusional relaxation rate, we are able to characterize yielding in soft materials such as colloidal glasses and gels. Of particular interest here are materials where the characteristic diffusion rate lies in a window where we can probe onset of nonlinear behavior at deformation frequencies above and below this relaxation rate. Using colloidal systems with near hard-sphere interactions and particles experiencing weak attractions we are able to explore yielding in the high frequency solid-like regime and the transition to nonlinear behavior in the low frequency, liquid-like regime. For this purpose we investigate the flow of suspensions of silica particles suspended in PEG (polyethylene glycol) of molecular weight 400g/mol and PTHF (Poly tetrahydrofuran) of molecular weight 250 mol/g. While the PEG system is near hard sphere, the particles experience attractions in PTHF. Nonlinearities in the flow properties under stress are studied using the asymptotic nonlinearities developed by Ewoldt and Bharadwaj (*Rheologica Acta*, 2013). Hard sphere systems have shown universal scaling behavior pertaining to their yielding and the variation in flow behavior as a function of attractive strength in the solution will be reported in the current study.

## **Symposium NF Non-Newtonian Fluid Mechanics**

Organizers: Paulo Arratia and R Sureshkumar

Monday 10:00 Frederick/Columbia

NF1

### **Drop impact on permeable meshes with yield-stress fluids**

Brendan C. Blackwell and Randy H. Ewoldt

University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Yield-stress fluids, such as pastes and gels, can stick and accumulate where they impact. To understand coating of complex topography, we experimentally study the ability of drops to accumulate on permeable solid meshes (rigid surfaces with small, evenly spaced openings). Whereas Newtonian fluids can adhere on meshes with sufficiently small lengthscales due to surface tension, yield-stress fluids can adhere due to rheological properties and accumulate much larger volumes. When inertial stresses are sufficiently high compared to the yield stress, a drop can pass through a mesh, breaking into smaller fluid particles with varying shapes, sizes, and velocities in the process. In contrast, when inertial stresses are sufficiently low compared to the yield stress, a drop can stick to the open mesh as though it were an impermeable solid surface. Drop size, impact velocity, mesh geometry, and rheological material properties are varied. Layers of spaced meshes are also examined, demonstrating a range of behaviors and the ability to coat internal aspects of complex topography. Dimensional analysis is performed to characterize material transmittance, velocity variations, and material spreading as a function of the geometric, kinematic, and rheological parameters.

Monday 10:25 Frederick/Columbia

NF2

**Drop deformation of viscoelastic drops in the presence of continuous air stream in the bag breakup regime**Varun Kulkarni, Arezoo Ardekani, Sharon Snyder, and Paul E. Sojka*School of Mechanical Engineering, Purdue University, West Lafayette, IN, United States*

In the present study, we analyze the deformation of a viscoelastic drop moving in a co-flowing air stream corresponding to Weber numbers in the bag breakup regime of secondary atomization. Although considerable attention has been given to secondary breakup of Newtonian drops relatively limited literature exists in the context of non-Newtonian drops. Before the drop atomizes completely it deforms gradually from a spherical shape to a flattened liquid entity. The extent of this deformation and the governing factors are important to understanding the atomization process in such a scenario. This work aims at studying this initial drop deformation including the effects of viscoelasticity. The Giesekus model is used to describe the viscoelastic nature of the drops and the governing momentum and mass conservation equations are derived and solved numerically to obtain the evolution of the cross-stream, stream-wise drop deformations. Furthermore, we estimate the magnitude of the initiation time, the time required by the drop to transition from the spherical shape to a flattened pan-cake like structure just before it bulges into a bag. These findings are then compared with experimental measurements on drops made of mixtures of Xanthan gum and DI water with concentrations varying from 0.1% to 1% and the role of viscoelasticity is therefore elucidated by examining the observed trends.

Monday 10:50 Frederick/Columbia

NF3

**Extensional necking in complex fluids: Beyond the Considere criterion**Suzanne M. Fielding and David M. Hoyle*Physics Department, Durham University, Durham DH1 3LE, United Kingdom*

We study the necking instability of an initially cylindrical sample of a complex fluid subject to extensional stretching. We move beyond the Considere criterion, which is widely discussed in the literature as applying universally in extensional stretching, but which we show in fact applies only rarely in complex fluids, under very particular circumstances, and subject to a very careful interpretation. We illustrate our findings in both polymeric fluids and also in soft glassy materials, which show a crossover as a function of sample age from a liquid-like to a solid-like mode of failure. Time permitting, we will discuss results not only for a constant Hencky strain rate protocol, but also for the protocols of constant velocity, constant stress and constant force.

Monday 11:15 Frederick/Columbia

NF4

**Extensional rheology of suspensions of motile cells**Ranganathan Prabhakar<sup>1</sup>, Amarin McDonnell<sup>1</sup>, James Friend<sup>2</sup>, and Leslie Yeo<sup>3</sup>*<sup>1</sup>Mechanical and Aerospace Engineering, Monash University, Clayton, Victoria 3800, Australia; <sup>2</sup>Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, CA 92093-0411, United States; <sup>3</sup>School of Civil, Environmental & Chemical Engineering, RMIT University, Melbourne, Victoria 3000, Australia*

We present here a comparison of theory against experiment for the extensional rheology of suspensions of motile cells. Extensional viscosities of cell suspensions have been measured using a novel acoustically-driven microfluidic capillary-breakup rheometer. Swimming speeds and rotational diffusivities of the cells were also measured independently. It is observed that motility increases the extensional viscosity of suspensions of algal pullers, but decreases it in the case of bacterial or sperm pushers. A recent model [Saintillan, Phys. Rev. E, 2010, 81, 56307] for dilute active suspensions is extended using a simple Krieger-Dougherty formulation to obtain predictions for higher volume fractions. We show that details of body and flagellar shape may have significantly determine macroscale rheological behaviour in extensional flows.

Monday 11:40 Frederick/Columbia

NF5

**Extensional flowSANS at NIST**Katie Weigandt<sup>1</sup> and Robert McAllister<sup>2</sup>*<sup>1</sup>NIST Center for Neutron Research, Gaithersburg, MD 20899, United States; <sup>2</sup>University of Delaware, Newark, DE, United States*

Extensional flows are commonly observed in nature and industry, but still poorly understood when compared with shear flows. This is due to inherent experimental difficulties in making precise structural and mechanical measurements of fluids undergoing extensional strain. In recent years, there have been a number of groups using microfluidic devices to accurately measure the extensional rheology and birefringence of various viscoelastic fluids. However, the relatively minimal available tools to probe the structure of complex fluids under extensional flow is in stark contrast to the variety of techniques used for similar materials in shear flow. For instance, at NIST we have a complementary suite of tools used to access the structure of complex fluids under shear relative to the 1-2, 1-3, and 2-3 shear planes. In an effort to address this unmet need we have recently designed a new modular flow cell for neutron scattering that will allow us to measure the structure of complex fluids in non-shear flows including extensional flow. Currently, we are using a cross slot geometry so that we can now quantify nanostructural changes that occur in complex fluids that are undergoing extensional deformation near a stagnation point. Recently, we have begun the process of optimizing the cross-slot geometry for both flow and neutron measurements. In particular, we have been investigating the effect of channel aspect ratio on the alignment of wormlike micelles near the stagnation point. In this poster we will describe the new flow cell and we will present the results of recent investigations into the structure of wormlike micelles solutions undergoing extensional flow at a stagnation point.

# Monday Afternoon

## Symposium SC

### Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Monday 1:30 Constellation C

SC6

#### **The suspension balance model revisited: Revisited**

Mu Wang and John Brady

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

We use Stokesian Dynamics to assess the particles' contribution to the suspension stress, which drives particle migration in the suspension balance model of Nott *et al.* [*Phys. Fluids* **23**, 043304 (2011)]. When computing this contribution, the choice of the hydrodynamic force is not unique due to the many-body, non-pairwise-additive hydrodynamic interactions. To select a proper partitioning of the hydrodynamic force, we appeal to Brownian suspensions where the equilibrium osmotic pressure is known. We find that the particles contribute the entire Brownian stress and the majority of the hydrodynamic stress. These results explain why the original suspension balance model of Nott & Brady [*J. Fluid Mech.* **275**, 157 (1994)] gives quantitative predictions of particle migration.

Monday 1:55 Constellation C

SC7

#### **Does suspension crowding screen hydrodynamic interactions?**

Yu Su<sup>1</sup>, James W. Swan<sup>2</sup>, and Roseanna N. Zia<sup>1</sup>

*<sup>1</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States; <sup>2</sup>Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

Resistance and mobility functions describe linear couplings between moments of the hydrodynamic traction on a suspended particle and the motion of that or other particles. For two isolated spheres, these functions are well known and have been applied directly in the solution of many important problems for dilute colloidal dispersions. We have devised a new stochastic technique to calculate an analogous set of functions for two spheres immersed in a suspension that are then used to model the near-equilibrium dynamics of concentrated dispersions, including viscoelasticity and long-time diffusion. These functions include coupling between particle translation/rotation and force/torque, as well as couplings with stresslet. Of interest is the degree of screening of hydrodynamic interactions by the intervening medium. We find that the mobility is unscreened at the pair level, even in suspensions of high concentration, confirming that hydrodynamic interactions are an essential part of the dynamics of crowded systems and cannot be neglected in favor of simple renormalization schemes. We compare our results for the hydrodynamic interactions between suspended particles to predictions from two-point microrheology. This technique can be used to infer the complex viscosity from long-ranged decay of the pair mobility in viscoelastic materials.

Monday 2:20 Constellation C

SC8

#### **Bulk rheology of suspensions of rigid particles in viscoelastic fluids**

Nick O. Jaensson, Martien A. Hulsen, and Patrick D. Anderson

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

Suspensions of rigid, non-Brownian particles in viscoelastic suspending fluids show interesting behavior that is not observed if the fluid is Newtonian. One of these behaviors is the formation of particle strings in a shear flow. Although this phenomenon is well-known, its influence on the bulk rheology has not been thoroughly investigated. We present direct numerical simulations of 2D particle suspensions in an Oldroyd-B fluid, and investigate the influence of string formation on the bulk viscosity and the bulk normal stress difference for varying Weissenberg numbers and particle concentrations. The use of mesh-refinement allows us to resolve the hydrodynamics in between particles, even for high particle concentrations, without the need for a repulsive potential. An averaging procedure over many random initial particle configurations is applied to obtain the true bulk response of the material. In accordance with experimental work by Lyon *et al.* [1], a decrease in the shear viscosity is observed, which can be related to the formation of particle strings. Furthermore, an increase in normal stress difference is observed, which we attribute to an increase in the effective shear in between particle strings. Lastly, flow cessation is simulated, and we show that the particle strings are preserved, indicating that the relaxation of elastic stresses does not break up the particle strings.

This research forms part of the research programme of the Dutch Polymer Institute (DPI), Project #746.

References: [1] M.K. Lyon *et al.* *Journal of Rheology*, 45(4), 881-890, 2001.

Monday 2:45 Constellation C

SC9

**Mixing and demixing in ternary particle-liquid-liquid mixtures**Samantha J. Heidlebaugh, Trystan Domenech, Steven Iasella, and Sachin S. Velankar  
*Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States*

We examine mixtures of two immiscible liquids and particles that are fully-wetted by one of the liquids. Experiments are conducted on various fluid pairs: oil/water, immiscible polymers, and air/water. The particle loading and the volume ratio of the two fluids are varied across a wide range. A variety of morphologies appear including pendular aggregates of particles, capillary aggregates, and a drops-in-suspension structure. Most interestingly, in a composition range when the particle loading is comparable to the wetting fluid loading, there is nearly-complete separation into two phases: one phase comprising a suspension of the particles in the wetting fluid, and the other phase being the non-wetting fluid. Within this composition range, the ternary mixture is strongly prone to macroscopic demixing, i.e. it is nearly impossible to achieve a good dispersion of the species. Such macroscopic demixing appears consistently across a variety of systems regardless of particle size, and regardless of the immiscible fluids pairs. Aggregation and separation do not happen if the particles are partially-wetted by both fluids, in which case Pickering emulsions appear at all compositions. Such demixing is rooted in the basic rheology of suspensions: if the combined (particles + wetting fluid) phase is highly concentrated in particles, it has a high viscosity or a weak yield stress. Under these conditions, drops of the combined phase can coalesce, but not break easily. This is a recipe for unbounded growth of the dispersed phase size, thus resulting in macroscopic separation. Rheological criteria for separation are proposed and compared with experimental results. Analogies are drawn to wet granulation and spherical agglomeration, two particle processing operations in which wetting phenomena and capillarity are important

Monday 3:10 Constellation C

SC10

**Rheology in hydrate formation at atmospheric pressure**Paulo H. de Lima Silva<sup>1</sup>, Alberto S. Stender<sup>1</sup>, Mauricio Barçante<sup>1</sup>, Monica F. Naccache<sup>1</sup>, Paulo R. de Souza Mendes<sup>1</sup>, and Aurora P. Gramatges<sup>2</sup><sup>1</sup>*Mechanical Engineering, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453900, Brazil;* <sup>2</sup>*Chemistry Department, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453900, Brazil*

The appearance of hydrates of natural gas is a major concern for the Oil & Gas Industry. Hydrates of natural gas are crystalline solids, formed when a water molecule entraps the gas molecule under appropriate conditions of pressure and temperature. Depending on the amount of hydrates formed, the resulting structure can be a slurry or a plug that resembles ice, with high bulk viscosity and shear modulus. The severe changes in fluid properties might cause flow assurance issues, so it is extremely important to evaluate the potential risk of blockage formation, and to seek solutions that would potentially delay hydrate nucleation or guarantee hydrate transportability. Typically, once hydrates are formed, the viscosity and the shear modulus increase very fast. Therefore, the understanding of the fluid rheology during this process can be a useful tool to better analyze this phenomenon. In this work, we obtain the rheology characterization of two different model systems, both hydrate formers at atmospheric pressure: the first system is a mixture of water and tetrahydrofuran (THF), and the other one is a water-in-oil emulsion with cyclopentane. The study shows results of each system, addressing the effects of the cooling rate, and water/hydrate former concentration on the fluid rheology during the hydrate formation process.

Monday 4:00 Constellation C

SC11

**A minimal model for the hydrodynamics of colloidal gelation**James W. Swan<sup>1</sup> and Zsigmond Varga<sup>2</sup><sup>1</sup>*Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States;* <sup>2</sup>*Massachusetts Institute of Technology, Cambridge, MA, United States*

Colloidal gels are formed during arrested phase separation. Sub-micron, mutually attractive particles aggregate to form a system spanning network with high interfacial area, far from equilibrium. Models for microstructural evolution during colloidal gelation have often struggled to match experimental results with long standing questions regarding the role of hydrodynamic interactions. In the present work, we demonstrate simulations of gelation with and without hydrodynamic interactions between the suspended particles. The disparities between these simulations are striking and mirror the experimental-theoretical mismatch in the literature. The hydrodynamic simulations agree with experimental observations, however. We explore a simple model of the competing transport processes in gelation that anticipates these disparities, and conclude that hydrodynamic forces are essential. Near the gel boundary, there exists a competition between compaction of individual aggregates which suppresses gelation and coagulation of aggregates which enhances it. The time scale for compaction is mildly slowed by hydrodynamic interactions, while the time scale for coagulation is greatly accelerated. This enhancement to coagulation leads to a shift in the gel boundary to lower strengths of attraction and lower particle concentrations when compared to models that neglect hydrodynamic interactions. Away from the gel boundary, differences in nearest neighbor distribution persist. This result necessitates a fundamental rethinking of how both microscopic and macroscopic models for gelation kinetics in colloids are developed.

Monday 4:25 Constellation C

SC12

**Gel formation and rheology of short range attractive nanocolloidal suspensions and their mixtures**Divya Bahadur<sup>1</sup>, Subramanian Ramakrishnan<sup>2</sup>, Robert L. Leheny<sup>3</sup>, and John Telotte<sup>1</sup><sup>1</sup>Florida State University, Tallahassee, FL, United States; <sup>2</sup>FAMU-FSU College of Engineering, Tallahassee, FL, United States;<sup>3</sup>Johns Hopkins University, Baltimore, MD, United States

We report a rheological study of moderately concentrated suspensions of silica colloids and their binary mixtures that form a gel on cooling. The suspensions are comprised of silica colloids (37nm, 98nm and 205 nm) coated with octadecyl-hydrocarbon chains and suspended in decalin at colloidal volume fractions ( $\phi$ ) ranging from 0.2 to 0.4. Different scaling relationships are explored to predict the elastic modulus and the limit of linearity. Gel temperatures of the different size particles and the elastic moduli, though different, collapse onto a single curve when scaled as  $G'D^3/\phi kT$  and plotted versus  $(1/T - 1/T_{gel})$ , where  $G'$  is the elastic modulus and  $T_{gel}$  is the gel temperature. This scaling is in line with predictions of mode coupling theory which emphasizes the importance of local structure (localization length) over longer-range correlations in determining the dynamical and mechanical properties of such gels. The observed scaling is extended to predict the elastic moduli of binary mixtures of particles with preliminary experimental data in good agreement with theoretical predictions. This highlights the effectiveness of predicting mechanical properties of the gel using the concept of localization. Efforts will be made to extend the scaling relationships to smaller particle sizes and their mixtures. Limitations of the theory in predicting the mechanical properties will also be discussed.

Monday 4:50 Constellation C

SC13

**Residual stresses in colloidal gels**Esmaeel Moghimi<sup>1</sup> and George Petekidis<sup>2</sup><sup>1</sup>University of Crete and IESL-FORTH, Heraklion, Greece; <sup>2</sup>Institute of Electronic Structure & Laser - IESL, Foundation for Research & Technology-Hellas - FORTH, Heraklion, Crete, Greece

We examined the internal stresses in colloidal gels which brought to the rest state from the steady shear of different rates by rheology and Brownian dynamics (BD) simulations. A model system of colloidal depletion gels with intermediate volume fraction ( $\phi=0.44$ ) is chosen and the attractions implemented between particles by adding non-adsorbing linear polymer chains. The gel release the stress in two distinct patterns after flow cessation: At high shear rates where shear forces dominate over the attractive forces, the shear melted gel behaves as liquids and releases the stresses to zero after flow cessation. For low shear rates, however, stresses relax only partially similar to the findings in the colloidal glasses [1] and jammed soft particles [2]. The balance between shear and attractive forces which determines the intense of structural distortion controls the amplitude of the residual stresses through a universal scaling. The macroscopic stress decay is connected to the microscopic subdiffusive particle motions which become arrested at long times due to network formation.

[1] Ballauff, M., J. M. Brader, S. U. Egelhaaf, M. Fuchs, J. Horbach, N. Koumakis, M. Kr€uger, M. Laurati, K. J. Mutch, G. Petekidis, M. Siebenkr€uger, Th. Voigtmann, and J. Zausch, "Residual stresses in glasses," Phys. Rev. Lett. 110, 215701 (2013). [2] Mohan, L., R. T. Bonnecaze, and M. Cloitre, "Microscopic origin of internal stresses in jammed soft particle suspensions," Phys. Rev. Lett. 111, 268301 (2013).

Monday 5:15 Constellation C

SC14

**Delayed yield in reversible colloidal gels: A micro-mechanical perspective**Roseanna N. Zia<sup>1</sup>, Benjamin J. Landrum<sup>1</sup>, and William B. Russel<sup>2</sup><sup>1</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States; <sup>2</sup>Chemical and Biological Engineering, Princeton University, Princeton, NJ 08540, United States

We study via dynamic simulation the nonlinear response of a reversible colloidal gel undergoing deformation under a fixed step stress, with a view toward elucidating mechanisms of macroscopic yield at the level of particle and network dynamics. Under shear, such gels may flow then regain solidlike behavior upon removal of the stress. The transition from solidlike to liquidlike behavior is a yielding process that is not always instantaneous but rather may occur after a finite delay. That the duration of the delay decreases as stress increases is well known, but the underlying microstructural origin of this delay, or the yield itself, has not been clear. Recent experiments reveal two yield regimes, suggesting multiple yield mechanisms. Theories advanced to link gel structure to rheology aim to predict the ultimate fate of a gel under an applied load. While these hypothesize a competition between bond breakage and reconnection rates, no such particle-scale dynamics have been directly observed, and it is not clear these theories reconcile with ongoing structural evolution. To study these behaviors, we conduct large-scale dynamic simulation to model structural evolution and particle transport in colloidal gels subjected to a step stress. A range of volume fraction, attraction strength, and stress is studied, with detailed connection between macroscopic response, microstructure, and particle dynamics.

Monday 5:40 Constellation C

SC15

**Structural anisotropy and rheological behavior of colloidal gel under start-up shear**Park Jun Dong<sup>1</sup>, Ahn Kyung Hyun<sup>1</sup>, and Norman J. Wagner<sup>2</sup><sup>1</sup>School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Republic of Korea; <sup>2</sup>University of Delaware, Newark, DE 19716, United States

The structural anisotropy and rheological behavior of colloidal gels under start-up shear flow are investigated by using Brownian Dynamics simulations. Shear induced structural change is analyzed in both real space and reciprocal space through pair distribution function and structure factor. Colloidal gel shows structural anisotropy represented by alignment along the compressional axis and vorticity axis. Structural anisotropy

is quantified through an alignment factor, which shows overshoot behavior. Based on the microstructure analysis, the evolution of the structural anisotropy is explained by rupture being preferred in the extensional direction as compared direction. This result suggests an explanation for how attractive interactions create anisotropic structure along the vorticity direction. The structural anisotropy is quantitatively related to rheological behavior via a stress-SANS rule. The stress-SANS rule is modified to include the rupture of the colloidal gel structure. It is shown that this modified stress-SANS rule effectively links the shear-induced structural anisotropy to the non-linear rheology.

## Symposium SM Polymer Solutions and Melts

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Monday 1:30 Constellation D

SM6

### The long-awaited universality in polymer physics

Sara Wingstrand<sup>1</sup>, Qian Huang<sup>1</sup>, Ole Hassager<sup>1</sup>, and Nicolas J. Alvarez<sup>2</sup>

<sup>1</sup>Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark; <sup>2</sup>Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA, United States

Predicting and manipulating dynamics of polymeric liquids is of great importance in the design and processing of soft materials. While fundamentals of slow flow dynamics were resolved half a century ago, fundamentals of fast flow dynamics are still unsolved, especially due to the lack of experimental data. Thus the primary goal in polymer physics is to develop a universal framework that will predict the linear and nonlinear flow behavior of polymer melts from a small number of physical parameters. Universality of molecular dynamics is the underlying framework of the most successful theoretical model, known as the "tube model". According to the tube model a polymer melt can be coarse-grained into four independent parameters: a tube diameter ( $a$ ), the number of entanglements per chain ( $Z$ ), the equilibration time of one entanglement ( $\tau_c$ ), and the number of Kuhn segments,  $N$ . The model predicts that different polymers (i.e. polymers with different chemical structures) exhibit identical rheological responses (normalized) if they have the same values of  $Z$  and  $\tau_{max}$ . To date, no two molecular systems involving melts or polymer solutions have exhibited identical nonlinear behavior. In this work, we first demonstrate the similarities between the nonlinear extensional flow dynamics of two melts, poly(methyl methacrylate) (PMMA) and polystyrene (PS), with identical  $Z$ , relatively similar  $N$ , but very different chemistry. Secondly, we manipulate a PMMA solution into exhibiting the same flow behavior as a PS melt, considering the latest concepts of monomeric friction reduction. Despite great differences in chemistry and fluid topology, strikingly similar responses of these fluids are observed for both slow flows and fast extensional flows. This unique data set confirms universality of nonlinear polymer dynamics and therefore clearly outlines the missing physics in our current models.

Monday 1:55 Constellation D

SM7

### Exploring the dynamics of star polymers in fast extensional flow and stress relaxation

Qian Huang<sup>1</sup>, Serena Agostini<sup>2</sup>, Ludovica Hengeller<sup>1</sup>, Maksim Shivokhin<sup>3</sup>, Nicolas J. Alvarez<sup>4</sup>, Lian R. Hutchings<sup>2</sup>, and Ole Hassager<sup>1</sup>

<sup>1</sup>Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark; <sup>2</sup>Department of Chemistry, Durham University, Durham, United Kingdom; <sup>3</sup>Department of Chemical and Biochemical Engineering, Illinois Institute of Technology, Chicago, IL, United States; <sup>4</sup>Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA, United States

Rheology of polymer melts is highly sensitive to branching. While a lot of work has been done for well-defined branched polymers in linear rheology, experimental data in non-linear rheology is very limited. Recently, Ianniruberto and Marrucci [1] reported that entangled melts of branched polystyrenes (PS) behave like linear PS in the steady state of fast extensional flow. This interesting conclusion is based on the data from Nielsen et al. [2], which is, to our knowledge, the only published data of steady-state viscosity in strong extensional flow for branched polymers of known structures.

In the present work, we explore the non-linear dynamics of the simplest branched polymers, which are star polymers with three arms. We measured three PS melts, a symmetric star, an asymmetric star and a linear PS, in both fast extensional flow and stress relaxation. All the three melts have the same backbone of molecular weight 180kg/mol, with an arm located in the center of the backbone with molecular weight 0kg/mol (linear), 20kg/mol (asymmetric star) and 90kg/mol (symmetric star), respectively. We show that the three melts behave identically in the steady state of fast extensional flow, which agrees with the observation from Ianniruberto and Marrucci [1]. However, in stress relaxation following steady extensional flow, the three melts behave differently due to the branch point as well as the length of the arm.

[1] Ianniruberto and Marrucci, *Macromol.* 46: 267-275 (2013). [2] Nielsen et al., *Macromol.* 39: 8844-8853 (2006)

Monday 2:20 Constellation D SM8  
**Issues with melt extension from non-isothermal condition, breakdown of time-temperature superposition to internal energy buildup**

Panpan Lin and Shi-Qing Wang

*Department of Polymer Science, University of Akron, Akron, OH 44325, United States*

We apply standard theoretical analysis and in situ IR thermal imaging measurements to show how specimen's temperature increases during uniaxial extension of well entangled polymer melts at high Hencky rates. The experimental condition far deviates from the isothermal condition when the melt extension becomes non-Gaussian. In the fast extension regime, there is a significant amount of energy missing, i.e., unaccounted for based on the measured temperature rise, suggesting storage of internal (potential) energy that is rarely reported in polymer melt rheology. The temperature measurements also allow us to confirm failure of the time-temperature superposition principle [1] to depict the transient stress responses during startup melt extension.

[1] Sun, H et al. *Macromolecules* 46, 4151 (2013).

Monday 2:45 Constellation D SM9  
**Small-angle neutron scattering study of the molecular deformation mechanism of entangled polymer melts in rapid uniaxial extension**

Jianning Liu<sup>1</sup>, Panpan Lin<sup>1</sup>, Shi-Qing Wang<sup>1</sup>, Luis E. Sanchez-Diaz<sup>2</sup>, Shiwang Cheng<sup>2</sup>, Kunlun Hong<sup>2</sup>, Wei-Ren Chen<sup>2</sup>, and Yangyang Wang<sup>2</sup>

<sup>1</sup>*Department of Polymer Science, University of Akron, Akron, OH 44325, United States;* <sup>2</sup>*Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

Understanding the viscoelastic properties of polymers is of fundamental and practical importance because of the vast and ever expanding demand of polymeric materials in daily life. Our current theoretical framework for describing the nonlinear flow behavior of entangled polymers is built on the tube model pioneered by de Gennes, Doi, and Edwards. On the basis of the barrier-free chain retraction on the Rouse time scale, the tube model predicts an elastic deformation mechanism that is fundamentally different from other alternative models such as the transient network model and yields excess strain softening in large deformation. The most convincing way to validate this ansatz of the tube model is to directly examine the molecular conformation of entangled polymers during rapid deformation. To this end, we have performed small-angle neutron scattering (SANS) measurements of uniaxially stretched polystyrene melts and analyzed the polymer dimensions as well as the deformation-induced conformational anisotropy in light of our recent SANS experiments of sheared colloids. Several implications from our analysis will be discussed in this talk.

Monday 3:10 Constellation D SM10  
**Nonlinear extensional behavior of an A-B-A thermoplastic elastomer near  $T_{g,A}$**

Luca Martinetti, Frank S. Bates, and Christopher W. Macosko

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

We investigated the behavior of a microphase-segregated PLA-PI-PLA triblock at a service temperature approaching the glass transition of the hard domains, an important application for thermoplastic elastomers (TPEs). The response was measured in start-up of steady uniaxial extension, at Hencky strain rates covering six orders of magnitude. Care was taken to ensure that the initial stress response accurately represented the material linear behavior, and the error associated with a random, small degree of anisotropy of the test specimens was minimized. By highlighting the viscous character of the response, use of the secant modulus allowed us to identify the effect of linear relaxation on tensile behavior. Strain hardening, whose onset could be predicted from the nonlinear elasticity of an entanglement strand, was preceded by strain softening possibly originating from entanglement slippage. Analyzing the experimental data at constant values of strain revealed a strain-induced relaxation associated with the glass-rubber transition of the microphase. The Rubinstein-Panyukov non-affine slip-tube model was unable to capture the observed strain dependence of the stress, while the Edwards-Vilgis slip-link model provided a reasonable description of the data even at the higher rates of strain. Based on the molecular picture of the strain-induced structural changes gained from exposing time and strain effects, the governing mechanism of rupture was identified with ductile/fragile rupture of PLA domains. To the best of our knowledge, this is the first experimental evidence linking the strain rate dependence of ultimate properties of triblock TPEs to the strain-induced glass-rubber transition of the domains. In addition, application of the Bailey criterion allowed us to quantitatively account for the deformation rate dependence of the ultimate properties in the regime of rubbery response.

Monday 4:00 Constellation D SM11  
**Linear and extensional rheology of butyl rubber**

Jon Bielby and Dana Adkinson

*LANXESS Inc, London, Canada*

Awareness of the differences in rheological properties between butyl rubber grades is crucial as they can have a significant impact on industrial processing and the intended application. The rheology was studied of various isobutylene-isoprene copolymers (known as butyl rubber). The

effects of small amounts of isoprene, as well as the introduction of a halogen and ionic groups to the copolymer were examined. The linear and extensional rheological properties were determined along with their dynamic mechanical behavior in the glass to rubber transition zone.

Isoprene in the polymer backbone acts as a branching agent as random long-chain branching was found in the isobutylene-isoprene copolymer. The terminal relaxation time, zero shear viscosity and extensional strain hardening increased as expected with long-chain branching. Whereas the glass transition temperature was found to be independent of long-chain branching, the glass to rubber transition was slowed by the topological interactions of the branches.

The introduction of a halogen to the copolymer slightly increased the terminal relaxation time, zero shear viscosity, extensional strain hardening, glass transition temperature and glass to rubber transition likely due to an increase in monomeric friction.

The addition of small amounts of ionic functionality along the halogenated copolymer backbone to form an ionomer produced large changes in the rheological properties. The presence of ionic groups generated an increase in the plateau modulus, the terminal relaxation time (including an additional relaxation process), zero shear viscosity and extensional strain hardening. An increase in the temperature dependence of the polymer was also found. The glassy modulus and the glass transition temperature increased, while the glass to rubber transition was narrower. The produced ionic groups in the copolymer aggregate into domains and behave as reversible physical cross-links.

Monday 4:25 Constellation D

SM12

### Recent developments in extensional rheology

Nicolas J. Alvarez<sup>1</sup>, Qian Huang<sup>2</sup>, Sara Wingstrand<sup>2</sup>, Ludovica Hengeller<sup>2</sup>, Aamir Shabbir<sup>2</sup>, and Ole Hassager<sup>2</sup>

<sup>1</sup>Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA, United States; <sup>2</sup>Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark

Based on the melt Filament Stretching Rheometer developed at DTU [1] we have constructed a smaller table-top FSR (the mini-FSR) with less inertia and thermal capacity in the system. Combined with updated on-line control of the kinematics [2] and a novel thermostat design, the operating range in extension rates and temperature has been extended. Available protocols include start-up of constant strain rate extension, constant stress (creep), constant force, stress relaxation after controlled flow, reverse flow and small amplitude oscillation. Windows in the thermostat allow visual observation of the liquid filament. This presentation will illustrate and discuss the operating ranges of the mini-FSR for a selection of model fluids including polymer melts, polymer solutions and ionomeric networks. Fracture of viscoelastic fluids and solids will be presented and discussed.

[1] Bach, Rasmussen and Hassager, J. Rheol. 47 (2003) 429-441. [2] Marin et al., Journal of Non-Newtonian Fluid Mechanics 194 (2013) 14-22.

Monday 4:50 Constellation D

SM13

### Exploring necking instability in polymeric solutions with single DNA molecules

Pouyan E. Boukany and Shaurya Sachdev

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

The addition of small amounts of polymers to a Newtonian fluid can exhibit complex rheological behaviour of the fluids in extensional flows. For instance, polymeric fluids produce strong filament thinning called necking when subjected to extensional flows. Coiled polymeric chains are expected to be stretched in this exponential necking regime. These stretched long chains induce elastic forces that resist the capillary forces trying to break the filament apart. Still, the molecular picture behind filament thinning and rupture of polymeric threads in extensional flow conditions is unknown. In this work, we investigate the flow instability with respect to neck formation of polymeric fluids undergoing extensional flow at the molecular level. Using single molecule approach, we unravel the underlying mechanism of thinning of a polymeric filament in different strain rates. Bulk flow and single molecule experiments have been done on both dilute and concentrated polymeric solutions. Direct visualisation of DNA molecules displays that majority of DNAs are stretched from their equilibrium coiled state in dilute systems ( $C < C^*$ ). In addition, we found that the strong flow in the thinning fluid provide sufficient forces to stretch and disintegrate single DNAs from other chains through chain disentanglement in concentrated polymeric system ( $C > C^*$ ). These new results allow us to pinpoint the molecular mechanism behind filament thinning and chain disentanglement in strong extensional flows of polymeric fluids.

Monday 5:15 Constellation D

SM14

### Stretch-relaxation of DNA molecules in semidilute solutions

Chandi Sasmal<sup>1</sup>, Hsiao Kai-Wen<sup>2</sup>, Charles M. Schroeder<sup>2</sup>, and J. Ravi Prakash<sup>1</sup>

<sup>1</sup>Chemical Engineering, Monash University, Melbourne, Victoria 3150, Australia; <sup>2</sup>Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Single molecule techniques have been used to directly observe the dynamics of fluorescently labelled linear semi-flexible DNA molecules in the semidilute concentration regime, subjected to planar extensional flow in a microfluidic cross-slot cell. Until recently, these methods have largely been confined to observations of DNA molecules in the ultra dilute limit. We study the conformational and stretching dynamics of DNA chains, and the relaxation following cessation of flow, as a function of concentration and Weissenberg number. Experimental observations have been complemented with numerical simulations, carried out with a computationally efficient multi-chain Brownian dynamics algorithm, which is capable of simulating polymer solutions at finite concentrations, and in which Kravynik-Reinelt periodic boundary conditions have been implemented to simulate planar extensional flow. A worm-like bead-spring chain model, with excluded-volume and hydrodynamic interactions taken into account, is used to represent DNA molecules. The successive fine graining technique, in which simulation data is accumulated for

chains with increasing numbers of beads,  $N$ , and then extrapolated to the limit  $N \rightarrow N_K$  (where  $N_K$  is the number of Kuhn steps), has been used to carry out a parameter-free comparison of experimental observations with numerical simulations. We observe that polymers in the semidilute regime exhibit key differences in dynamics compared to dynamics in the dilute regime. This work extends the field of single polymer dynamics to semidilute solutions, and addresses important questions in classical polymer physics on chain dynamics at the molecular level in this concentration regime.

Monday 5:40 Constellation D

SM15

### **Extensional rheology and printability of polymer solutions**

Jelena Dinic, Leidy N. Jimenez, Yiran Zhang, and Vivek Sharma

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

Many advanced manufacturing technologies like inkjet and 3D printing, nano-fiber spinning involve complex free-surface flows, and the formation of columnar necks that undergo spontaneous capillary-driven thinning and pinch-off. The progressive self-thinning of neck is often characterized by self-similar profiles and scaling laws that depend on the relative magnitude of capillary, inertial and viscous stresses for simple (Newtonian and inelastic) fluids. Stream-wise velocity gradients that arise within the thinning columnar neck create an extensional flow field that can orient and stretch macromolecules, contributing extra elastic stresses and extensional viscosity that change thinning and pinch-off dynamics for polymeric complex fluids. Polymeric fluids exhibit a much larger resistance to flow in an elongational flow field than Newtonian fluids with same shear viscosity. Characterizing the filament thinning and break-up kinetics in jetting, dripping and stretching liquid bridge provides invaluable insight into the interplay of elastic, viscous, capillary and inertial stresses relevant for these applications. In this talk, we elucidate how polymer composition, flexibility and molecular weight determine the thinning and pinch-off kinetics in our experiments. Both effective relaxation time and transient extensional viscosity are found to be strongly concentration dependent even for dilute solutions. Further, we show how finite extensibility of polymers dramatically changes the kinematics from elastocapillary to viscocapillary under strong extensional flow fields that can lead to coil-stretch transition.

## **Symposium IR Interfacial Rheology**

Organizers: Gordon Christopher and Sachin Velankar

Monday 1:30 Constellation E

IR6

### **Rheological behavior of bacteria at fluid interfaces**

Liana Vaccari<sup>1</sup>, Nima Sharifi-Mood<sup>1</sup>, Tagbo H. Niepa<sup>1</sup>, Robert L. Leheny<sup>2</sup>, and Kathleen J. Stebe<sup>1</sup>

<sup>1</sup>*Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA, United States;* <sup>2</sup>*Johns Hopkins University, Baltimore, MD, United States*

The interactions of bacteria and their surroundings have been central in understanding many fundamental processes in biology, such as biofilm formation, biofouling, biodegradation and deterioration. While most of these issues involve bacteria at solid-fluid interfaces, the proliferation of bacteria at fluid-fluid interfaces have been reported as a cause of infections in cystic fibrosis patients, and linked to the deterioration of dairy products. We have previously reported that bacteria can form elastic films at oil-water interfaces, Films of Bacteria at Interfaces (FBI), where the interface undergoes a transition from an active colloidal stage, to a viscoelastic one, eventually evolving into the aforementioned elastic film. To study these stages, we utilize particle tracking and pendant drop techniques, probing the evolution of the rheological properties of the oil-water interface in the presence of bacteria. Our previous particle tracking statistics took place over relatively short lagtimes - we have since had a unique opportunity with a species, *Pseudomonas aeruginosa* PA14, which remained active over an extended period of time (at least 24 hours). The actions by the bacteria trapped at the interfaces are interesting biologically, aiding our understanding of their reaction to stress, and are of further interest in answering important fundamental questions about the statistical mechanics of an active system that is not necessarily bound to the fluctuation dissipation theorem. Additionally, we have previously used pendant drop elastometry in conjunction with a linear Hookean model to determine the material parameters of an anisotropic elastic FBI. In this work, we extend our analysis to capture stresses associated with any elastic film, including the FBIs, without the aid of constitutive equations. This allows us to better characterize the material properties of a wider variety of elastic films.

Monday 1:55 Constellation E

IR7

### **Wrinkling of thin interfacial films by viscous stress**

Sourav Chatterjee<sup>1</sup>, McDonald Christina<sup>1</sup>, Peng Wang<sup>2</sup>, Rui Huang<sup>2</sup>, and Sachin S. Velankar<sup>1</sup>

<sup>1</sup>*University of Pittsburgh, Pittsburgh, PA 15261, United States;* <sup>2</sup>*Aerospace Engineering and Engineering Mechanics, University of Texas, Austin, TX, United States*

We examine the buckling of a thin elastic film floating on a viscous liquid layer which is itself supported on a prestretched rubber sheet. Releasing the prestretch in the rubber induces a viscous stress in the liquid, which in turn induces a compressive stress in the elastic film, leading to buckling. An approximate shear lag model is developed to predict the evolution of the stress profile in the unbuckled film. Three parameters arise from this analysis: the rate at which the prestretch is released, the thickness of the liquid layer, and the length of the elastic film, all suitably normalized by geometric and material parameters. A linear perturbation analysis is developed to predict the wavelength of wrinkles. Numerical simulations are

conducted to predict nonlinear evolution of the wrinkle wavelength and amplitude. Experiments conducted using 25 micron thick elastic polymer films floating on a viscous polymer liquid show trends that are qualitatively consistent with the predictions. The relevance of this research to rheology lies in the observation that the wrinkle wavelength is predicted to scale with the square root of the film modulus; thus, this approach may provide a way to measure the modulus of thin solid-like films at interfaces. Unlike conventional interfacial rheometry which becomes challenging as the bulk viscosity increases, this buckling-based method becomes easier to apply as the bulk viscosity increases. Thus, it has the potential to measure interfacial properties of compatibilizer-laden interfaces between molten polymers.

Monday 2:20 Constellation E

IR8

### **Disentangling the mechanisms underlying the dilatational modulus of irreversibly adsorbed layers**

Anthony P. Kotula<sup>1</sup>, Stephanie M. Kirby<sup>2</sup>, Todd M. Moyle<sup>2</sup>, Lynn M. Walker<sup>2</sup>, and Shelley L. Anna<sup>3</sup>

<sup>1</sup>*Materials Science and Engineering, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States;*

<sup>2</sup>*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States;* <sup>3</sup>*Chemical Engineering and*

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

Macromolecules or nanoparticles adsorbed on fluid-fluid interfaces impart unique interfacial mechanical properties. The response of an interface to dilatation (expansion or compression) impacts the stability of emulsions and foams, and the deformation and migration of droplets and bubbles with complex fluid interfaces. We determine dilatational interfacial rheology independent of shear and elongational deformation by applying small amplitude pressure oscillations across a microscale spherical cap. We obtain irreversibly adsorbed layers using a fluid exchange procedure. We examine a variety of complex interfaces including well-studied insoluble lipids and fatty acids, irreversibly adsorbed components of dispersant mixtures, semi-fluorinated alkane monolayers, and layers of surface-active nanoparticle complexes. For these systems, the Gibbs modulus arising from surface pressure changes alone and contributions from extra stresses arising from intermolecular and inter-particle interactions can be determined independently by combining simultaneous surface pressure and dilatational modulus measurements. No extra stresses are observed for the simplest surface-active molecules, while more complex macromolecules and nanoparticles exhibit large extra stresses, indicating the presence of a significant interfacial microstructure in these cases.

Monday 2:45 Constellation E

IR9

### **Impact of composition on the interfacial mechanics of multicomponent fluid-fluid interfaces**

Stephanie M. Kirby<sup>1</sup>, Shelley L. Anna<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 and*

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

Dynamic interfacial tension and interfacial rheology measurements are extremely useful for quantifying the adsorption behavior of surfactants, proteins, and polymers at oil/water and air/water interfaces. However, interfacial rheology measurements can be complicated by the presence of bulk surfactant that diffuses to the interface. Species that irreversibly adsorb to an interface allow for the investigation of interfacial behavior without the added complication of surfactant exchange with the bulk. We present a method for generating air/water and oil/water interfaces coated with an irreversibly adsorbed surfactant or protein. The surfactant adsorbs to the interface from a bulk solution for a specified amount of time before the bulk solution is exchanged with deionized water. The amount of surfactant adsorbed on the interface correlates directly with the interfacial tension at the time of rinsing; manipulating the rinsing procedure allows for direct control over the amount of surfactant or protein on the interface. Using a microtensiometer, we then measure the interfacial tension and interfacial rheology of the irreversibly adsorbed layers with no species present in the bulk. We also introduce a second surfactant to the system and observe disruption or displacement of the initial irreversibly adsorbed layer as a function of initial coverage and secondary surfactant concentration. This sequential adsorption procedure allows us to measure the interfacial tension and interfacial rheology of multi-component systems while avoiding bulk interaction. This approach has been applied to polymeric surfactants (Tween), biosurfactants (rhamnolipid) and globular proteins (hydrophobins) and competition with small molecule surfactants.

Monday 3:10 Constellation E

IR10

### **Interfacial self-assembly in the elasto-capillary regime**

Arthur A. Evans

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

When particles are adsorbed to a fluid interface, their interactions are mediated by deformations of the surface. A common strategy for assembling interfacial structures relies on exploiting these interactions by tuning particle anisotropy, either by constructing particles with heterogeneous wetting properties or fabricating particles that have a naturally anisotropic shape. In this talk I will discuss the implications for inducing anisotropy using elasticity-mediated energy scales, both in the deformation of particles and in the case of fluids with an elastic component.

Monday 4:00 Constellation E

IR11

**Influence of interfacial rheology on the volume of liquid entrained in a foam film**John M. Frostad<sup>1</sup>, Daniele Tammaro<sup>2</sup>, Luciano Santollani<sup>1</sup>, Simone Bochner de Araujo<sup>1</sup>, and Gerald G. Fuller<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Stanford University, Stanford, CA, United States;* <sup>2</sup>*Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, University of Naples Federico II, Napoli, Italy*

Bubble columns that produce foam are commonly found in waste water treatment and other industrial processes. The head on a glass of beer is another familiar example of foam formed by bubbles rising through a liquid and collecting on the surface. The characteristics of the foam that is formed in these systems such as the foam height, density and lifetime are all dependent on the properties of the surface-active compounds that are present in the liquid. In the present work, a fundamental study of single bubble interactions at a planar air-liquid interface is performed. When a single bubble moves upward and reaches the interface, a thin film of liquid is formed that drains and eventually ruptures. The volume of liquid initially entrained in this film is important in determining the properties of the resulting foam. For example, thicker films will tend to produce "wetter", more dense foams. A thicker film may also take longer to drain and therefore result in taller foam heights and/or more stable foams. Using interferometry, the volume of liquid entrained in the film is measured for several different surfactant systems. The interfacial rheological properties of the surfactants are then related to the volume of fluid entrained in the film.

Monday 4:25 Constellation E

IR12

**Effect of pH changes on the rheology of unsaturated zwitterionic and anionic phospholipids at the air-water interface**Saba Ghazvini<sup>1</sup> and Prajnaparamita Dhar<sup>2</sup><sup>1</sup>*Bioengineering, The University of Kansas, LAWRENCE, KS 66045, United States;* <sup>2</sup>*Chemical Engineering, The University of Kansas, Lawrence, KS 66045, United States*

We demonstrate changes in surface viscosity of four unsaturated phospholipid monolayers at the air-water interface induced by changes in the pH, using active interfacial microrheology. Unsaturated phospholipids are the major components of cell membranes, as well as intracellular organelles. These phospholipids could experience a change in pH; from 6.5~7 in early endosomes to 4.5~5 in late endosomes and lysosomes. The goal is to quantify how changes in pH affect the membrane fluidity of model phospholipid membranes with differences in size and charge of headgroups. We measured the surface viscosity of 1-hexadecanoyl-2-(9Z-octadecenoyl)-sn-glycero-3 phosphocholine (POPC), 1-hexadecanoyl-2-(9Z-octadecenoyl)-sn-glycero-3-phosphoethanolamine(POPE), 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (POPS), and 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (POPG) monolayers at pH 4.4 and pH 7.4. Fluorescence microscopy imaging confirmed no crystalline order for any of these unsaturated phospholipids, at air-water interface, which explains the very low surface viscosity (less than 10 nN s/m) measured at pH 7.4. Interestingly, we observed an increase in surface viscosity at pH 4.4 for POPC (3-fold), POPE (7-fold increase), and POPS (2.5 fold increase), but not for POPG, even though no change is observed in the fluorescence microscopy images. Moreover, this increase was not just dependent on headgroup charge (POPS becomes zwitterionic at this pH, while POPG remains anionic), and headgroup size, suggesting that the ability of the different headgroups to form hydrogen bonds with water molecules also modulates the surface viscosity. Our results demonstrate that our active interfacial microrheology set-up with sensitivity of 1 nNs/m is uniquely capable of determining minute changes in surface viscosity induced by changes in pH in unsaturated phospholipids monolayers even in systems that lack crystalline order, and therefore cannot be easily detected by higher resolution spectroscopic techniques.

Monday 4:50 Constellation E

IR13

**Estimating strain-dependent interfacial rheological properties of the encapsulation of lipid-coated monodisperse microbubbles using broadband attenuation at different pressure amplitudes**Kausik Sarkar<sup>1</sup>, Lang Xia<sup>1</sup>, and Tyrone M. Porter<sup>2</sup><sup>1</sup>*The George Washington University, Washington D.C, DC 20052, United States;* <sup>2</sup>*Boston University, Boston, MA, United States*

The surface rheological properties (surface tension, surface dilatational elasticity and surface dilatational viscosity) of the lipid encapsulation of a monodisperse microbubble are measured using broadband attenuation measured at four different acoustic excitation amplitudes. The rheological properties are determined by applying three different interfacial rheological models to the attenuation data. Although different models result in very similar rheological properties, attenuation measured at different excitation levels (4kPa-110kPa) leads to different values for them. With increasing excitation amplitude, the dilatation elasticity decreased from 0.56 N/m to 0.18 N/m, while dilatational viscosity decreased from  $2.4 \times 10^{-8}$  Ns/m to  $1.52 \times 10^{-8}$  Ns/m. However, attenuation being dependent on excitation levels raises a serious concern as to the validity of the assumption of a linear dynamics and thereby mode independence which underlies the theory of attenuation computation. We investigate it by numerically simulating the scattered response of the microbubble dynamics. Nonlinear energy transfer between frequencies are shown to be negligible, thereby establishing the suitability of the attenuation data. There is a second concern arising from shell properties being dependent on excitation amplitude--it is not a proper constitutive variable--which is resolved by arriving at a strain-dependent rheology for the encapsulation.

Monday 5:15 Constellation E

IR14

**A mesoscale computational study on the effectiveness of surface-active molecules on droplet dynamics and break-up**Arman Boromand<sup>1</sup>, Rosa D Apolito<sup>2</sup>, Safa Jamali<sup>1</sup>, Valentina Preziosi<sup>2</sup>, Giovanna Tomaiuolo<sup>2</sup>, Stefano Guido<sup>2</sup>, and Joao Maia<sup>1</sup><sup>1</sup>Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States; <sup>2</sup>Department of Chemical, Materials and Production Engineering, Università di Napoli Federico II, Napoli 80125, Italy

The use of different types of surface-active agents is ubiquitous in different industrial applications ranging from cosmetic and food industries to polymeric nano-composite and blends. This allows to produce stable multiphase systems like foams and emulsions whose stability and shelf-life are directly determined by the efficiency and the type of the surfactant molecules. Moreover, the presence and self-assembly of these species on an interface will display complex dynamics and structural evolution under different processing conditions. Analogous to bulk rheology of complex systems, surfactant-covered interfaces will respond to an external mechanical force or deformation differently depending on the molecular configuration and topology of the system constituents. Although the effect of molecular configuration of the surface-active molecules on the planar interfaces has been studied both experimentally and computationally, it remains challenging from both experimental and computational aspects to track the efficiency and the effectiveness of different surfactant molecules with different molecular geometries on curved interfaces. Using Dissipative Particle Dynamics, we have studied the effectiveness and the efficiency of different surfactant molecules on a curved interface in equilibrium and far from equilibrium. Interfacial tension is calculated for linear and branched surfactants with different hydrophobic and hydrophilic tail and head groups with different branching densities. Results from numerical simulations have been compared to experimental data of droplet deformation in water/oil emulsions with surfactants undergoing shear flow. The effects of surfactant concentration and shear rate have been investigated by measuring the deformation parameter as a function of the capillary number.

Monday 5:40 Constellation E

IR15

**The role of interfacial charge transport on the deformation and relaxation of a low-conductivity drop exposed to a DC electric field**Javier Lanauze, Lynn M. Walker, and Aditya S. Khair

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

We examine the transient deformation of a weakly conductive, millimeter-sized oil drop immersed in another oil exposed to a uniform DC electric field. Additionally, we examine the relaxation of the drop upon removal of the field. First, the transient deformation of a drop that attains a final oblate configuration is predicted using the leaky dielectric model, which is solved via an axisymmetric boundary integral method that accounts for surface charge convection and a finite relaxation timescale over which the interface charges. Our computations are compared against an experimental system consisting of a silicone oil droplet suspended in a castor oil medium. Next, the deformation-relaxation profile of a prolate low-conductivity drop is analyzed through experiments, analytical theory, and boundary integral simulations. Here, we find a marked asymmetry between the temporal evolution of the drop shape during deformation and relaxation, which we demonstrate is due to the finite relaxation time over which the interface charges (and discharges). In conclusion, our work highlights that interfacial charge transport plays an important role in the deformation and relaxation of weakly conductive drops exposed to electric fields.

**Symposium BM****Biological Macromolecules: Proteins, Cellulosic Biomass and other Biomaterials**

Organizers: Jai A. Pathak and Patrick Underhill

Monday 1:30 Constellation F

BM6

**Redefining the role of the gluten network in the rheology of wheat dough**Mathieu Meerts<sup>1</sup>, Ruth Cardinaels<sup>2</sup>, Filip Oosterlinck<sup>3</sup>, Christophe M. Courtin<sup>4</sup>, and Paula Moldenaers<sup>1</sup><sup>1</sup>Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium; <sup>2</sup>Department of Mechanical Engineering, TU Eindhoven, Eindhoven 513, The Netherlands; <sup>3</sup>Materials Science Center, DSM Ahead B.V., Geleen 6167, The Netherlands;<sup>4</sup>Laboratory of Food Chemistry and Biochemistry, KU Leuven, Leuven 3001, Belgium

Although bread making has been practised for millennia, the fundamental understanding of the relations between dough microstructure and rheology is still surprisingly limited. It is well known that the dough matrix consists of a hydrated gluten network filled with starch granules. There is, however, no consensus yet about the specific contribution of each of these major constituents (gluten and starch) to the overall dough behavior. We have tackled this research question by investigating the rheological behavior of both components individually, and by studying mixtures of different gluten-to-starch ratios as well as dough made from weak and strong flours. Oscillatory and creep-recovery experiments are implemented to investigate respectively the linear and nonlinear viscoelastic behavior in shear. Uniaxial extensional tests are performed by means of an extensional viscosity fixture on a rotational rheometer. In the nonlinear region, dough behavior appears to be primarily determined by the response of the gluten network, which is in line with the findings of previous studies. Surprisingly, this conclusion does not seem to hold for the linear dough behavior, which is also strongly affected by the starch granules. As a result, only nonlinear rheological tests are able to distinguish strong from weak flour dough. The value of the strain hardening index (SHI) clearly reflects differences in both gluten quantity and quality, and is also affected by changes in water content and mixing time. To further elucidate the precise role of the gluten network in dough behavior, we have studied the effect of glucose oxidase on dough rheology. This enzyme is believed to modify the existing gluten network by creating additional

disulfide crosslinks. Changes in the gluten network are again most apparent in nonlinear rheological tests, and with the SHI we are able to quantify the concentration-dependent strengthening effect of glucose oxidase on the gluten network.

Monday 1:55 Constellation F

BM7

### **Fracture patterns and failure criteria for soft solid gels**

Mathieu Leocmach<sup>1</sup>, Bavand Keshavarz<sup>2</sup>, Christophe Perge<sup>1</sup>, Gareth H. McKinley<sup>2</sup>, Thibaut Divoux<sup>3</sup>, and Sébastien Manneville<sup>1</sup>

<sup>1</sup>Laboratoire de Physique, ENS Lyon, Lyon 69364, France; <sup>2</sup>Hatsopoulos Microfluids Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, United States; <sup>3</sup>Centre de Recherche Paul Pascal - CNRS, Pessac 33600, France

Biomaterials such as protein or polysaccharide gels are known to behave qualitatively as soft solids and to rupture under sufficiently large external loading. Combining optical imaging with shear rheometry we study the brittle rupture of a model casein gel in a Taylor-Couette geometry following two different rheological protocols, namely: creep experiments and large amplitude oscillatory shear under constant stress. Both protocols lead to the delayed (viscoelastic) failure of the gel, yet through quantitatively very different scenarios. The time to failure follows a decreasing power law with the applied shear stress, similar to the Basquin law of fatigue for solids in the two types of experiments, but the casein gels break sooner under oscillatory stress and exhibit a smaller Basquin exponent. Furthermore, the fracture patterns observed during the two protocols show quantitative differences. Creep experiments lead to the logarithmic growth of periodic cracks perpendicular to the direction of shear, while cyclic fatigue tests result in the formation of a heterogeneous fracture network. In the latter case, the casein gel is shattered into pieces with a characteristic size that strongly depends on the oscillation frequency and which are subsequently further eroded during the failure process. This extensive data set raises the following questions that we will discuss during the talk: what criterion best describes the onset of yielding: a critical strain or a critical energy input? Does the yielding criterion depend on the nature of the rheological test? Finally, can we propose a unified framework to describe the failure of soft solids in creep and fatigue experiments?

Monday 2:20 Constellation F

BM8

### **An investigation of the capillary thinning dynamics of saliva using a sticky gel network model**

Caroline E. Wagner and Gareth H. McKinley

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

There is increasing interest in using rheological measurements of saliva and other non-invasive bodily secretions such as cervical and respiratory mucus as diagnostics for pathology and disease. Despite this, there is only limited literature available on the extensional rheology of saliva, and nearly no consideration of its temporal stability in the face of biological degradation. Indeed, capillary breakup extensional rheometry (CaBER) data of saliva samples at various ages conclusively shows that both the time to breakup and relaxation time decrease as a function of age. Since the viscoelastic properties of saliva can primarily be attributed to the presence of large glycoproteins (MUC5B mucins) in solution, an initial modeling attempt involved treating saliva as a suspension of finitely extensible non-linearly elastic (FENE) dumbbells. Limited success was attained: the duration of the viscocapillary thinning period was overestimated, and, more importantly, the 'rupture-like' failure dynamics observed at the end of the thinning process for saliva and other biopolymer solutions was not captured. It is well known that the large salivary mucins physically associate and interact with each other and their surroundings via ion-mediated crosslinking and hydrogen bonding interactions (Schipper 2007), suggesting that modeling saliva as a weak physically-associated gel may be a more appropriate modeling choice. This motivated the development of a Sticky Network model in which saliva is modeled as an entangled and associated network of finitely extensible elastic segments with a stretch-dependent 'stickiness' energy parameter that must be overcome in order for the chains to be able to dissociate from the rest of the network. We show that this model is able to accurately capture the capillary thinning and filament rupture behaviour of saliva using biologically-derived parameters, and can systematically account for temporal changes through a progressive decrease in the molecular weight of the MUC5B chains.

Monday 2:45 Constellation F

BM9

### **Synergistic interaction between kappa-carrageenan and methylcellulose and the effect of salts on sol-gel transition**

Nalinda Almeida<sup>1</sup>, Leela Rakesh<sup>2</sup>, and Jin Zhao<sup>3</sup>

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Methylcellulose (MC) and kappa-carrageenan (KCG) are both widely used in food and pharmaceutical industries as a viscosity modifier, a gelling aid, and a film former due to their reversible thermal gelation properties. This research focused on the gelation effect of KCG and KCG with salts on sol-gel transition of MC solutions. The polymer solutions of 7 wt% MC (METHOCEL(tm) A15 LV Premium cellulose of low-molecular-weight grade) and 0.1% or 0.3% KCG (CPKelco, GENUCEL carrageenan CG-130) were made with various concentrations of NaCl, KCl, and CaCl<sub>2</sub> salts (0.01M to 0.5M). Rheological data were obtained using AR2000 rheometer (TA Instruments) with concentric cylinder geometry. Differential Scanning Calorimetry (DSC) was used to determine the thermal characteristics of MC/KCG/salts system using DSC Q-2000 (TA Instruments). Shear thinning behavior was observed for the blend of A15/KCG systems. With the addition of KCG, viscosity was increased one order of magnitude compared to A15 solutions. The highest viscosity was observed in the presence of low concentration salts. As salt concentration is increased viscosity is decreased to lower values. With the addition of KCG, elastic modulus has increased one order of magnitude compared with A15 solution. In the presence of low concentration of KCl, A15/ KCG, elastic modulus increased two orders of magnitude. However, with

higher concentration of salt, the influence of KCG on elastic modulus is not significant. Differential Scanning Calorimetry (DSC) was used to calculate free water and bound water content in the blend and bound water was detected only in the presence of KCl.

Monday 4:00 Constellation F

BM11

### **Characterizing and understanding protein stability and rheology at high concentrations**

Wei Qi, Stacy Kenyon, Steven Blake, Madhabi Majumdar, Samiul Amin, and E.Neil Lewis

*Malvern Biosciences Inc, Columbia, MD, United States*

The combination of dynamic light scattering (DLS), DLS-microrheology and Raman spectroscopy offers concomitant measurements of protein conformation viscosity and size. By linking the changes observed in the molecular structure as measured by Raman with the nanoscale physical properties derived from DLS and DLS-microrheology, unique insights into the optimum solvent (formulation) conditions that stabilize the native state of the protein can be obtained. In particular the Raman measurements provide insight into secondary and tertiary structural changes as well as the conformations around the disulfide linkages and changes in intermolecular (protein-protein) interactions as measured by changes in the extent of hydrogen bonding. In addition a number of kinetic and thermodynamic parameters can also be obtained through temperature studies and/or the use of deuterium exchange experiments. Specifically we have studied a number of mAbs and simple smaller proteins under a variety of solvent conditions to demonstrate the utility of the approach. We will present data that demonstrates the tool can be used to gain insight into the mechanism and pathways of protein aggregation as well as some of the driving forces associated with changes in viscosity.

Monday 4:25 Constellation F

BM12

### **Dilatation air bubbles in solution: A rheological study of their effects on therapeutic antibody stability**

Gigi L. Lin<sup>1</sup>, Jai Pathak<sup>2</sup>, Valeria Riguero<sup>3</sup>, Marcia Carlson<sup>3</sup>, Jean Buff<sup>4</sup>, and Gerald G. Fuller<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, Stanford University, Stanford, CA, United States;* <sup>2</sup>*Formulation Sciences Department, Medimmune, Gaithersburg, MD 20878, United States;* <sup>3</sup>*MedImmune, Inc., Gaithersburg, CA, United States;* <sup>4</sup>*Food Process Engineering, ETH Zurich, Zurich, Switzerland*

Monoclonal antibody drugs are a growing class of biologic therapeutics with high specificity in the treatment of cancer and various other indications. Although interfacial hydrodynamic stresses that are distinct from bulk shear are routinely encountered by monoclonal antibodies under typical manufacturing, filling and shipping conditions, the physics underlying molecular instability in the form of aggregate and particle formation is poorly understood and lumped under the moniker "shear." Our rheological studies examine well-characterized interfacial modes of fluid kinematics: equal-area shear and dilatation. We find visual evidence that dilatational deformation of the air-solution (A/S) interface is more detrimental to antibody stability when compared to constant-area shear at the interface. This was accomplished with the construction of a dilatational device that uses simultaneous pressure and shape measurements to study the protein's mechanical stability under interfacial aging. This approach has advantages over traditionally used methods that invoke the Young-Laplace equation, as they inaccurately describe viscoelastic interfaces formed by proteins adsorbed at solution/water interfaces. It offers multiple possibilities for rheological experiments, including step-strain and exponential strain studies. Results indicate that aging time, concentration, and magnitude of dilatational strain influence the onset of yielding of the protein-adsorbed solution/water interface, which can be used to characterize the extent of protein destabilization at the interface.

Monday 4:50 Constellation F

BM13

### **Correlating protein-protein interactions and solution viscosities at high concentration**

Mahlet A. Woldeyes, Eric M. Furst, and Christopher J. Roberts

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

Therapeutic monoclonal antibody (mAb) proteins have the ability to bind tightly and selectively to drug targets. However, high doses are necessary for these proteins to be effective therapeutics. Currently there are two methods of mAb drug administration: intravenous, large volume at dilute condition and subcutaneous, small volume at high concentration. The subcutaneous route is preferred due to its convenience and the possibility of patient self-administration. However, high concentrations lead to undesirable solution behaviors such as increases in viscosity, aggregation, and protein instability.<sup>1</sup>

Recent research has attempted to understand the relation between viscosity changes at high protein concentrations with measurements of protein-protein interactions (PPI).<sup>2</sup> This presentation will focus on work conducted using *alpha*-chymotrypsinogen A (aCgn) and mAb, where we have experimentally determined the PPI and viscosities over a broad range of protein concentrations. Static and dynamic light scattering were used to measure PPI over a range of ionic strengths and pH conditions. The osmotic second virial coefficient ( $B_{22}$ ) was used to quantify PPI in dilute regime. Colloidal intermolecular interaction potentials, such as square-well, screened electrostatics, and dipole interactions are used to calculate PPI at dilute protein concentrations. These experimental and modeling results will be presented and the effectiveness of simple colloidal models in predicting PPI from low to high protein concentrations will be discussed. The viscosity of aCgn and mAb solutions was measured using multiple-particle tracking microrheology. The results of these experiments will be presented and discussed in terms of its application in elucidating the connection between PPI and changes in viscosity with increasing protein concentration.

[1] Saluja, A., et al. *Int. J. Pharm.* 2008, 358 (1-2), 1-15. [2] Neergaard, M. S., et al., *Eur. J. Pharm. Sci.* 2013, 49 (3), 400-410.

Monday 5:15 Constellation F

BM14

**Deciphering the thermodynamic underpinnings of increased solution viscosity in crowded monoclonal antibody solutions**Rose Keeling<sup>1</sup>, Peng Ke<sup>2</sup>, Robin Curtis<sup>1</sup>, Prasad S. Sarangapani<sup>3</sup>, Sofia Ekizoglou<sup>2</sup>, Ronald L. Jones<sup>4</sup>, Shahid Uddin<sup>2</sup>, Christopher F. van der Walle<sup>2</sup>, and Jai Pathak<sup>3</sup><sup>1</sup>Chemical Engineering & Analytical Science, The University of Manchester, Manchester, United Kingdom; <sup>2</sup>Formulation Sciences, MedImmune, Cambridge, United Kingdom; <sup>3</sup>Formulation Sciences Department, Medimmune, Gaithersburg, MD 20878, United States; <sup>4</sup>Materials Science and Engineering, National Institute of Standards and Technology, Gaithersburg, MD, United States

Therapeutic protein formulation development could benefit from sound approaches for predicting concentrated solution properties from dilute solution data. Recent studies have suggested a link between dilute and concentrated solution behavior, although notable exceptions exist. We have carried out a detailed investigation of a monoclonal antibody solution using a combination of temperature-resolved dynamic and static light scattering (DLS/SLS), small angle neutron scattering (SANS), and rheological measurements spanning a protein concentration range between 1 g/L and 200 g/L. The systematic measurements have been made on a model IgG1 antibody under seven different solvent conditions (pH and ionic strength) chosen to tune non-specific protein-protein interactions from highly repulsive to strongly attractive. We have identified three solution conditions in D2O, used in SANS to achieve contrast between the macromolecule and the solvent, with similar strength of attractive protein-protein interactions, quantified by the DLS interaction parameter  $kD$  and the zero wavevector structure factor  $S(q)$  from SANS. These buffer conditions are 25 mM ionic strength in Tris buffer at pH 9, which is close to the protein iso-electric point, citrate buffer at pH 6.5 and an ionic strength of 25 mM, and at a high ionic strength of 275 mM in pH 5 acetate buffer with added chaotropic thiocyanate (SCN<sup>-</sup>) anions. We expect the range and anisotropy of the protein-protein interaction potential to vary across these conditions. Unlike the similar dilute solution behaviour in each buffer, the thermodynamic properties of the concentrated solutions are markedly different. High ionic strength solutions containing SCN<sup>-</sup> ion phase separate at a higher temperature due to weaker protein-protein attraction between 50 and 100 g/L. The solutions at low ionic strength are much more viscous than the one with SCN<sup>-</sup> anions at pH 5.0, suggesting that tuning the range and strength of the interaction potential may affect solution viscosity.

Monday 5:40 Constellation F

BM15

**A "syringe-on-chip" device for quantitative injectability study of concentrated protein solutions**Alfredo Lanzaro<sup>1</sup>, Robin Curtis<sup>1</sup>, Jai Pathak<sup>2</sup>, and Xue-Feng Yuan<sup>3</sup><sup>1</sup>School of Chemical Engineering and Analytical Science, the University of Manchester, Manchester, Greater Manchester M1 7DN, United Kingdom; <sup>2</sup>Formulation Sciences Department, Medimmune, Gaithersburg, MD 20878, United States; <sup>3</sup>The National Supercomputer Centre, Interdisciplinary Institute of High-Performance Computing, Guangzhou, China

We present a systematic study of the flow of well-characterised protein solutions in microfluidic syringe-like flow geometries, motivated by the objective of developing scaled-down models for measuring syringe performance - "syringeability." We focus on well-characterised monoclonal antibody formulations, as well as bovine and human albumin solutions prepared over a range of concentrations (1 g/L < c < 400 g/L) and with different formulation conditions such as buffer pH. The rheometric properties of protein solutions are characterised in the range of deformation rates typical of syringeability tests using the Rheo-chip platform developed at Univ. of Manchester (1). The available data include transient and steady shear viscosity measured over a range of shear rates as high as 10<sup>5</sup> s<sup>-1</sup>, and also extensional viscosity measured using our microfluidic "cross slot" device up to 10<sup>4</sup> s<sup>-1</sup>. It is important to measure both shear and extensional viscosity to describe syringe flow, as both flow kinematics exist in a syringe/needle and contribute to the total pressure drop. The complex flow of protein solutions is studied by means of a novel microfluidic "syringe-on-chip" device, which mimics the shear rate conditions encountered by concentrated protein solutions during injection using different needle gauge sizes. Measurements of pressure drop, velocity field and birefringence are performed (2,3). The results obtained in microfluidic flow conditions are critically compared with the outcomes of conventional syringeability tests performed with texture analysis systems. This systematic approach will lead to an effective scale down of syringe injection tests, with consequent minimisation of required sample, and will allow for optimisation of the design of drug delivery devices.

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## Symposium SG Solids, Glasses, and Composites

Organizers: Lynden Archer and Anne Grillet

Monday 1:30 Baltimore/Annapolis

SG6

### Convective cage release in model colloidal glasses

Alan R. Jacob<sup>1</sup>, Andreas Poulos<sup>2</sup>, Sunhyung Kim<sup>3</sup>, Jan Vermant<sup>4</sup>, and George Petekidis<sup>1</sup>

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<sup>4</sup>*Materials Science, ETH Zürich, Zürich 8093, Switzerland*

The mechanism of flow in glassy materials is probed using mechanical spectroscopy applied to colloidal glasses of model nearly hard sphere particles. Superimposing a small strain oscillatory motion orthogonal onto a steady state shearing motion, enables a direct measurement of the viscoelastic spectra during simple shear flow. Near the crossover frequency, a strain rate-orthogonal frequency superposition (SROFS) is obtained, due to a convective cage release that introduces a structural relaxation linearly dependent on shear rate. Although convective cage release is the dominant mechanism, deviations are observed both at low and high frequencies. At high frequencies in-cage motion is observed to be slowed down with increasing rate of deformation. Brownian dynamics simulations confirm that this is due to a shear induced cage distortion. Comparison between experiments and simulations further suggest that low frequencies deviations from a simple terminal flow response in SROFS are caused by hydrodynamic interactions. We further utilize the same approach to probe the shear induced dynamics of colloidal glasses of ultrasoft particles and attractive colloidal gels.

Monday 1:55 Baltimore/Annapolis

SG7

### What are the minimal interparticle interactions necessary to successfully simulate soft particle glasses?

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, University of Texas at Austin, Austin, TX 78712, United States;* <sup>2</sup>*ESPCI ParisTech, Paris, France*

Soft particle glasses (SPG) are highly concentrated suspension of deformable particles that have both solid- and liquid-like rheological behavior. The shear stress flow curve for these materials are well-described by a Herschel-Bulkley model with a shear thinning exponent of  $\frac{1}{2}$ . Several 2D and 3D simulations have been developed to predict and understand the rheology. A variety of interparticle interactions have been proposed in these simulations with varying results in terms of predicting the shear thinning exponent and the general rheology of the SPGs. In this talk we identify the minimal interparticle interactions necessary for a molecular dynamics simulation to successfully predict the structure and flow behavior SPGs. Generally, two kinds of forces must be accounted for in simulations of SPGs: viscous or frictional drag forces and elastic contact forces, which can be of different forms. Drag forces are a necessary component to dissipate energy in the simulation and capture the effect of the rheology of the suspending fluid. In general elastic forces are dominant compared to drag or other forms of friction forces. In this regime the Herschel-Bulkley flow curve, including the shear thinning exponent of  $\frac{1}{2}$ , is recovered, surprisingly, regardless of the form of the drag forces. To understand the origin and robustness of the  $\frac{1}{2}$  exponent, we compute the effective pairwise mobility between two soft particles in a concentrated suspension of soft particles in shear. We show how the mobility depends on concentration, particle elasticity, and the shear rate. We find that the shear rate dependence of the mobility determines the flow behavior of SPGs and its form is the same regardless of drag and elastic forces. This result explains the universal rheology of SPGs ranging from jammed emulsions and microgels suspensions to concentrated star solutions.

Monday 2:20 Baltimore/Annapolis

SG8

### Structure, rheology and transport properties of binary soft colloids

Akanksha Agrawal, Snehashis Choudhury, and Lynden A. Archer

*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

We report on jamming, yielding, and flow of binary mixtures of self-suspended silica nanoparticles densely grafted with Polyethylene glycol (PEG)(MW~5000g/mol). We find that addition of larger particles to a suspension of smaller ones softens the suspensions, and in the limit of large size disparities, completely fluidize the material. We show that these behaviors coincide with a speeding-up of de-correlation dynamics of all particles in the suspensions using XPCS measurements and are accompanied by reduction in the energy dissipated at the yielding transition as observed from oscillatory shear rheology measurements. We discuss our findings in terms of ligand-mediated jamming and un-jamming of hairy particle suspensions and propose an experimental state diagram as a function of variation in particle size ratio and relative fraction of large particles. These hybrid binary nanoparticles exhibit high ionic conductivity when they are used as electrolytes. These findings are explained in terms of variation in transport and structural properties that occurs due to size disparities as observed from impedance spectroscopy and SAXS measurements.

Monday 2:45 Baltimore/Annapolis

SG9

**WLF to Arrhenius dynamic transition in nanocomposites**Guilhem P. Baeza<sup>1</sup>, Claudia Dessi<sup>1</sup>, Dan Zhao<sup>2</sup>, Angel Alegria<sup>3</sup>, Dimitris Vlassopoulos<sup>1</sup>, and Sanat K. Kumar<sup>2</sup><sup>1</sup>*Institute of Electronic Structure and Laser, Foundation for Research and Technology, Heraklion, Crete 70013, Greece;*<sup>2</sup>*Chemical Engineering Department, Columbia University, New-York City, NY, United States;* <sup>3</sup>*Centro de fisica de materiales, Universidad del País Vasco, San Sebastian, Basque country 20018, Spain*

We investigate the dynamics of nanocomposites consisting of poly(2 vinyl pyridine), P2VP, matrix and well dispersed nanosilica spheres [1] by means of rheology and dielectric spectroscopy. Master curves are obtained via time-Temperature superposition but, remarkably, the temperature dependence of the frequency shift factors changes from William-Landel-Ferry behavior to an Arrhenius-like as the filler fraction increases (to about 50% wt). Dielectric spectroscopy reveals a significant decrease in the strength of the  $\alpha$ -process and its broadening at lower frequency (called  $\alpha_2$  [2]) becoming noteworthy at high silica content. The significant dynamic change with increased silica loading implies strong physico-chemical interactions between silica particles and polymer matrix. NMR and FTIR revealed the presence of physical H-bond between silanols at the silica surface and nitrogen atoms of the P2VP chains, which we claim to give rise to the bridging of particles through the polymer chains forming a network. This is consistent with recent results suggesting a transition from soft to glassy bridges in the same nanocomposite system at the same filler fraction [3]. The huge activation energy of about 380 kJ/mol is rationalized by estimating the density of bonds per particle and polymer chain, yielding a "Velcro" picture for the network. The effects of matrix molar mass and nonlinear strain are also addressed.

1. Jouault, N., D. Zhao, and S.K. Kumar, Role of Casting Solvent on Nanoparticle Dispersion in Polymer Nanocomposites. *Macromolecules*, 2014. **47**(15): p. 5246-5255. 2. Holt, A.P., et al., Dynamics at the Polymer/Nanoparticle Interface in Poly(2-vinylpyridine)/Silica Nanocomposites. *Macromolecules*, 2014. **47**(5): p. 1837-1843. 3. Chen, Q., et al., Mechanical Reinforcement of Polymer Nanocomposites from Percolation of a Nanoparticle Network. *ACS Macro Lett.*, 2015. **4** (4): p. 398-402.

Monday 3:10 Baltimore/Annapolis

SG10

**Design of yield-stress fluids: A rheology-to-structure inverse problem**Arif Z. Nelson and Randy H. Ewoldt*University of Illinois at Urbana-Champaign, Urbana, IL, United States*

A desired rheological property can often be achieved by multiple material structures, transcending the typical organization of the academic discipline into separate material classes. Our typical conceptual organization leads from structure-to-rheology, but property-driven design requires the inverse. The purpose of this work, which focuses on yield-stress fluids, is to apply methodologies of material design (both selection and creation) to rheologically-complex materials. Through implementation of these methodologies, microstructures are organized according to the different mechanisms capable of producing a yield-stress fluid (attraction-dominated and repulsion-dominated). The organization leads to a more creative yet focused design-space for these rheologically-complex materials and inspires new material design opportunities. This rheology-to-structure inverse problem reveals trade-offs in designing yield-stress fluids, demonstrating that multiple material classes can achieve a target yield stress, providing the opportunity for creative design to achieve both the yield stress and other secondary design criteria.

Monday 4:25 Baltimore/Annapolis

SG12

**Shear banding in time dependent flows of soft glassy materials**Rangarajan Radhakrishnan and Suzanne M. Fielding*Physics Department, Durham University, Durham DH1 3LE, United Kingdom*

Many soft materials, such as foams, pastes, and slurries exhibit features of structural disorder and metastability and are classified as soft glassy materials (SGMs). Time dependent flows that are used to characterize SGMs can sometimes give rise to distinct bands of shear rates across the sample. We investigate the emergence of shear banding in such flows of SGMs by a mesoscopic soft glassy rheology (SGR) model. From a kinetic Monte Carlo simulation of the SGR model, we find that transient shear banding appears both above and below the glass transition point. The magnitude and persistence of transient banding depends on sample age, and flow history. We compare the results of the SGR model with that of fluidity models used to represent SGMs.

Monday 4:50 Baltimore/Annapolis

SG13

**The Kovacs aging signatures in colloidal glasses**Xiaoguang Peng and Gregory B. McKenna*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

In this work we have synthesized and characterized a thermo-responsive core-shell PS-PNIPAM/AA latex system [1,2] and have investigated the aging behaviors of its colloidal dispersions subsequent to temperature (or concentration)-jump perturbations using sequential creep experiments to probe the response of the colloidal system. The aging experiments were conducted in the vicinity of the glass transition concentration or temperature as evidenced by the strongly varying relaxation time with decreasing temperature (or increasing concentration). The aging results from the current colloidal glass study are compared with those expected in the Kovacs' catalogue of experiments in structural recovery of glassy polymers, viz., intrinsic isotherms, asymmetry of approach and memory events [3]. We found that the colloidal glasses display aging behavior and time-aging time superposition is valid here. There are similarities in aging dynamics between colloidal glasses and molecular glasses, and differences also persist.

1. X. Di, X. Peng and G. B. McKenna, *The Journal of Chemical Physics* 140, 054903 (2014). 2. X. Peng and G. B. McKenna, *Physical Review E* 90, 050301(R) (2014). 3. A.J. Kovacs, *Fortschritte der Hochpolymeren-Forschung*, 3, 394-507 (1963).

We gratefully thank the National Science Foundation under the Grant No. CBET 1133279 and the John R. Brandford Endowment at Texas Tech University and each partially support this work.

Monday 5:15 Baltimore/Annapolis

SG14

### **A model for aging under deformation field, residual stresses and strains in soft glassy materials**

Yogesh M. Joshi

*Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar pradesh 208016, India*

A model is proposed that considers aging and rejuvenation in a soft glassy material as respectively a decrease and an increase in free energy. The aging term is weighted by inverse of characteristic relaxation time suggesting greater mobility of the constituents induce faster aging in a material. A dependence of relaxation time on free energy is proposed, which under quiescent conditions, leads to power law dependence of relaxation time on waiting time as observed experimentally. The model considers two cases namely, a constant modulus when aging is entropy controlled and a time dependent modulus. In the former and the latter cases the model has respectively two and three experimentally measurable parameters that are physically meaningful. Overall the model predicts how material undergoes aging and approaches rejuvenated state under application of deformation field. Particularly model proposes distinction between various kinds of rheological effects for different combinations of parameters. Interestingly, when relaxation time evolves stronger than linear, the model predicts various features observed in soft glassy materials such as thixotropic and constant yield stress, thixotropic shear banding, and presence of residual stress and strain.

Monday 5:40 Baltimore/Annapolis

SG15

### **Rheology of polyethylene/oxidized polyethylene blends and blend-nanocomposites with graphene and surface functionalized graphene**

Muhammad Z. Iqbal<sup>1</sup>, Frederick C. Prehn Jr.<sup>2</sup>, Abdala A. Ahmed<sup>3</sup>, Boyes G. Stephen<sup>2</sup>, and Matthew W. Liberatore<sup>1</sup>

<sup>1</sup>*Chemical and Biological Engineering, Colorado School of Mines, USA, Golden, CO 80401, United States;* <sup>2</sup>*Department of Chemistry, Colorado School of Mines, USA, Golden, CO 80401, United States;* <sup>3</sup>*Qatar Environmental and Energy Research Institute, Doha, Qatar*

Graphene is known to poorly disperse in non-polar polymers due to aggregation and van der Waals stacking of graphene sheets. In this presentation, improvement in graphene dispersion in polyethylene (PE) is shown by 1) blending PE with oxidized polyethylene (OPE), and 2) by chemically functionalizing the surface of graphene. The effects of these modulations on polymer-polymer and polymer-particle interactions are presented by means of melt rheology, small angle x-ray scattering (SAXS), wide angle x-ray scattering (WAXS), thermal and mechanical properties. OPE is observed to be completely miscible in PE, confirmed by a very low but positive value of the Flory-Huggins interaction parameter,  $\chi \sim 0.06$ , and by small fluctuations in constructing the time-temperature superposition master curves. OPE acts as a plasticizer for PE, which is shown by decreasing zero shear viscosity with increasing OPE concentration. On the other hand, OPE decreased the long period order in PE by reducing the amorphous regions in PE lamella and eventually increased elastic moduli with increasing OPE concentration (i.e., increased brittleness). PE/OPE blend-graphene nanocomposites exhibit improvements in graphene-network formation at lower loadings. The viscosity of blend-nanocomposites is found to be the same as that of neat PE indicating the ease of processability of these nanocomposites. The dispersion of graphene is observed to increase by the inclusion of OPE. Moreover, the effect of graphene surface functionalization on its dispersion in PE/OPE blends will be shown by melt rheology, mechanical properties and SEM morphology.

## **Symposium NF Non-Newtonian Fluid Mechanics**

Organizers: Paulo Arratia and R Sureshkumar

Monday 1:30 Frederick/Columbia

NF6

### **Stress gradient diffusion in dilute polymer solutions: Two model problems**

Ronald G. Larson, Gurui Zhu, and Xiaoyi Wang

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

When velocity gradients vary on length scales comparable to polymer molecules, polymer migration can occur, due to stress gradient diffusion. In some formulations, the driving force is written in terms of the second derivative of the local velocity, while in others it is given as a divergence of the stress tensor. To examine the relationship between these descriptions and to determine their accuracy, we deploy both molecular simulations and analytical theory to determine the steady-state polymer concentration field for dilute solutions in tight geometries. The two model two dimensional problems are electro-osmotic flow in a straight channel with spatially periodic wall charge and Taylor vortex flow, with sinusoidally varying velocities in the x and y directions. The first problem is solved by both Stochastic Rotation Dynamics (SRD) simulations, which includes hydrodynamic interactions (HI), and Brownian Dynamics (BD) simulations that omit HI. We tune the strength of HI in the SRD simulations using the solvent particle number density, and find that the steady state concentration field converges very slowly towards the no-HI BD case as the hydrodynamic interaction strength  $h^*$  decreases, with HI having a strong effect on concentration even at low  $h^*$ . Even without HI, stress gradient diffusion produces very pronounced concentration variations at modest Weissenberg number. In the second problem, Taylor vortex flow, we omit

HI, and solve for the concentration field of a Hookean dumbbell by BD and by analytical theory using a perturbation expansion out to third order in the Peclet number  $Pe$ , which we show is the appropriate expansion variable, rather than the Weissenberg number. We show that out to second order in  $Pe$ , both formulations of stress gradient diffusion give identical concentration fields, and we show how the BD results converge to the analytical results at low  $Pe$ . The results allow quantitative assessment of the accuracy of current theories of stress gradient diffusion.

Monday 1:55 Frederick/Columbia

NF7

### **Stress diffusion in models for shear banding**

Elian M. Masnada and Peter D. Olmsted

*Department of Physics, Georgetown University, Washington, DC 20057, United States*

Understanding shear banding is of utmost importance from both theoretical and experimental point of view and consequently it has been studied for several decades [1,2]. Despite this study numerous aspects of shear banding remains poorly understood. Because of the intrinsic inhomogeneity in the shear banded state, applicable constitutive models must include spatial inhomogeneities, leading to a so-called 'diffusive' term in the equation of motion for the slow variables that carry stress [3-6]. Such terms are also vital in describing the interaction of bulk shear banding flows with walls and incorporation of wall slip. In this work, we consider different sources of 'diffusion' in polymer models in which concentration degrees of freedom are negligible [7]. The simplest models used are consistent with diffusive terms whose origin is intrinsically dissipative, such as due to hydrodynamic interactions. By contrast, models in which elastic effects such as finite chain stiffness contribute to stress diffusion are inconsistent with simple diffusive models, and we propose alternative consistent models.

[1] P. D. Olmsted, *Rheol. Acta*, 47, 283-300 (2008). [2] S. M. Fielding, *Soft Matter*, 3, 1262-1279 (2007). [3] C.-Y. D. Lu, P. D. Olmsted and R.C. Ball, *Phys. Rev. Lett.*, 84, 642 (2000). [4] A. W. El-Kareh and L. G. Leal, *J. Non-Newton. Fluid Mech.*, 33, 257 (1989). [5] X. F. Yuan, *Europhys. Lett.*, 46, 542-548 (1999). [6] O. S. Agimelen and P.D. Olmsted, *Phys. Rev. Lett.*, 110, 204503 (2013). [7] J. K. G. Dhont and W. J. Briels, *Rheol. Acta*, 47, 257-281 (2008).

Monday 2:20 Frederick/Columbia

NF8

### **Evaluation of stress diffusion coefficient for wormlike micellar systems**

Hadi Mohammadigoushki and Susan J. Muller

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

In this work, we use rheometry and flow visualization to study the dynamics of the interface between shear bands in a wormlike micellar solution sheared between concentric cylinders, i.e., in a Taylor-Couette (TC) cell, and to evaluate the stress diffusion coefficient and stress correlation length in the Johnson-Segalman model. The wormlike micellar solutions are CTAB/NaNO<sub>3</sub> and CPCI/NaSal. These systems are highly elastic, exhibit Maxwellian behavior in linear viscoelasticity experiments, and shear banding in nonlinear experiments. A large, custom-built, computer controlled TC cell allows us to rotate both cylinders independently and to visualize the flow field in the r-z plane using a CCD camera. At low shear rates, the flow is stable and the fluid appears homogeneous throughout the gap between the cylinders. Above a critical shear rate, a shear banding transition occurs. This manifests itself in the formation of two distinct bands in the r-z plane, with an interface between the two bands. For sufficiently high ramp speeds, multiple steps of interface evolution are identified. We quantify the interface travel using direct visualization and use these measures, as well as rheometry, to determine the stress diffusion coefficient  $D$ , and stress correlation length  $\lambda$  in the Johnson-Segalman model. These parameters are evaluated at different temperatures, shear rates, and gap sizes for different systems. Our results show that the diffusion coefficient is independent of shear rate and increases with temperature in a manner consistent with kinetic theory. The stress correlation length is found to be independent of shear rate and temperature for the range of parameters studied in this work. However, we find that the stress diffusion coefficient and stress correlation length depend strongly on the gap of the Couette cell.

Monday 2:45 Frederick/Columbia

NF9

### **Disclination in nematic liquid crystal**

Chiquan Zhang<sup>1</sup>, Xiaohan Zhang<sup>1</sup>, Amit Acharya<sup>1</sup>, Noel Walkington<sup>1</sup>, and Dmitry Golovaty<sup>2</sup>

<sup>1</sup>*Carnegie Mellon University, Pittsburgh, PA, United States;* <sup>2</sup>*The University of Akron, Akron, OH, United States*

Liquid crystals (LC) are matter in a state whose properties are between liquids and solids. Research on liquid crystals is currently advancing quite rapidly motivated by applications in material science as well as in biological systems. In this work, we are primarily interested in modeling disclinations in a uniaxial nematic liquid crystalline medium, treated by an augmentation of the director model where the director is represented by a vector. It is well known that the universally accepted Oseen Frank energy function gives infinite energy solutions for disclination line defects treated classically. Recently, a kinematic augmentation of classical Leslie-Ericksen theory has been devised that allows alleviating the singularity, with results being demonstrated for the case where the defect field is not allowed to evolve. In this work, we study this augmented model with further natural modifications in the context of line defects, including those of half-integer strength. First, a gradient flow dynamics of the augmented energy is utilized and applied to calculate equilibrium solutions. However, we find that the gradient flow dynamics, for this energy, is not capable of adequately addressing the defect evolution problem; we explain why. Inspired by the crystal dislocation case, a 2D model based on the augmented energy, thermodynamics, and the kinematics of conservation of defect topological charge is built to analyze disclination dynamic behaviors. We demonstrate this model and computations for disclination annihilation, repulsion, and splitting.

Monday 3:10 Frederick/Columbia

NF10

**An immersed boundary method for fluid-structure interactions in a nematic liquid crystal**Saverio E. Spagnolie*Mathematics, University of Wisconsin-Madison, Madison, WI 53711, United States*

The nematic phase of a liquid crystal is characterized by a spontaneous local molecular alignment leading to fluid anisotropy (direction-dependent response to deformation). A body moving through such a phase can induce complex viscous and elastic structures in the surrounding environment, and the fluid's anisotropic response can generate surprising forces on the immersed body. Bacteria swimming in a liquid crystal, for instance, have been observed to align with the orientation of the underlying director field. In other settings the fluid stresses may couple to the shapes of immersed particles or membranes. The complexity of such problems makes analysis generally intractable, and even computing solutions can still be very challenging. In this talk I will discuss an immersed boundary method for computing fluid-structure interaction problems in an Ericksen-Leslie model fluid with relative ease. The immersed structure communicates forces onto the fluid as in Peskin's original method, but also communicates torques on the nematic director field through molecular anchoring boundary conditions. Sample applications will also be discussed, including the locomotion of undulatory bodies in anisotropic fluids.

Monday 4:00 Frederick/Columbia

NF11

**Morphology and rheology of micelle and micelle-nanoparticle solutions: A molecular dynamics study**Abhinandan Sambasivam, Subas Dhakal, and Radhakrishna Sureshkumar*Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13210, United States*

We present a systematic molecular dynamics (MD) study of the structure, dynamics and rheology of cationic micellar solutions in the presence of explicit solvent and highly binding organic salt. We use a coarse-grained (CG) MARTINI-based force field which has been shown to accurately predict shape transitions and binary interactions in such micelle systems [1, 2]. We simulate systems that contain up to a million CG beads, and access microsecond timescales, while still preserving the underlying physical chemistry. Our simulations have been able to capture the configurational dynamics and rupture of rodlike micelles in shear flow [3] as well as the morphological changes that cause anomalous variations in zero-shear viscosity as a function of salt concentration observed experimentally in CTAC/NaSal solutions [4]. For the first time, estimates of micelle size distribution, persistence length, end-cap energy and recombination time are obtained from MD simulations. Further, the addition of nanoparticles (NPs) to wormlike micellar fluids result in the formation of electrostatically stabilized junctions. Effect of NP surface charge and volume fraction on the equilibrium structure and shear rheology of such solutions will be discussed. Non-equilibrium MD simulations of such mixtures exhibiting complex rheological behavior including shear thinning, shear thickening and shear-induced isotropic-nematic transition will be presented.

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Monday 4:25 Frederick/Columbia

NF12

**Immersed boundary methods for particles in viscoelastic fluids**Sreenath Krishnan<sup>1</sup>, Eric S. Shaqfeh<sup>2</sup>, and Gianluca Iaccarino<sup>1</sup>*<sup>1</sup>Mechanical Engineering, Stanford University, Stanford, CA, CA 94305, United States; <sup>2</sup>Chemical Engineering, Stanford University, Stanford, CA, CA 94305, United States*

Suspensions of rigid particles in Newtonian and viscoelastic fluids are common in many engineering applications like hydraulic fracture stimulation, fluidized beds, coal based combustion etc. The capability to numerically simulate these flows would not only improve our understanding of the underlying physics, but also allow one to engineer fluids for these applications. This study is concerned with fully resolved simulations (FRS), wherein all scales associated with the particle motion and the surrounding flow are resolved. The present effort is based on the Immersed Boundary (IB) methods, in which the domain grids do not conform to particle geometry and for simplicity are chosen to be Cartesian. Cartesian grids cannot, however, efficiently represent complex geometries often encountered in engineering applications. Hence our approach is focused on the development of an IB method for viscoelastic flows using unstructured domain grids. The combination of IB forcing formulations within an unstructured non-Newtonian flow solver has not been presented before and this represents one of the major challenges tackled herein. In this approach, the conservation of momentum equations, which include both Newtonian and non-Newtonian stresses, are solved over the entire domain including the region occupied by the particles. It is assumed that this region is filled with a fluid with density equal to the particle density. The particle is defined on a separate mesh that is free to move over the underlying grid. The motion of the material inside the particle is constrained to be a rigid body motion by adding a body force in the momentum equation. This method is implemented in a massively parallel, unstructured finite-volume-based incompressible fluid solver developed at Stanford. The main focus of the presentation will be the description of the algorithm, including the measures taken to enable efficient parallelization. As a very interesting example, results for sedimentation under orthogonal shear will be presented.

Monday 4:50 Frederick/Columbia

NF13

**Computational modeling of suspension flow in pipes with generalized Newtonian matrix fluids**Nicos S. Martys<sup>1</sup>, Chiara F. Ferraris<sup>1</sup>, and William L. George<sup>2</sup><sup>1</sup>*Materials and Construction Research Division, National Institute of Technology, Gaithersburg, MD 20899, United States;*<sup>2</sup>*Applied Computational and Mathematics Division, National Institute of Technology, Gaithersburg, MD 20899, United States*

The flow of suspensions in pipe systems is important for a wide variety of applications including pumping of concrete and slurries. In this presentation, results of a study of suspension flow in a pipe geometry, based on the Smooth Particle Hydrodynamics approach will be given. Flow fields and the spatial distribution of solid inclusions in the pipe will be shown as a function of the matrix fluid properties, (including Newtonian, shear thinning and shear thickening), driving force, and volume fraction of particles. A simple model is presented which captures the salient features of an effective slip phenomena in such systems. Results will be compared to experiments and previous simulation work

Monday 5:15 Frederick/Columbia

NF14

**Migration of rigid particles in two-phase shear flow of viscoelastic fluids**Nick O. Jaensson, Martien A. Hulsen, and Patrick D. Anderson*Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands*

In the Stokes regime, non-Brownian, rigid particles in a shear flow will not migrate across streamlines if the fluid is Newtonian. In viscoelastic fluids, however, particles will migrate across streamlines away from areas of higher elastic stresses, e.g. towards the outer cylinder in a wide-gap Couette flow. This migration is believed to be due to a difference in normal stresses. We simulate the two-phase case where this difference in normal stresses is not due to the flow field, but rather due to the properties of the fluids. We apply the diffuse-interface model for the interface between the two fluids, which can naturally handle a changing topology of the interface, e.g. during particle adsorption. Furthermore, the diffuse-interface model includes an accurate description of surface tension and can be used for a moving contact line. A sharp interface is assumed between the particles and the fluids. Initially, a particle is placed close to an interface of two fluids with different viscoelastic properties in a shear flow. We show that based on the properties of the fluids and the interfacial tension, four regimes can be defined: 1) migration away from the interface, 2) halted migration towards the interface, 3) adsorption of the particle at the interface and 4) penetration of the particle into the other fluid.

This research forms part of the research programme of the Dutch Polymer Institute (DPI), Project #746.

Monday 5:40 Frederick/Columbia

NF15

**Non-equilibrium depletion interactions: First particles attract, then they repel**Benjamin E. Dolata and Roseanna N. Zia*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

Non-Equilibrium depletion interactions in colloidal dispersions are studied theoretically via a combination of asymptotic and numerical solutions of the Smoluchowski equation. A pair of probes at arbitrary separation is driven by an external force at arbitrary orientation through a suspension, deforming the surrounding microstructure. The degree to which the structure is distorted, and the shape of this deformation, depends on the separation between the probes, on the orientation of the pair to the driving force, and on the strength with which the probes are forced relative to the entropic restoring force of the suspension particles, defined by the Peclet number,  $Pe = U(a+b)/D$ , where  $U$  is the probes' velocity,  $a$  is the probe size,  $D$  is the diffusivity of the background particles of size  $b$ . The resultant non-equilibrium osmotic pressure gradients give rise to both drag and interactive forces between the probes. When the external force is zero, the depletion attraction of Asakura and Oosawa is recovered. When an external force is applied, the interactive force can lead either to attraction or repulsion, as well as deterministic re-orientation of the probes relative to the external force, depending on initial separation, orientation, and strength of forcing. The use of this model for interrogation of non-continuum and elastically networked materials is explored.



## Tuesday Morning

### Symposium PL Plenary Lectures

#### *Bingham Lecture*

Tuesday 8:30 Constellation D-F

PL2

#### **Slow dynamics of components in miscible polymer blends**

Hiroshi Watanabe

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Blends of chemically different but miscible polymers exhibit very rich dynamic features. For example, the component concentration distribution in those blends is heterogeneous in a segmental (local) length scale because of the self-concentration effect. Consequently, the segmental relaxation times of the components have different temperature dependence, which results in the thermo-rheological complexity of the segmental relaxation of the blend as a whole. Even more striking features can be noted for slow relaxation occurring in larger length scales, in particular when the components have a large asymmetry. This talk focuses on such slow component dynamics in miscible blends of cis-polyisoprene (PI) and poly(*p*-tert-butyl styrene) (PtBS), the former having the type-A dipole and exhibiting slow dielectric relaxation that reflects the end-to-end fluctuation. Linear viscoelastic data showed that the entanglement length in high-M PI/PtBS blends, determined at high temperatures (*T*), obeys a blending rule weighed with the number fractions of Kuhn segments of respective components, rather than with the component volume fractions. At low *T*, the Rouse equilibration of the fast component (PI) over this length was retarded by the slow component (PtBS), as noted from comparison of viscoelastic and dielectric data. This retarded Rouse equilibration at low *T* masked the high-frequency entanglement plateau sustained by both PI and PtBS, so that the slow relaxation in the linear regime was thermorheologically complex not only for the blends as a whole but also for respective components. These experimental findings will be discussed in relation to the asymmetry of the components (PI and PtBS), and a brief discussion will be presented also for the nonlinear relaxation of the PI/PtBS blends under large step strains.

### Symposium SC Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Tuesday 10:00 Constellation C

SC16

#### **Shear stress induced microstructure in concentrated silica dispersions**

Jonghun Lee, Xiao-Min Lin, Alec R. Sandy, and Suresh Narayanan

*Argonne National Laboratory, Lemont, IL 60439, United States*

Concentrated colloidal dispersions show non-equilibrium phase behavior when shear is applied. The particles are hexagonally ordered in layers, and these layers stack in the velocity-vorticity plane. Under a small amplitude strain, these layers oscillate due to shear gradients, and scattering pattern corresponds to a twinned FCC lattice. With increasing strain amplitude, the layers slide past each other, exhibiting six-fold scattering pattern. Such ordered structures are often accompanied with abrupt shear thinning. At very high strain amplitude, the ordered structures break down by shear thickening. These structures have been studied by light, neutron and x-ray scattering, confocal microscopy, and simulations, but the link between rheology and microstructure is still unclear. Here, we studied the microstructure of concentrated silica dispersions under shear with varying sizes and volume fractions using in situ small angle x-ray scattering. We found that the microstructural changes are closely related to the changes in  $G'$  versus  $\tau/G'_0$ . Twinned FCC scattering pattern appears with slight increase in  $G'$  (strain overshooting), and six-fold scattering pattern appears with a large degree decrease in  $G'$ . More importantly, independent of volume fraction and the oscillation frequency, the changes in  $G'$  and the associated microstructural changes appear at the same  $\tau/G'_0$ . Our study concludes that shear stress versus equilibrium loss modulus is a characteristic measure to explain the microstructure, and that the microstructural changes induce the dissipation energy change.

Tuesday 10:25 Constellation C

SC17

#### **Timescales of microstructure relaxation in sheared colloidal hard sphere suspensions**

Rick Dannert, Roland Sanctuary, and Jörg Baller

*Physics and Materials Science Research Unit, University of Luxembourg, Luxembourg, Luxembourg*

We have investigated the influence of quasi-spherical silica nanoparticles (average radius  $a=12.5$  nm) on the linear viscoelastic behavior of the glass-former Diglycidyl Ether of Bisphenol A. Interestingly a low-frequency process emerged additionally to the  $\alpha$ -process of the matrix in the sheared suspensions. We interpreted the low frequency process as the relaxation of the strain-induced perturbations of the isotropic filler distribution [1]. We have shown that the timescales of the microstructure relaxation depends in a complex manner on the volume concentration:

for dilute systems, the relaxation frequency increases with the concentration, whereas for concentrated systems the opposite behavior can be observed. This non-monotonic concentration dependency of the relaxation frequency can no longer be modelled by the commonly used Peclet frequencies  $\omega_p = D/a^2$ , since the Peclet frequencies depend only on the suspension viscosity. Rearrangement of the microstructure requires interactions between filler particles. Therefore at low filler concentrations the particle radius is no longer an appropriate length scale. To address this problem we have introduced a modified Peclet frequency by replacing the filler radius by the mean particle distance  $\langle r \rangle$ . The competition between the increasing viscosity and decreasing interparticle distance with growing filler content leads to the observed concentration dependency of the relaxation frequency [1]. To check the limits of the validity of the modified Peclet frequency we have investigated the microstructure relaxation on altered colloidal suspensions obtained by changing the viscosity of the matrix or by filling the original matrix by fractal alumina nanoparticles. As we will show even for these suspensions the non-monotonic concentration dependency of the relaxation frequency appears and is well described by the modified Peclet time.

[1] R. Dannert, R. Sanctuary, J. Baller; *Journal of Rheology*, 59(2) (2015) 391-404.

Tuesday 10:50 Constellation C

SC18

### **Rheology and microstructure of soft to rigid shear-thickening colloidal suspensions**

Safa Jamali<sup>1</sup>, Arman Boromand<sup>1</sup>, Norman J. Wagner<sup>2</sup>, and Joao Maia<sup>1</sup>

<sup>1</sup>*Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States;* <sup>2</sup>*University of Delaware, Newark, DE 19716, United States*

For decades shear-thickening of a suspension has been thought to be due to the lubrication forces between colloidal particles that give rise to formation of hydroclusters. However, computational efforts based on lubrication theory have not been able to explain discontinuous shear-thickening (DST) in suspensions. Recently, some reports have incorporated frictional contacts and their dissipative role in colloidal interactions and have successfully reproduced higher viscosity ratios including DST at high shear rates in the shear-thickening regime. Nevertheless, as one would expect, the predominance of tangential frictional forces in this regime gives rise to positive N1 measurements, which is in contradiction with recent experimental developments. In this work, we study the effect of contact forces (both frictional and normal) and lubrication potential in rheological behavior of the colloidal suspensions. To do so, we have modified DPD method in order to include the lubrication potentials. Furthermore, different types of contact potentials have been included in our DPD potentials in order to understand the physical nature of contact forces and their effect on the rheology of suspensions. A complete rheological picture is drawn regarding the rate-dependent properties of soft to rigid colloidal suspensions using computational models. We show that a contact force defined based on an elasto-hydrodynamic deformation theory captures the main rheological signatures of colloidal suspensions: while near hard-sphere particles exhibit a strong and continuous shear-thickening at high Péclet numbers, soft suspensions undergo a second shear-thinning regime in qualitative agreement with scaling laws (Mewis & Wagner 2012). This regime occurs when the lubrication stresses become comparable to the elasticity of the colloidal particles. We measure N1 and N2 to be large and negative in the shear-thickening regime; however, in the second shear-thinning regime N2 reduces in magnitude and eventually becomes positive.

Tuesday 11:15 Constellation C

SC19

### **Nanoparticle-induced gelation in bimodal slurries of highly size asymmetric particles**

Jooyoung Lee<sup>1</sup>, Seong Jae Lee<sup>2</sup>, Kyung Hyun Ahn<sup>1</sup>, and Seung Jong Lee<sup>1</sup>

<sup>1</sup>*School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea;* <sup>2</sup>*Department of Polymer Engineering, The University of Suwon, Gyeonggi, Republic of Korea*

Coating fluids that include highly size asymmetric particles are widely used in many applications such as Li-ion batteries, multi-layer ceramic capacitors, and electrical conductors. They include different types of particles to improve the performance of the product. In these liquids, the size of the particles is very different; one is micron and the other nano-meter scale, for example. Because of distinctively different size of the particles, these bi-modal dispersions show more complex flow behavior compared to colloids of a single size. However, most studies for bi-modal dispersions assumed well-stabilized nanoparticles, thus they have not been relevant to the behavior of the materials used in industry. In this study, we design a model system consisting of two kinds of particles with highly asymmetric size to offer a valuable description of complex behavior of the slurries. Their surface potentials were tuned by varying the solution pH, setting up large particles (PS latex, 500nm) to be electrostatically stabilized and small particles (alumina coated silica, 12nm) to be attractive to each other. We show highly charged microspheres are subsequently aggregated by the addition of very small amount of nanoparticles, altering the rheological behavior from viscous to gel-like. The bimodal gels are not described by the typical power law scaling for fractal clusters. Their elastic moduli have a unique scaling behavior on particle volume fraction with two distinct power-law indices. We show that the unique scaling behavior is due to the bridging clusters, formed by minute amount of small particles in the region between the lower and the upper critical boundary of small particle volume fraction.

Tuesday 11:40 Constellation C

SC20

### **Thixotropy and viscosity bifurcation in fluid fine tailings**

Babak Derakhshandeh

*Fluid Dynamics Division, Coanda Research and Development Corporation, Vancouver, British Columbia V3N 4A3, Canada*

One of the most pressing environmental issues that the Canadian Oil Sands Industry is currently facing is the growing quantity of fluid fine tailings (FFT) which are stockpiled in large open ponds in northern Alberta. FFT is a colloidal suspension composed of a mixture of various clay particles, sand, bitumen, silt, and some processing aids in water. These suspensions experience various shear fields in the processing plants, from nearly

quiescent conditions in the ponds to relatively high shear rates in pipes, pumps, and mixers. Therefore, knowledge of FFT rheological behaviour is of great importance to the design of new facilities and the remediation of the existing ponds. In this work, the rheology of FFT suspensions are studied systematically using conventional rheometry in rotational and oscillatory modes. FFT suspensions are found to be thixotropic fluids with rheological properties that depend on the shear history and age of the samples. The structure buildup and break down at rest and under flow are studied in detail and models are proposed to predict the transient flow behaviour of the suspensions. Additionally, a Pulsed Ultrasonic Doppler Velocimeter (PUDV) is coupled with a conventional rheometer to measure the steady-state velocity profiles of the suspensions at various shearing conditions. The velocity profiles are found to exhibit a discontinuity in transition from yielded to un-yielded regions of the wide gap rheometer implying shear-banding instability in the flow. These observations are also confirmed by creep experiments under stress-controlled experiments.

## Symposium SM Polymer Solutions and Melts

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Tuesday 10:00 Constellation D

SM16

### **Exact analytical solution for large-amplitude oscillatory shear flow**

Chaimongkol Saengow<sup>1</sup>, Alan J. Giacomin<sup>2</sup>, and Chanyut Kolutawong<sup>1</sup>

<sup>1</sup>Mechanical Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; <sup>2</sup>Chemical Engineering, Queen's University, Kingston, ON K7L 3N6, Canada

When polymeric liquids undergo large-amplitude shearing oscillations, the shear stress responds as a Fourier series, the higher harmonics of which are caused by fluid nonlinearity. Previous work on large-amplitude oscillatory shear flow has produced analytical solutions for the first few harmonics of a Fourier series for the shear stress response (none beyond the fifth) or for the normal stress difference responses (none beyond the fourth) [JNNFM, 166, 1081 (2011)], but this growing subdiscipline of macromolecular physics has yet to produce an exact solution. Here, we derive what we believe to be the first exact analytical solution for the response of the extra stress tensor in large-amplitude oscillatory shear flow. Our solution, unique and in closed form, includes both the normal stress differences and the shear stress for both startup and alternance. We solve the corotational Maxwell model as a pair of nonlinear coupled ordinary differential equations, simultaneously. We choose the corotational Maxwell model because this two-parameter model is the simplest constitutive model relevant to large-amplitude oscillatory shear flow, and because it has previously been found to be accurate for molten plastics (when multiple relaxation times are used). By relevant we mean that the model predicts higher harmonics. We find good agreement between the first few harmonics of our exact solution, and of our previous approximate expressions (obtained using the Goddard integral transform). Our exact solution agrees closely with the measured behavior for molten plastics, not only at alternance, but also in startup.

Tuesday 10:25 Constellation D

SM17

### **Fingerprinting the non-linear response of a polystyrene solution: Comparison of strain controlled and stress controlled mechanical spectral hole burning**

Zhiyuan Qian and Gregory B. McKenna

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

It is well known that large amplitude oscillatory shear (LAOS) has become a powerful tool to fingerprint the nonlinear response of polymers and other complex fluids. In a recent work, Shamim and McKenna [J. Rheol. 58(1), 43-62, 2014] used the strain controlled mechanical spectral hole burning (MSHB) which was developed in our labs, to expand the fingerprinting Lissajous-Bowditch (LB) loop and Fourier transform rheology (FTR) method to characterize the nonlinearity of linear polystyrene solution. They observed a linear relationship between the horizontal hole intensity and the square of pump strain amplitude. A similar quadratic dependence was found for the third harmonics from FTR. However, the origins are not same for these two signatures. In the current work, we address the hole burning spectroscopy by using stress controlled MSHB and the compare the results with the strain controlled method. In addition, a comparison will be made among the methods in order to build more complete fingerprint of the non-linear response.

The authors are thankful to the American Chemical Society, Petroleum Research Fund 53205-ND7, for the support of this project.

Tuesday 10:50 Constellation D

SM18

### **A library of rheological fingerprints for medium amplitude oscillatory shear: Models and experiments**

N Ashwin K. Bharadwaj and Randy H. Ewoldt

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

Rheologists have expectations for signatures of linear viscoelastic properties, such as shapes of  $G'(\omega)$  and  $G''(\omega)$ , and use these signatures to compare model predictions to experimental measurements. Here, we develop a library of expectations for the four asymptotically-nonlinear material functions associated with medium amplitude (or asymptotically-nonlinear) oscillatory shear,  $[e_1](\omega)$ ,  $[e_3](\omega)$ ,  $[v_1](\omega)$ ,  $[v_3](\omega)$ , defined in [Ewoldt and Bharadwaj, Rheol. Acta 52, 201-209 (2013)]. Beyond linear viscoelasticity, these nonlinear fingerprints differentiate constitutive models and when compared to experimental measurements, can potentially allow inverse problems to infer structure, select constitutive models, and calibrate model parameters. We consider seven different constitutive models with analytical solutions for these material functions (corotational Maxwell, Giesekus, Time-strain separable memory integral, Rigid rod-like polymer solutions, Curtiss-Bird, Dilute emulsions, and Fourth Order

fluid). We identify general trends and highlight key differences within this library of constitutive model fingerprints. We then demonstrate a fingerprint matching exercise with experimental measurements on two material systems: a polymer melt (which allows fitting by multiple models) and a transiently cross-linked hydrogel system (which matches none of the analytical fingerprints and requires new models to be developed). Experimental challenges will also be discussed, including (i) an exact correction for measurements with a parallel disk geometry, and (ii) propagation of uncertainty in making these measurements.

Tuesday 11:15 Constellation D

SM19

### **Complex polymer orientation in LAOS**

Peter H. Gilbert and Alan J. Giacomin

*Chemical Engineering, Queen's University, Kingston, ON K7L 3N6, Canada*

In our previous work, we explored the dynamics of a dilute suspension of rigid dumbbells as a model for polymeric liquids in large-amplitude oscillatory shear (LAOS) flow. We derived the expression for the dumbbell orientation distribution, and then we decomposed this function into its first five harmonics (the zeroth, first, second, third and fourth harmonics). In this work, we separate each harmonic into its components in and out of phase with and use three-dimensional images to investigate complex polymer motion undergoing LAOS. Our analysis focuses on the nonlinear viscoelastic regime, where both and exceed unity. We learn that harmonic components in and out of phase with contribute orientation differently, and that out-of-phase components tend to give more probable orientation away from the flow direction. We find that the total orientation distribution is peanut-shaped for non-linear viscoelasticity. The peanut-shaping is caused by the zeroth harmonic and the tilting of the shape is a result of the second harmonic.

Tuesday 11:40 Constellation D

SM20

### **Design intuition and user experience: Stress-input rheology with viscoelastic polymer systems**

R E. Corman, Jill Godman, and Randy H. Ewoldt

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

The complex, function-valued properties of rheologically-complex materials present a challenge for both design intuition and design for user experience (e.g. tactile perception). Here, we introduce a stress-amplitude Pipkin Space to connect perception to rheology. The stress-controlled paradigm can (i) correlate with human tactile perception of material properties, (ii) simplify the presentation of rheological complexity, and (iii) guide experimental characterization to be within stress amplitudes and timescales relevant to user experience. Two case studies in room temperature viscoelastic polymer systems are used. First, we study a series of polymer melts known as physical therapy putties, designed for a range of user experience for strengthening hand muscles (extra-soft, soft, medium, medium-firm, firm, extra-firm). These are commercially available, intended for user experience, and easily accessible for developing tactile intuition with viscoelasticity. Second, we consider transiently cross-linked polymer solutions (PVA-Borax: polyvinyl alcohol cross linked with sodium tetraborate). This system is more controlled and readily made in the lab for the interested tactile-investigator. One of these materials (therapy putties) shows a range of both time scales and viscous resistance while the other (PVA-Borax) shows an approximately constant relaxation timescale. Although all linear viscoelastic material functions are inter-related and inter-changeable, we show that a judicious choice can reduce the complexity of the description. Here, stress-input descriptions (namely dynamic compliance and fluidity) achieve a simpler description than dynamic moduli, making connections to intuition and perception more direct. This understanding of the "psycho-rheology" of the materials leads to improved tactile intuition for both understanding and designing viscoelasticity.

## **Symposium SA**

### **Self-assembled Systems and Gels**

Organizers: Surita Bhatia and Kelly Schultz

Tuesday 10:00 Constellation E

SA1

### **Dynamic transitions of colloidal gels measured using multiple particle tracking microrheology**

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

<sup>1</sup>*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States;* <sup>2</sup>*Product Supply, Procter & Gamble, West Chester, OH 45069, United States*

Rheological diversity of colloidal gels makes them ideal for an array of applications ranging from biomaterials to personal care products. The structure and function of these materials is greatly influenced by environmental conditions. Understanding the gel-sol transition and the conditions that lead to this critical transition will aid in the design of stable products. Multiple particle tracking microrheology (MPT) is used to determine the properties and structure of a hydrogenated castor oil (HCO) colloidal gel in water-surfactant environments. MPT extracts rheological properties from measurements of the Brownian motion of embedded probe particles using the Generalized Stokes-Einstein Relation. HCO rod-like particles are formed through crystallization and dehydrated with 20 wt% water, a composition similar to those used in home care products. The osmotic gradient between the solution and gel drives material expansion and contraction. Probe particle movement is tracked during these dynamic transitions of the colloidal gel over six hours in a series of surfactant solutions with varying water content (0-100% water). Complete expansion of the material outside of the measurement apparatus occurs over six hours, while contraction occurs in one hour. Heterogeneity of the material microstructure during expansion and contraction is quantified by comparing particle trajectories using an F-test with a 95% confidence interval to

quantify if particles are probing the same microenvironment. During expansion, the colloidal gel contains heterogeneous microenvironments that are homogeneously distributed throughout the field of view. MPT also characterizes particle cage jumping. Cage jumping occurs when the colloidal gel structure is heterogeneous with microscopic islands of gel and sol. A particle can become stuck within the colloidal gel structure and is able to "jump" between two islands of gel. The frequency of cage jumping in this colloidal gel is linearly related to the bulk viscosity in both expansion and contraction.

Tuesday 10:25 Constellation E

SA2

### **Avalanche-like fluidization of a colloidal gel**

Aika Kurokawa<sup>1</sup>, Valérie Vidal<sup>2</sup>, Kei Kurita<sup>1</sup>, Thibaut Divoux<sup>3</sup>, and Sébastien Manneville<sup>2</sup>

<sup>1</sup>*Earthquake Research Institute, The University of Tokyo, Tokyo, Japan;* <sup>2</sup>*Laboratoire de Physique, ENS Lyon, Lyon 69364, France;* <sup>3</sup>*Centre de Recherche Paul Pascal - CNRS, Pessac 33600, France*

We report on the transient dynamics of a colloidal gel that displays strong physical aging. Extensive rheology coupled to ultrasonic velocimetry allows us to characterize the global stress response together with the local dynamics of the gel during shear startup experiments. In practice, after being rejuvenated by a preshear, the gel is left to age during a given time before being submitted to a constant shear rate. We investigate in detail the effects of both aging time and shear rate on the fluidization dynamics and build a complete phase diagram of the gel behavior. At large enough shear rates, the gel is fully fluidized and flows homogeneously independently of its age. Under lower shear rates, the strong interplay between aging and shear rejuvenation leads, together with wall slip, to a more complex phenomenology. The gel may either display transient shear banding towards complete fluidization, or steady-state shear banding. In the former case, we unravel that the progressive fluidization occurs by successive steps that appear as peaks on the global stress relaxation signal. Flow imaging reveals that the shear band grows up to complete fluidization of the material by sudden avalanche-like events that are correlated to large peaks in the slip velocity at the moving wall. In the case of steady-state shear banding, we recover the classical scenario involving a critical shear rate below which no homogeneous steady flow is possible. We show here that the critical shear rate displays a non-monotonic behavior with the aging time. Our work paves the way for a thorough description of transient flows of weak attractive gels, and highlights the subtle interplay between shear, wall slip and aging that constitutes a major challenge in terms of modeling that has yet not been met.

Tuesday 10:50 Constellation E

SA3

### **Aging promoted work-hardening of a colloidal gel**

Davide Calzolari<sup>1</sup>, Irmgard Bischofberger<sup>2</sup>, and Veronique Trappe<sup>1</sup>

<sup>1</sup>*Department of Physics, University of Fribourg, Fribourg 1700, Switzerland;* <sup>2</sup>*Department of Physics, University of Chicago, Chicago, IL, United States*

We investigate the mechanical properties of a colloidal gel formed by particles with attractive interactions that are conveniently tuned by temperature. Quenching a suspension with a particle volume fraction of 18% from a temperature of 15°C to 27°C leads to the formation of a colloidal gel, that exhibits considerable aging evidenced by a continuous increase of both the relaxation time and the high frequency modulus with the samples age. Applying a constant stress over a limited time lapse leads to a further increase of the elastic modulus, while the relaxation time remains unchanged. This shows that the temporal application of stress does not lead to an over-aging of the gel, but rather to simple work hardening. Surprisingly, however, we find that the magnitude of work-hardening obtained during creep directly relates to the aging relaxation time and the age dependent modulus.

Tuesday 11:15 Constellation E

SA4

### **On the relaxation and dynamics of colloidal gel**

Mehdi Bouzid, Jader Colombo, and Emanuela Del Gado

*Department of Physics, Georgetown University, Washington, DC, United States*

Colloidal gels belong to the class of amorphous systems, they are disordered elastic solids that can form at very low volume fraction, via aggregation into a rich variety of networks. They exhibit a slow relaxation process in the aging regime similar to the glassy dynamics [1]. A wide range of experiments on colloidal gels show unusual compressed exponential of the relaxation dynamical properties [1, 2, 3].

We use molecular dynamics simulation to investigate how the dynamic change with the age of the system. Due to the breaking and the reorganization of the network structure [4, 5], the system displays stretched or compressed exponential relaxation. We show that the transition between these two regimes is associated with the interplay between the thermal fluctuations and the elastic relaxation [6]. The ballistic behavior emerges from the non-local relaxation of internal stresses mediated by a series of "micro-collapses" [7]. When the thermal effects dominate, the gel restructuring involves instead short range displacements, leading to a stretched exponential type of relaxation.

[1] L. Cipelletti and L. Ramos, *J. Phys. Condens. Matter.* 17, R253 (2005). [2] L. Cipelletti, S. Manley, R. C. Ball and D. A. Weitz, *Phys. Rev. Lett.* 84, 10 (2000). [3] H. Guo, S. Ramakrishnan, J. L. Harden, and R. L. Leheny, *J. Chem. Phys.* 135, 154903 (2011). [4] J. Colombo, A. Widmer-Cooper and E. Del Gado, *Phys. Rev. Lett.* 110, 198301 (2013). [5] J. Colombo and E. Del Gado, *J. Rheol.* 58, 1089 (2014). [6] J. Colombo and E. Del Gado, *J. Rheol.* 58, 1089 (2014). [7] E. E. Ferrero, K. Martens and J-L. Barrat, *Phys. Rev. Lett.* 113, 248301 (2014). [8] J.-P. Bouchaud and E. Pitard, *Eur. Phys. J. E.* 6, 231 (2001).

Tuesday 11:40 Constellation E

SA5

**Tuning structure in short-range attractive colloidal gels via the flow history**Arman Boromand, Safa Jamali, and Joao Maia*Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

In colloidal gel systems, the presence of multiple interactions over multiple length scales such as Van der Waals, depletion attractions, and electrostatic repulsions makes these systems challenging from both experimental and simulation aspects. Recently there has been growing interest to tune and manipulate structural and dynamics properties of those systems without adjusting interparticle interactions and just by taking them out of equilibrium. In this work we used Core-modified dissipative particle dynamics (CM-DPD) with modified depletion potential, as a coarse-grain model, to address the gel formation process in short ranged-attractive colloidal suspensions for a range of volume fraction and attraction strength. It is suggested that at high volume fractions near glass transition there is a transformation from non-bonded glass to bonded-glass for which the effect of topological frustration (caging) will be alleviated by presence of attractive potentials (bonding) i.e. melting upon cooling. In the first part of the presentation, we discuss our similar findings for attractive bimodal colloidal gels at equilibrium for semi-dilute regime, which can be explained through local densification of attractive colloidal gels. In the second part, structural and dynamics properties of arrested gels will be studied under shear and after cessation of shear to study how the different flow profiles and history will alter final morphology of the gel systems. Using CM\_DPD enable us to consider the effect of multi-body hydrodynamic interactions that are missing in other common simulation techniques such Brownian Dynamics.

**Symposium BM****Biological Macromolecules: Proteins, Cellulosic Biomass and other Biomaterials**

Organizers: Jai A. Pathak and Patrick Underhill

Tuesday 10:00 Constellation F

BM16

**Macroscopic rheology of human blood: Effects of cholesterol and triglycerides**Alex J. Apostolidis and Antony N. Beris*Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States*

Blood is a concentrated suspension of deformable red blood cells in plasma with proteins, white blood cells, platelets, various metabolites, etc. As a result, blood's flow behavior is Non-Newtonian characterized by yield stress and thixotropy. The non-Newtonian blood rheology has been recently studied for steady [1] and transient [2] shear flows, respectively. Most importantly, parametric relationships have been established that connect the yield stress and model viscosity appearing in the Casson model to important physiological parameters such as the hematocrit and the fibrinogen concentration [1]. However, those parametric relations were developed for healthy blood and therefore are restricted to physiological conditions.

We examine here the effect of cholesterol and triglycerides to the steady state shear flow properties of human blood. We use viscosity data of both high and low cholesterol donors, well characterized both with respect to cholesterol (total, LDL and HDL) and triglycerides, as well as hematocrit and fibrinogen [3]. We show that while the Casson model continues to describe well the blood viscosity, the model parameters need to be significantly modified from their physiological values, parametrized with indices formed from the supplied cholesterol and triglycerides information.

Acknowledgement: This material is based upon work supported by the National Science Foundation (USA) under Grant No. CBET 1033296.

References: [1] Apostolidis, A.J., Beris, A.N, "Modeling of the blood rheology in steady-state shear flows." *J. Rheol.*, 58(3), 607-633 (2014). [2] Apostolidis, A.J., Armstrong, M.J., Beris, A.N, "Modeling of the human blood rheology in transient shear flows." *J. Rheol.*, 59(1), 275-298 (2015). [3] Moreno L. et al., "Effect of cholesterol and triglycerides levels on the rheological behavior of human blood." *Korea-Australia Rheology Journal*, 27(1),1-10 (2015).

Tuesday 10:25 Constellation F

BM17

**The rheology of nanoparticles in blood for improved cancer therapy**Erik Carboni<sup>1</sup>, Yang Guo<sup>2</sup>, Grant Bouchillon<sup>3</sup>, Andrea Kadilak<sup>1</sup>, Leslie Shor<sup>1</sup>, and Anson Ma<sup>2</sup>*<sup>1</sup>Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States; <sup>2</sup>Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States; <sup>3</sup>Department of Civil and Environmental Engineering, University of Connecticut, Storrs, CT 06269, United States*

There has been a growing interest in using nanoparticles as drug carriers, especially for cancer treatment (1). However, little is known about the rheology of nanoparticles in blood flow, which must be understood if the nanoparticles are to be administered intravenously. Decuzzi *et al.* and Kumar and Graham (2, 3) showed in their modeling that nanoparticles can undergo a "margination" phenomenon wherein the nanoparticles trend toward the periphery of blood vessels. The implication is a higher chance for the nanoparticles to diffuse into the tumor through the leaky vasculature typically found near tumor sites. Experimentally, most existing studies use particle adhesion to channel walls during flow as a mechanism for quantifying the margination propensity of particles but adhesion is also affected by other factors, further complicating the interpretations of experimental results (4). In this presentation, we will disclose our findings on directly tracking the motion and distribution of

nanoparticles within microfluidic devices that mimic blood vessels. In order to unravel the fundamentals of margination, particles of different sizes have been studied in both water and bovine blood.

References: [1] Davis, ME. Fighting cancer with nanoparticle medicines - The nanoscale matters. *MRS Bulletin*. 2012;37:828-835. [2] Decuzzi P, Lee S, Bushan B, Ferrari M. A theoretical model for the margination of particles within blood vessels. *Annals Biomed. Eng.* 2005;33(2):179-190. [3] Kumar A, Graham MD. Margination and segregation in confined flows of blood and other multicomponent suspensions. *Soft Matter*. 2012;8(41):10536-48. [4] Carboni E, Tschudi K, Nam J, Liu X, Ma A. Particle margination and its implications on intravenous anticancer drug delivery. *AAPS PharmSciTech*. 2014;15(3):762-71.

Tuesday 10:50 Constellation F

BM18

### **Rheological properties of electrosterically stabilized nanocrystals of cellulose in the semi-dilute regime**

Gilles Lenfant<sup>1</sup>, Marie-Claude Heuzey<sup>1</sup>, Theo G. M. van de Ven<sup>2</sup>, and Pierre J. Carreau<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Polytechnique Montreal, Montreal, Quebec H3T 1J4, Canada;* <sup>2</sup>*Pulp and Paper Research Centre, McGill University, Montreal, Quebec H3A 2A7, Canada*

Electrosterically stabilized nanocrystals of cellulose (ENCCs) are a new kind of colloidal particles resulting from a two steps oxidation process applied to bleached woodpulp. ENCCs are nanocrystals with cellulosic amorphous chains protruded at each endcaps bearing carboxylic groups at the C2 and C3 position. In this work, the semi-dilute regime of ENCC aqueous suspensions has been investigated as a step forward to our previous work in the dilute regime based on viscometric flow [1]. ENCCs suspensions are studied in the range of 0.3 wt% to 7 wt% (taking  $L/d = 15$ ) in order to fully cover the semi-dilute regime. All suspensions are tested at pH 7 and 2.5 in order to quantify the effect of charges on the rheological properties of the suspensions. At a pH of 2.5 the rigid rod-like state was reached while at pH 7 the amorphous chains protruded at each endcaps of ENCCs affected their interactions due to the presence of deprotonated carboxylic acid groups. Up to 3 wt% the suspensions still had a water-like behavior while at 7 wt% a weak gel was formed. Decreasing the pH protonated the carboxylic groups and made the amorphous chains collapse decreasing the relative viscosity of the suspensions. Steady shear viscosity and storage and loss moduli were examined as functions of both volume fraction and pH to characterize the structure due to ENCC interactions and orientation under flow.

[1] Lenfant G, Heuzey MC, van de Ven TGM, Carreau PJ (2015) Intrinsic viscosity of suspensions of electrosterically stabilized nanocrystals of cellulose *Cellulose* doi:10.1007/s10570-015-0573-7.

Tuesday 11:15 Constellation F

BM19

### **Shear-induced crystallization of poly (L-lactic acid)**

Amirjalal Jalali

*Chemical Engineering, University of Sherbrooke, Sherbrooke, Quebec, Canada*

Effect of shear flow on the crystallization of Poly (L- Lactic acid), PLLA, with different molecular weights, (MW) was carried out by the startup shear flow tests. Accordingly, PLLA samples were subjected to a specific experimental procedure consisting of heating samples to 190 ° C to erase thermal history and, subsequently, rapidly cooled down to desired isothermal temperatures and finally subjected to shear flow with varying shear rates. Effects of shear rate, strain as well as the temperature on the shear-induced crystallization of PLLA were examined. Although the low-MW sample demonstrated the highest rate of crystallization in quiescent conditions, a remarkable effect of MW on the shear-induced crystallization of PLLA with increasing MW was observed. An attempt was also made to study the effect of shear flow on the crystalline phases of PLLA. For this, different molecular weight 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,  $t$ . Thermal behavior and the microstructures of the pre-sheared samples were studied by Differential Scanning Calorimetry, DSC, and Wide-angle X-ray Diffraction, WAXD, respectively.

Tuesday 11:40 Constellation F

BM20

### **Viscoelastic properties of cartilage polymers**

Wan-Kyu Oh<sup>1</sup>, Srinivasa Raghavan<sup>2</sup>, Peter J. Basser<sup>1</sup>, and Ferenc Horkay<sup>1</sup>

<sup>1</sup>*Section on Tissue Biophysics and Biomimetics, PPITS, NICHD, National Institutes of Health, Bethesda, MD 20892, United States;* <sup>2</sup>*Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States*

Aggrecan is a proteoglycan, which is a critical component of cartilage extracellular matrix (ECM). Its molecular mass is large (1000 kDa <  $M < 3000$  kDa). Aggrecan exhibits a bottlebrush configuration. It contains glycosaminoglycans (mainly chondroitinsulfate (CS) and keratansulfate chains) attached to a core protein. Aggrecan forms complexes with hyaluronic acid (HA) that provide the osmotic properties necessary for tissue function. Aggrecan/HA complexes are enmeshed in a collagen network. The high charge density of the aggrecan bottlebrush induces a large osmotic pressure, which leads to tissue swelling. Understanding the biomechanical properties of aggrecan and aggrecan/HA complexes are essential for modeling cartilage ECM. The aim of our work is to determine the viscoelastic properties of solutions of CS, HA, aggrecan and aggrecan-HA complex. CS, HA and aggrecan show concentration-dependent modulus increment and viscosity increase. In the presence of calcium and sodium ions, both the moduli ( $G'$  and  $G''$ ) of the solutions and the corresponding viscosities decrease. The solution of aggrecan/HA complexes exhibits gel-like behavior as indicated by the increase of  $G'$ . The results also show that complex formation only weakly affects  $G''$ . The rheological findings will be related to the supramolecular structure and biological function of cartilage ECM.

## Symposium SG Solids, Glasses, and Composites

Organizers: Lynden Archer and Anne Grillet

Tuesday 10:00 Baltimore/Annapolis

SG16

### **The role of polymer composite binder on mechanics and performance of lithium ion battery electrodes**

Thomas Humplik<sup>1</sup>, Anne M. Grillet<sup>1</sup>, David A. Barringer<sup>1</sup>, Emily K. Stirrup<sup>1</sup>, Kevin N. Long<sup>1</sup>, Hector Mendoza<sup>1</sup>, Scott A. Roberts<sup>1</sup>, Chelsea Snyder<sup>2</sup>, Christopher A. Apblett<sup>3</sup>, and Kyle R. Fenton<sup>3</sup>

<sup>1</sup>*Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185, United States;* <sup>2</sup>*Rensselaer Polytechnic Institute, Troy, NY, United States;* <sup>3</sup>*Power Sources Technology Group, Sandia National Laboratories, Albuquerque, NM, United States*

Battery electrodes are complex multiphase composites which must provide efficient bicontinuous networks for transport of electrons (through the particle phase) and positive lithium ions (through the electrolyte filled pores of the electrode). A crucial but often neglected element of battery electrodes is the binder, typically a mixture of polyvinylidene fluoride (PVDF) and carbon black. The binder has two primary roles - to provide mechanical integrity and to improve electrical conduction of the electrodes. Migration of the binder has also been implicated as a potential mechanism of capacity fade in rechargeable lithium ion batteries.

We will present experimental characterization of the polymer binder for battery applications. Mechanical properties of the composite binder will be shown for both dry films and also binder swollen with carbonate electrolytes used in rechargeable batteries. Additionally we will examine the impact of mechanical stresses on the retention electrolyte and also the electrical conductivity.

Mesoscale simulations will be presented using experimentally determined three dimensional structures of battery cathodes. As batteries charge and discharge, the particles within the electrodes expand and contract as lithium is transferred into and out of the active material. The role of complex particle geometry and polymer binder properties on peak mechanical stresses due to particle swelling during cycling will be examined. Implications for battery performance and cycling stability will be discussed.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Tuesday 10:25 Baltimore/Annapolis

SG17

### **A comprehensive constitutive framework for describing the non-isothermal rheology of waxy crude oil**

Michela Geri and Gareth H. McKinley

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

Waxy crude oils are known to exhibit many complex rheological features whenever their temperature falls below a critical threshold known as the Wax Appearance Temperature (WAT). This temperature characterizes the onset of a phase transition that involves nucleation and growth of wax crystals within the oil. The new solid phase percolates to form a sample-spanning network that gives the material a gel-like behavior as well as a complex yielding behavior even at low volume fractions of the paraffinic component. It has been known for a long time that the rheology of waxy crude oils is extremely sensitive to both the shear and thermal history of the sample. This observation holds even for simpler model waxy oils comprised from binary solutions of mineral oil and paraffin wax. We have previously shown that it is possible to obtain reliable and repeatable experimental results by following specific protocols and we have used such data to develop a constitutive framework (IKH model) that can capture all of the most important features of waxy oil rheology under isothermal conditions. [Dimitriou and McKinley, *Soft Matter*, 2014, 10, 6619]. In this work we address the behavior of model waxy oils under non-isothermal conditions. In particular, we investigate first the effect of temperature using both steady-state and startup of steady shear experiments. We show that the experimental trends observed with changes of temperature can be very well explained by considering the compositional changes of the system microstructure underlying phase transition. To do this we use the theory of concentrated, non-spherical suspensions with an attractive interaction potential and incorporate this within the existing IKH model to obtain a comprehensive constitutive model for non-isothermal waxy crude oils. Finally, we address the case of thermal transients and show how they can also be explained by considering the presence of crystal nucleation and growth.

Tuesday 10:50 Baltimore/Annapolis

SG18

### **Low-temperature glassy dynamics of bitumen and proposed relaxation time spectrum for polydisperse glass formers**

Olli-Ville Laukkanen<sup>1</sup> and H. Henning Winter<sup>2</sup>

<sup>1</sup>*Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003-3110, United States;* <sup>2</sup>*Chemical Engineering and Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003-3110, United States*

The low-temperature rheological properties of bitumen play a major role in the thermal cracking performance of asphalt pavements. Recently, a technique using 4-mm parallel plate geometry on a rheometer with torsional instrument compliance corrections has been introduced to measure these properties. However, because of the newness of this measurement technique, there is still scarcity of data and associated analysis techniques in the contemporary literature. This paper presents and analyzes dynamic rheological data measured for various neat bitumens both above and

below their glass transition temperatures ( $T_g$ ). Based on the van Gurp-Palmen plots, the studied bitumens are found to be thermorheologically simple in the vicinity of  $T_g$ . However, modulus (vertical) shifts are also needed to produce smooth master curves near and below  $T_g$ , as is evident from the Cole-Cole plot  $G''(G')$ . The temperature dependence of horizontal shift factors, obtained from the time-temperature superposition, is found to accurately follow the Kaelble-WLF equation over the entire experimental temperature range ( $T_g-30$  K to  $T_g+115$  K). Finally, the constructed master curves are used to calculate the relaxation time spectrum of the bitumen with its broad glass transition. The bitumen spectrum differs greatly from previously studied glass formers, which are narrowly distributed. While all of these glass formers are characterized by a powerlaw spectrum with positive exponent, the spectrum of the narrowly distributed glass formers is abruptly cut off at long relaxation times [1] whereas the spectrum of the broadly distributed bitumen requires a broad cutoff: a power law with positive exponent and stretched exponential cutoff is able to describe the experimental data. The powerlaw spectrum with broad cutoff is speculated to be universal for polydisperse glasses.

[1] Winter HH (2013) *Macromolecules* 46:2425-2432

Tuesday 11:15 Baltimore/Annapolis

SG19

### **A combination of large amplitude oscillatory shear and Fourier transform rheology to determine the fatigue behavior of polymers**

Valerian Hirschberg<sup>1</sup>, Dimitri Merger<sup>1</sup>, Manfred Wilhelm<sup>1</sup>, and Denis Rodrigue<sup>2</sup>

<sup>1</sup>*Institut für Technische und Polymerchemie, Karlsruhe Institute of Technology, Karlsruhe, Baden-Württemberg 76128, Germany;*

<sup>2</sup>*Chemical Engineering, Université Laval, Quebec, Quebec G1V0A6, Canada*

In this work, large amplitude oscillatory shear (LAOS) measurements were combined with Fourier transform rheology to propose a criterion for the break-up of polymers under fatigue testing. In particular, polystyrene (PS) samples were studied using the torsion rectangular geometry on a strain controlled ARES rheometer. All the tests were performed in the solid state at room temperature and the effect of strain amplitude and frequency was studied via time sweep tests. The idea is to use higher harmonics to detect the inception of part failure and to predict the end of life conditions of polymer materials. Each experiment was also followed by a video camera to visualize changes in the samples. The results show that variations in the storage ( $G'$ ) and loss ( $G''$ ) moduli are not sensitive enough to predict the sample point of rupture. On the other hand, strong variation in the first odd ( $I_{3/1}$ ) and even ( $I_{2/1}$ ) harmonics were detected. This behavior can be related to morphological changes in the sample leading to crack initiation and propagation which can be used as a criterion to predict sample break-up.

Tuesday 11:40 Baltimore/Annapolis

SG20

### **Applying Boltzmann superposition principle to aging soft glassy materials**

Asheesh Shukla and Yogesh M. Joshi

*Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar pradesh 208016, India*

Aging soft glassy materials demonstrate evolution of physical properties such as viscosity and modulus as a function of time. This invalidates time - translational invariance, and consequently the fundamental principle of linear viscoelasticity - the Boltzmann superposition principle (BSP) is not applicable to this class of materials. Recently it has been proposed that the Boltzmann superposition principle can be made applicable to aging soft materials by transforming the material from the real time domain to the effective time domain. The effective time is defined by normalizing the real time by time dependent mean relaxation time so that the time dependency ceases to exist in the effective time domain. In this work we test applicability of BSP for aging colloidal suspensions of Laponite subjected to step-up and step-down stress jumps, and other stress fields. We observe that influence of applied deformation field on the shape of evolving spectrum of relaxation times is crucial to the validation of BSP.

## **Symposium NF Non-Newtonian Fluid Mechanics**

Organizers: Paulo Arratia and R Sureshkumar

Tuesday 10:00 Frederick/Columbia

NF16

### **Testing an elastic instability criterion in a planar elongational flow**

Simon J. Haward<sup>1</sup>, Gareth H. McKinley<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>*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

There is now a well-established dimensionless criterion [1] for understanding the critical conditions that control the onset of many elastic instabilities. However, most of the elastic flow instabilities analysed to date are dominated by shearing kinematics. Here, we use a range of model viscoelastic fluids to test this criterion in the context of a well-defined, extensionally-dominated flow field in a cross-slot-type geometry [2]. The results of combined micro-particle image velocimetry ( $\mu$ -PIV) and flow-induced birefringence (FIB) measurements performed over a wide range of Weissenberg numbers ( $Wi$ ), reveal a much richer sequence of instabilities than has previously been reported. As the Weissenberg number is increased beyond  $Wi > 0.5$ , the development of a birefringent strand localized along the outflowing stagnation-point streamline indicates the expected local orientation of polymer molecules. For these low values of  $Wi$ ,  $\mu$ -PIV measurements show a Newtonian-like flow field with a centrally-located stagnation point and hyperbolic streamlines. However, for  $0.5 < Wi < 2.0$ , the stagnation point becomes laterally displaced from its central location towards one or the other exit channels of the flow geometry, and with further increases in  $Wi$  begins to oscillate erratically

between the exit channels. Interestingly, the birefringent strand maintains localization and uniformity throughout this range of  $Wi$ . Finally, beyond another fluid-dependent critical  $Wi$ , the flow breaks symmetry globally and spatio-temporal fluctuations are apparent in both the  $\mu$ -PIV and the FIB measurements. Prior to the onset of the first flow instability, the FIB measurements can be used to quantify the spatial distribution of stresses, allowing spatial evaluation of the dimensionless instability criterion. The critical values of this criterion at onset of elastic instability compare well with values reported for torsional, shearing-dominated flows.

[1] Pakdel & McKinley (1996), PRL 77: 2459. [2] Haward et al. (2012), PRL 109: 128301.

Tuesday 10:25 Frederick/Columbia

NF17

### **Dynamics and flow structures of the laminar-turbulent edge state for understanding polymer drag reduction**

Li Xi

*Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada*

Recent advances in viscoelastic turbulence research indicate that answers to some most prominent questions in this field are likely held in the laminar-turbulent transition region. Questions such as the maximum drag reduction (MDR) -- the universal upper limit for polymer drag reduction, transition to turbulence and onset of drag reduction (DR) have remain unsolved after decades of efforts. Although the exact nature of MDR is still unclear, it becomes increasingly apparent that MDR is probably dominated by a class of weak or marginal turbulent states, characterized by significantly lower levels of turbulent activity, drastically reduced friction drag, and distinctly different flow features than Newtonian turbulence. The current study focuses on the edge state, a pivotal (both literally and figuratively) point in the dynamics of laminar-turbulent transition. Edge states are computed for various parameters (Reynolds number, Weissenberg number, and box size) and their flow statistics, structure and dynamics are analyzed. These states show a strongly shear-dominated flow pattern that is distinct from Newtonian turbulence and closely resembles MDR. Polymers are not significantly extended at moderate Weissenberg numbers. As a result, flow statistics do not notably depend on viscoelasticity -- the defining characteristic of MDR. Dynamics of edge states are much less chaotic than regular turbulence and are normally dominated by a few key states. This systematic investigation into the edge state paves way for further exploration of the near-transition regime, which holds the key to solving the mystery of MDR as well as interpreting the conflicting observations of the laminar-turbulent transition in polymer solutions.

Tuesday 10:50 Frederick/Columbia

NF18

### **Spatial-temporal dynamics of Newtonian and viscoelastic turbulence**

Sung-Ning Wang and Michael D. Graham

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

Introducing a trace amount of polymer into the liquid turbulent flows can result in substantial reduction of friction drag. This rheological drag-reducing phenomenon has been widely used in fluid transport, such as the Alaska crude oil pipeline. However, the mechanism or the theoretical picture behind the phenomenon is not well understood. In order to gain more insight into this issue, we conduct direct numerical simulations (DNS) of fully-developed Newtonian and viscoelastic turbulent flows in large domains that imitate experiment length scales. In large-domain simulations, the flow shows different characteristics in different regions. In some areas hibernating turbulence is occurring, while in other areas the turbulent motions are much more active. To identify these characteristic regions, we apply a statistical method capable of partitioning a data set by its own algorithm based on a certain criterion. K-means clustering partitions the observations into  $k$  clusters by assigning each observation to its nearest mean called centroid. The resulting partition maximizes the between-cluster variance. In large-domain simulations, the observations are the flow variables from mesh points at the walls. Regions with different levels of drag are automatically identified by the partitioning algorithm. We find that the velocity profiles of the centroids exhibit characteristics similar to the individual coherent structures observed in minimal domain simulations. In addition, we observe that as viscoelasticity increases, polymer stretch becomes strongly correlated with wall shear stress. How viscoelasticity modifies the spatial-temporal dynamics in large-domain simulations is to be determined in this work.

Tuesday 11:15 Frederick/Columbia

NF19

### **Elastic turbulence in parallel shear flows at low Reynolds numbers**

Boayng Qin and Paulo E. Arratia

*Dept. Mechanical Engineering & Applied Mechanics, University of Pennsylvania, Philadelphia, PA, United States*

In this talk, we present an experimental investigation on the flow of viscoelastic fluids in parallel channel flows in a microfluidic device. The dimensions of the microchannel are small enough (100  $\mu$ m wide x 100  $\mu$ m depth) such that inertial effects are negligible. The flow of a viscoelastic fluid is initially perturbed by a linear array of cylinders, and velocimetry measurements are performed immediately after the perturbation region (linear array of cylinders) as well as far downstream (200 x channel width). We find signatures of turbulence, namely large and non-periodic velocity fluctuations in the wake of the initial perturbation, where the streaks are highly three-dimensional and unsteady. Such velocity fluctuations occur over a broad range of frequencies and spatial wavelengths. Furthermore, the temporal and spatial power spectra of the stream-wise velocity fluctuation follow a power law that resembles that of the purely elastic turbulence previously reported in flows of curved geometries. Beyond a set of critical conditions, the turbulent velocity fluctuation persists far downstream and evolves to follow a different spectra decay scaling. Energy contained in the fluctuations is seen to dissipate from large length scales and to transfer from high frequencies to lower ones.

Tuesday 11:40 Frederick/Columbia

NF20

**Elastic instabilities around periodic cylinder arrays and their role on oil displacement**Xueda Shi and Gordon F. Christopher*Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Microfluidics have increasingly been used as an effective analog for the study of viscoelastic porous flows because of their ability to create dynamically similar conditions. Using such techniques, we have characterized new classes of instabilities that occur at moderate viscoelastic Mach numbers around individual cylinders, which model idealized single pores in porous media. In this work, we expand our examination to multi-cylinder arrays in order to understand how single pore instabilities are affected by neighboring geometry, and how these instabilities can be leveraged to effectively displace oil out of porous media.

Using both streakline imaging and excess pressure drop, we characterize instability onset and the changes in flow behavior. We have systematically characterized the roles of cylinder placement and density on the onset and interaction of previously observed single cylinder instabilities. As cylinder density increases, we note new flow patterns emerging, creating both mirrored vortices around cylinders and eventually much greater chaotic flows. The changes in flow behavior heavily depend on the center-to-center distance between cylinders in the flow direction, the blockage ratio of individual cylinders, total porosity and viscoelastic Mach number. We have estimated how instabilities affect the effective mobility of these flows using pressure measurements and evaluated the efficacy of these reduced motilities in displacing residual oil.



## Tuesday Afternoon

### Symposium SC Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Tuesday 1:30 Constellation C

SC21

#### **Yield and flow of non-colloidal suspensions in a pendular state**

Junyi Yang, Trystan Domenech, and Sachin S. Velankar

*Chemical Engineering, University of Pittsburgh, Pittsburgh, PA, United States*

We examine the yielding of pendular suspensions composed of silica particles in polyisobutylene with a small quantity of polyethylene oxide (PEO) added. The PEO is preferentially-wetting towards the particles and therefore forms narrow necks, called pendular menisci, between the particles. Since the pendular menisci induce a capillary attraction between particles, a percolating particle network is formed. This network has strongly non-Newtonian flow characteristics with yield-like rheology analogous to the yield stress of a wet sandpile which has exactly this kind of pendular network structure.

We show that the yield stress increases with volume fraction of the particles and of the wetting fluid as long as a pendular state is maintained. The pendular state is lost at sufficiently high wetting fluid fraction, when the fluid engulfs the particles leading to a decrease in yield stress. In steady shear, pendular suspensions show strongly shear-thinning rheology. All the flow curves can be collapsed into a single mastercurve by normalizing the shear stress by the yield stress, and the viscosity by the viscosity of a corresponding suspension without pendular attractions. The pendular networks soften after being subjected to high stress, however subsequent shearing at lower stress can restore the stiffness again. In creep, the pendular networks show delayed yielding where the shear rate may first reduce to near-zero values before fluidization. Finally in LAOS, the networks show behavior typical of attractive particulate systems: as strain increases, the storage and loss moduli cross each other indicative of a transition from solid-like to fluid-like behavior. We compare various measures of the yield strain: (1) the crossover strain in strain sweep experiments; (2) the strain beyond which creep recoil shows a plateau; (3) the strain beyond which the oscillatory modulus decreases irreversibly. All of these measures show that the yield strain is a few percent and increases with the wetting fluid volume fraction.

Tuesday 1:55 Constellation C

SC22

#### **Theory of margination in confined multicomponent suspensions**

Rafael G. Henríquez Rivera, Kushal Sinha, and Michael D. Graham

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

In blood flow, leukocytes and platelets tend to segregate near the vessel walls; this phenomenon is known as margination. Margination of leukocytes and platelets is important, for example, in physiological processes (e.g., hemostasis, response to inflammation), medical diagnostics (e.g., microfluidic cell separation) and drug delivery (the margination properties of a drug delivery particle influences its distribution in the vessel and thus its effectiveness). A mechanistic theory is developed to describe flow-induced segregation in confined multicomponent suspensions of deformable particles such as blood. The theory captures the essential features of margination by describing it in terms of two key competing processes in these systems at low Reynolds number: (1) wall-induced migration and (2) hydrodynamic pair collisions. The theory also includes the effect of physical properties of the deformable particles as well as the effect of molecular diffusion. Several regimes of segregation are identified, depending on the value of a "margination parameter",  $M$ . Moreover, there is a critical value of  $M$  below which a sharp "drainage transition" occurs: one component is completely depleted from the bulk flow to the vicinity of the walls. Direct hydrodynamic simulations also display this transition in suspensions where the components differ in size or flexibility. The developed mechanistic theory leads to substantial insight into the origins of margination and will help in guiding development of new technologies involving blood and other multicomponent suspensions.

Tuesday 2:20 Constellation C

SC23

#### **The effects of particle deformability and size on single particle lateral migration in low Reynolds number flow**

Margaret Y. Hwang and Susan J. Muller

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

Lateral migration of suspension components in pressure-driven flow has been observed (e.g. margination in capillary blood flow) and has been previously found to depend on particle deformability, shape, and size, suspension concentration, and Reynolds number, but how these properties result in migration is not well understood. In this work, we attempt to elucidate the roles of particle deformability and particle size on lateral migration in low Reynolds number, pressure-driven channel flows through the use of model suspensions. Deformable alginate microspheres were generated using a modified flow-focusing microfluidic device. Monodisperse particles of specific size and deformability were produced by respectively tuning flow rate ratios and alginate concentration. Particle deformability was quantified using capillary micromechanics in a tapered capillary. Dilute suspensions of particles were flowed through long, straight microchannels. Tracking single deformable particles as they flowed

through the channel revealed lateral migration at  $Re = 0.1$ . The effects of particle size and deformability on migration entry lengths and steady state particle positions will be discussed.

Tuesday 2:45 Constellation C

SC24

### **Relative viscosity trends of bimodal suspensions containing rigid and soft particles**

Anik Chaturbedi, Brian Schendt, and Nina C. Shapley

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

The steady shear rheology of a bimodal suspension of neutrally buoyant, noncolloidal spheres in a viscous, Newtonian liquid is investigated. The smaller particles are alginate gel microbeads, which are deformable and porous, and the larger particles are rigid PMMA spheres. Potential applications of such a system include composites processing and separation column packing. This work extends a prior study of the steady shear rheology of a concentrated bimodal suspension to cover a broader concentration range, including values of the total particle volume fraction beyond 0.4 and 0.5, and to examine various particle diameter ratios. Measurements are acquired in a parallel plate rheometer under shear rates ranging from 0.1 to 100  $s^{-1}$ . We seek to identify the total and relative concentration ranges and diameter ratios over which enhanced shear thinning or non-monotonic viscosity curves are observed. Mapping the regions of rheological behavior over a broader parameter space will provide further insight into the flow of bimodal suspensions containing both rigid and soft particles.

Tuesday 3:10 Constellation C

SC25

### **Dependence of shear-induced particle migration on inner/outer fluid viscosity ratio**

Yeng-Long Chen, Shih-Hao Wang, and Wei-Ting Yeh

*Institute of Physics, Academia Sinica, Taipei 11529, Taiwan*

Shear-induced particle migration is a well-known phenomenon that has been utilized in microfluidic cell-sorting [1] and large scale stream-bed particle-sorting [2]. For soft particles such as droplets and cells, both the inertial-driven and deformation-driven lift can contribute to the steady state particle position in microfluidic flow [3,4]. A recent experiment [1] found that the steady state droplet position has non-monotonic dependence on the inner/outer viscosity ratio, which could significantly affect cell-sorting. In this work, we investigate this phenomenon using lattice Boltzmann-immersed boundary method. We found that the steady state particle position strongly depends on the particle deformation, which in turn depends on the inner/outer fluid viscosity ratio. For higher shear rates and larger particle deformation, the steady state position moves monotonically towards the wall as the inner fluid becomes more viscous. At lower shear rates and smaller particle deformation, the steady state particle position is between the wall and the channel center at low and high inner fluid viscosity, and the position moves towards the center when the viscosity ratio is approximately 1. The results could be applied to design optimized sorting strategies for droplets and cells by controlling the outer fluid viscosity.

[1] S. C. Hur, A. J. Mach and D. Di Carlo, *Biomechanics*, 2011, 5, 22206. [2] A. Karnis, H. L. Goldsmith and S. G. Mason, *Can. J. Chem. Eng.*, 1966, 44, 181. [3] P. C. H. Chan and L. G. Leal, *J. Fluid Mech.*, 1979, 92, 131. [4] Y.-L. Chen, *RSC Advances*, 2014, 4, 17908.

Tuesday 4:25 Constellation C

SC27

### **Towards a continuum modeling of shear thickening suspensions?**

Romain Mari<sup>1</sup>, Ryohei Seto<sup>2</sup>, Jeffrey F. Morris<sup>3</sup>, and Morton M. Denn<sup>3</sup>

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There is an emerging consensus that the mechanism for shear thickening in dense suspensions is a transition from a "frictionless" rheology, where close interactions between suspended particles are lubricated, to a "frictional" rheology, where particles make unlubricated frictional contacts. Particle-scale simulation now can quantitatively reproduce the non-Newtonian behavior of thickening suspensions. However, we still do not have a macroscopic continuum description of these suspensions, which would allow to predict e.g. flows of shear thickening fluid when the shear conditions are not spatially uniform. To tackle this challenging issue, we explore some relations between microscopic properties, like the interparticle force distribution and the particle motion correlations, and the macroscopic rheology.

Tuesday 4:50 Constellation C

SC28

### **A population balance based, coarse grained, evolution equation for microstructure in thixotropic colloidal dispersions**

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A systematic study of an evolution equation to describe the structural dynamics in a thixotropic suspension is presented. Starting from a population balance equation, a monodisperse closure rule is used to develop a coarse grained structure evolution equation. Improvements to incorporate the effect of yield stress on aggregation dynamics are made. This population based model can now simulate a thixotropic fluid with yield stress using a single structural parameter. This model is tested and validated against rheological data using a simple constitutive relationship for stress that considers the viscous and elastic stresses of interacting aggregates. The predictions from this model are also compared against existing phenomenological structural models [1]. Similarities and differences will be discussed. Next, improvements are incorporated to include the effects

of polydispersity by applying a 6-moment closure to the population balance. This represents the suspension as an equivalent tri-modal suspension. Subsequently an improved constitutive relationship is presented to account for the effects of polydispersity on the viscosity and yield stress in this tri-modal representation of the thixotropic dispersion. This updated model provides a good representation of experimental data and captures general thixotropic phenomena seen. The resulting structure predictions are now amenable to independent verification via optical techniques, an advantage over purely phenomenological structural models. Finally, the fit of the experimental data suggests that primary clusters and not primary particles are the basic units of the thixotropic suspension studied in this work. This result is supported by neutron scattering and small angle x-ray scattering measurements on the system.

[1] Mewis, Jan, and Norman J. Wagner. Colloidal suspension rheology. Cambridge University Press, 2011.

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Tuesday 5:15 Constellation C

SC29

### **Making jammed particle suspensions flow: Slow and high shear rate cooperative rearrangements**

Vishwas Venkatesh<sup>1</sup>, Sudeep Dutta<sup>2</sup>, Emanuela Del Gado<sup>2</sup>, and Daniel Blair<sup>2</sup>

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We have combined confocal microscopy imaging of jammed emulsions under shear with molecular dynamics simulations of dense soft sphere suspensions. The experiments performed at volume fractions above the jamming transition, for various shear rates, follow the Hershel-Bulkley flow curve. The confocal microscopy measurements carried out in tandem with the shearing unravel important features at the droplet level. They indicate that at low enough shear rates, the flow becomes localized and the rearrangements of the emulsion droplets are slow and intermittent. Increasing the imposed shear rate makes the emulsion flow with an increasingly linear flow profile but the local rearrangements remain cooperative in nature. Using extensive numerical simulations of a model soft sphere suspension with a polydispersity of 10%, we understand these experimental results. The simulations support the idea that, at sufficiently high volume fractions, particle mobility strongly depends on the accumulated local shear strain, both at low and high shear rates. The local changes in displacements of the particles are analysed by computing the non-Gaussian parameter and cage correlation function. Using these results, we understand the rearrangement of particles at various local shear strains. We have also computed the local structural order parameter to understand the correlation between dynamical cooperativity and structural changes.

Tuesday 5:40 Constellation C

SC30

### **Wall slip in suspensions of thermo-responsive particles**

Thibaut Divoux<sup>1</sup>, Véronique Lapeyre<sup>2</sup>, Valérie Ravaine<sup>2</sup>, and Sébastien Manneville<sup>3</sup>

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Suspensions of particles are often subject to wall slip, that is the fluid velocity  $v_f$  differs from the velocity of the boundary  $v_w$  due to the presence of a thin lubrication layer. The slip velocity  $v_s$ , defined as  $v_s = |v_f - v_w|$ , displays a universal power-law scaling with the stress  $\sigma$  at the wall. If slip velocities in dilute suspensions robustly follow  $v_s \propto \sigma^p$ , with  $p \approx 1$ , no consensus currently exists for jammed suspensions of soft particles experiencing wall slip above the yield stress. Indeed, slip velocities are either reported as a function of the stress, or of the viscous stress, and exponents range inconsistently from  $p=0$  to  $2$  on similar systems. Here, we report an extensive experimental data set obtained from velocimetry coupled to rheometry on a suspension of thermo-responsive particles. We demonstrate that the slip velocity always scales as a power law of the viscous stress  $\sigma - \sigma_c$ , where  $\sigma_c$  denotes the yield stress. Experiments performed at different temperatures further reveal that such scaling holds true over a large range of packing fractions on both sides of the jamming point, and that the exponent  $p$  goes continuously from  $p=1$  to  $p=2$  as a dilute suspension of hard particles is turned into a jammed assembly of soft particles. We finally revisit data sets from the literature that further confirm our results and show that above jamming, for stresses larger than the yield stress, the slip velocity depends on the packing fraction.

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

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Tuesday 1:30 Constellation D

SM21

### **Tube deformation, chain stretching, yielding and shear thinning in entangled polymer melts: A force-level statistical mechanical approach**

Kenneth S. Schweizer

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A force-level, self-consistent theory of the tube field has been recently developed for rod and (at the primitive path level) chain polymer liquids [1]. Distinctive predictions are that the dynamic confinement potential is anharmonic and the entanglement force preventing transverse motion is of finite strength, which are in good agreement with equilibrium F-actin experiments and chain melt simulations. For entangled rods, a rheological theory has been constructed under step strain and continuous startup shear conditions [2]. In the former, the tube can be transiently destroyed beyond a strain of order unity, providing a microscopic basis for the elastic yielding concept proposed by S.Q.Wang. For continuous shear

deformation, a stress overshoot, emergent convective constraint release (CCR), a monotonic flow curve, shear thinning and tube dilation are predicted. Building on these advances, an initial theory is formulated for flexible chain melts subjected to continuous shear. Theoretical analysis of the tube confinement force and the deformation-induced force required to stretch chains leads to the prediction that strands do not retract until the intrachain elastic force becomes sufficiently large. Predictions are made for the strain and applied rate dependence of the tube diameter, degree of orientation and stretch ratio, and the magnitude and shear rate dependence of the critical strain required for chain retraction. Overall, the results are consistent with the experiments, qualitative physical picture, and simulations of Wang and coworkers. In the steady state, a CCR-like process and stress plateau emerge from a self-consistent treatment of orientation, relaxation and tube constraints.

[1] D.M.Sussman and K.S.Schweizer, PRL,107,078102(2011);PRL,109,168306(2012). [2] Macromolecules, 45, 3270 (2012); 46, 5684 (2013); JCP, 139, 234904 (2013).

Tuesday 1:55 Constellation D

SM22

### **Transition from homogeneous flow to a shear banded state before and after the stress overshoot in start flow of entangled polymer melts: The influence of flow ramp speed**

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To date, ample experimental observations and a single molecular simulation (average entanglement points per chain,  $\langle Z \rangle = 10$  at equilibrium) have demonstrated the existence of shear banding in highly entangled polymeric solutions and melts. In this study, we have performed hi-fidelity Dissipative Particle Dynamics (DPD) simulations in unidirectional flow of polymeric melts over a broad range entanglement density, i.e.,  $13 = \langle Z \rangle = 28$ . In turn, comprehensive flow microstructure analysis has been performed to pave the way for a molecular understanding of the origin of shear banding in this class of industrially important flow. Overall, we have demonstrated that the stress overshoot in a typical start-up setting gives rise to spatially inhomogeneous chain deformation and thus spatially inhomogeneous chain disentanglement; the localized jump in entanglement density along the velocity gradient direction and a commensurate jump in normal stress and viscosity ultimately leads to shear banding. Moreover, a plausible explanation for different responses of the transient and steady shear banding to in the initially localized disturbances is presented based on interfacial instability analysis. Finally, we observed multiple steady states of shear banded structures at a given deformation rate if the flow was ramped quickly enough from the rest, but homogeneous linear flow otherwise. Specifically, if the flow is ramped slowly, the orientational relaxation process has the required time to homogenize the system, thus formation of spatially inhomogeneous chain disentanglement and therefore development of shear banding is prevented. In this presentation the dependence of level of the stress overshoot in terms of the initially imposed shear rates as a function relevant time scales of the system will be discussed.

Tuesday 2:20 Constellation D

SM23

### **Wall slip of HDPEs: MW, MWD and surface conditions effects**

Marzieh Ebrahimi and Savvas G. Hatzikiriakos

*Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia V6T1Z3, Canada*

The slip behavior of several high-density polyethylenes (HDPEs) including bimodals is studied as a function of molecular weight (Mw) and its distribution. The slip velocity increases with decrease of molecular weight, as reported for several other linear polymer systems in the literature. The double reptation theory that relates the polymer viscosity as a function of number of entanglements thus molecular weight characteristics is extended to predict the slip velocity of the studied polymers based on their molecular weight distribution (MWD). It is found that this theory is applicable for unimodal HDPEs. However, for bimodal HDPEs, migration effects are present and the segregation of low molecular weight chains to the wall should be considered. The effect of surface conditions such as surface topology and energy on slip of these polymers have also been studied. Laser ablation has been used to micro/nano-pattern the surface of slit dies in order to examine their effect on slip of HDPEs. In addition, fluoropolymer and silane-based coatings on smooth and patterned substrates were used to understand the effect of surface energy on slip. It was found that surface conditions affect slip at various degrees depending on the presence of micro/nano roughness and coatings.

Tuesday 2:45 Constellation D

SM24

### **Stick-slip transition and shear banding in entangled solutions based on polybutadiene of ultra high molecular weight**

Mengchen Wang, Tianbo Liu, and Shi-Qing Wang

*Department of Polymer Science, University of Akron, Akron, OH 44325, United States*

This presentation reports rheological behavior of two polybutadiene (PB) solutions based on PB of molecular weight  $M_w \sim 4$  million g/mol. Small molecule solvents were used to make 5 % solutions with extrapolation length  $b$  reaching 600 nm so that massive wall slip can be readily studied in both rate-controlled and stress-controlled modes. The measurements are found to have no gap dependence in presence of massive wall slip, violating the standard formula that shows the shear stress at a constant nominal rate to decrease when the gap distance  $H$  is lowered. The solutions also show a massive stick-slip transition in rotational cone-plate shear. When the hydrocarbon solvent is replaced by oligomeric PB, wall slip can be suppressed sufficiently to allow emergence of shear banding at a concentration 3.5 %. Because of the low concentration, the solutions are incapable of developing any edge effects.

Tuesday 3:10 Constellation D

SM25

**Edge fracture and shear banding in a highly entangled polystyrene solution**Yanfei Li and Gregory B. McKenna*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The possibility of shear banding has become an important problem. Does it exist? If it does, is it a steady-state or a transient phenomenon? What are the mechanisms for its occurrence? The answers to these questions would help rheologists better evaluate the validity of the Doi-Edwards tube model [1]. Experimentally, if shear banding had occurred, many observational rheological measurements [2] would need to be reevaluated since these experiments were based on the assumption of a homogeneous strain field. The visualization of steady-state shear banding was first reported in 2006 [3] using particle tracking velocimetry with a polybutadiene solution. On the other hand, other findings suggested shear banding is transient and its occurrence is not embedded in the constitutive equation [4]; instead, it could be attributed to edge effects. In the present work, to evaluate the banding phenomenon, we focused on a highly entangled polystyrene solution with entanglement density  $Z=61$  and  $PDI=1.14$ . Using particle tracking velocimetry, startup shear tests were carried out deep into the nonlinear regime where the Weissenberg number  $Wi$  reaches up to 255. With wall slip prevented by surface roughening, edge fracture occurs at  $Wi > \sim 3$ . We found that the velocity profiles are linear, except at  $Wi = 255$ , where transient weak banding occurs. These findings suggest that banding is transient, and its occurrence could relate to the edge fracture, which serves as a stress concentrator that either perturbs the monotonic constitutive response or that directly induces shear banding due to, e.g., strong secondary flows that propagate into the sample from the free edge.

[1] Doi M, Edwards SF, *J Chem Soc Farad T 2* 75:38 (1979). [2] Shamim N, McKenna GB, *J Rheol* 58:43 (2014). [3] Tapadia P, Wang SQ, *Phys Rev Lett* 96:016001 (2006). [4] Hu YT, *J Rheol* 54:1307 (2010).

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Tuesday 4:00 Constellation D

SM26

**Molecular dynamics and slip-spring model simulations of branched polymer**Jian Zhu, Zuowei Wang, and Alexei E. Likhtman*School of Mathematical and Physical Science, University of Reading, Reading, Berkshire RG6 6AX, United Kingdom*

Understanding the relaxation dynamics of entangled branched polymers is highly desired for developing theories for the rheology of entangled polymer melts. Such understanding is however hard to achieved from macroscopic experiments. In principle, molecular dynamics simulations involve the complicated combination of relaxation mechanisms, such as arm retraction, constraint release and branch-point hopping, while the time cost is extremely high due to the exponentially slow dynamics. The slip-spring method is considered to be one promising solution to this problem due to its high efficiency and the ability to separate different relaxation mechanisms. In this work, a detailed discussion on the end-to-end relaxation and the mean-square displacement is presented for typical branched polymers, such as symmetric star, asymmetric star and H-polymer. By comparing slip-spring model and the MD simulations, we propose a mechanism of entanglements passing through the branch-point, which potentially provides a universal mechanism for the relaxation of branched polymers.

Tuesday 4:25 Constellation D

SM27

**Solution and melt rheology of symmetric star-shaped poly (hydroxybutyrate) generated from immortal ring opening polymerization of  $\beta$ -butyrolactone**Ebrahimi Tannaz<sup>1</sup>, Mehrkhodavandi Parisa<sup>2</sup>, and Savvas G. Hatzikiriakos<sup>3</sup><sup>1</sup>*Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia V4P 3L5, Canada;*<sup>2</sup>*Chemistry, The University of British Columbia, Vancouver, British Columbia V6T-1Z1, Canada;* <sup>3</sup>*Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia V6T1Z3, Canada*

High molecular weight symmetric star shaped poly (hydroxybutyrate)s were synthesized via immortal ring opening polymerization (ROP) of  $\beta$ -butyrolactone (BBL) using indium (1) and zinc (2) complexes bearing tridentate NNO type ligand in the presence of a triol (tris(hydroxymethyl) benzene (THMB)) and a hexol (dipentaerythritol (DPET)) as chain transfer agents. While catalyst system 2 generates moderately syndiotactic 6-armed star shaped PHBs with maximum molecular weights of ( $M_w > 114,000$  Da), synthesis of 3-armed star PHBs of the molecular weights up to 230,000 Da is possible using catalytic system 1. The solution and melt viscoelastic properties of the various molecular weight linear and star-shaped PHBs were also investigated. Power-law relationships of the  $R_g$  and  $R_h$  with molecular weights, and lower amounts of the intrinsic viscosity and compactness factors of the stars compared to that of the linear PHBs indicated the self-similar and symmetric topology of the star PHBs. From melt rheology, the entanglement molecular weights of the linear and star shaped PHB homopolymers are estimated. The zero-shear viscosity of the linear PHBs has shown a scaling of  $\eta_0 \propto M_w^{3.42}$  to be consistent with those reported for linear monodisperse polymers, while  $\eta_0$  for symmetric stars scales exponentially with the arm molecular weight. Furthermore, transient shear viscosity growth of the samples indicates more shear thinning behavior of the stars compared to the linear PHBs due to the dynamic dilution effect of arm tips and lower entanglement densities of the stars, which eases the shear alignment of the chains. The shear viscosity of the aforementioned polymers is also investigated using the K-BKZ constitutive equation.

Tuesday 4:50 Constellation D

SM28

**Classification of thermorheological complexity in polyethylene and other single phase polymer melts**Florian J. Stadler*College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China*

Thermorheological complexity in polyolefins has been reported many times but so far it has not been systematically investigated. Here, a classification of the different types of thermorheologically complex behavior is proposed, which categorize the available data in 5 different types and describe key characteristics. These definitions are based on polyethylene, but other polymers show similar patterns for materials with comparable branching structure. Linear materials are thermorheologically simple as long as many very long short chain branches do not introduce phase separation. Sparsely branched materials show the biggest thermorheological complexity, with significant shape changes of rheological functions with temperature, while higher amounts of branching (such as combs) reduce thermorheological complexity. Low density polyethylene shows a significant modulus shift at different temperatures probably due to excessive low molecular components.

Tuesday 5:15 Constellation D

SM29

**Conversion of creep compliance to dynamic moduli using Laplace transform and complex decomposition method**Sang Hun Lee and Kwang Soo Cho*Department of Polymer Science and Engineering, Kyungpook National University, Daegu 702701, Republic of Korea*

Linear viscoelastic theory provides mathematical relations between measurable viscoelastic functions such as creep compliance and dynamic moduli. Hence, it is possible, at least principle, to convert a viscoelastic function to another. Although they are exact, it is difficult to implement them from experimental data because experimental data are obtained in a finite interval.

Measurement of dynamic moduli is highly reproducible and quite easy. However, without time-temperature superposition, the measurement is restricted to considerably narrow interval of frequency. Especially, polymeric fluid of high molecular weight usually does not show the terminal region. On the other hand, creep test gives reliable data of long time regime where creep compliance is linearly increases as time. Hence, it is important to convert creep compliance data to dynamic ones.

Evans *et al.* (2009) developed a nice method to convert creep compliance directly to dynamic moduli. However, this algorithm includes the numerical integration of the numerical derivative of creep compliance. Although numerical integration is stable for experimental errors, conventional numerical differentiation such as forward scheme is very weak for experimental errors. Looking at their results, it can be said that the ill-posedness of numerical differentiation overcomes the stabilization of integration. They developed the algorithm in order to detour numerical inversion of Laplace transform.

Different from the algorithm of Evans *et al.*, our algorithm uses the Laplace transform of creep compliance. The core of our algorithm is the regression of the Laplace transform by double logarithmic power series in terms of Chebyshev polynomial and complex decomposition of the power series to obtain dynamic moduli. Our algorithm reduces the effect of experimental error by regression. Our algorithm does not contain any numerical differentiation procedure, the calculated moduli are free from rapidly oscillating noise.

Tuesday 5:40 Constellation D

SM30

**Power series approximation of continuous relaxation spectrum by the Fuoss-Kirkwood relations**Sang Hun Lee, Jung-Eun Bae, and Kwang Soo Cho*Department of Polymer Science and Engineering, Kyungpook National University, Daegu 702701, Republic of Korea*

Relaxation spectrum is important not only because other viscoelastic functions can be determined from it but also because it gives an insight on molecular relaxation of relaxation. Fuoss and Kirkwood (1941) derived the relation between loss modulus and relaxation spectrum by use of Fourier transform. The uniqueness of Fourier transform pair supports the reality of relaxation spectrum although it cannot be measured. Modern molecular theory of linear viscoelasticity of polymer fits experimental data with two or more parameters irrespective of molecular weight and molecular weight distribution. However, the ill-posedness of relaxation spectrum implies that such agreement in measurable viscoelastic quantities may not be sufficient criterion on the soundness of the molecular theory. Slight difference in dynamic moduli is apt to mean absolutely different spectra. Hence, relaxation spectrum must be an acid test for good molecular theories.

Although the Fuoss-Kirkwood relation is exact, if measurable viscoelastic function is not exactly known, then no spectrum can be obtained exactly. The Weierstrass theorem is that any continuous function on a closed interval can be approximated by a power series with a desired precision if the order of the power series can be increased at will. We developed an algorithm to calculate the coefficients of the power series of spectrum from those of modulus by use of the Fuoss-Kirkwood relations. Furthermore, we analyzed the error in spectrum in terms of the error in the approximation of modulus. This error analysis provides how to obtain spectrum whose error bound is equivalent to that of modulus.

Reference: Fuoss, R. M. and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 385~394 (1941).

## Symposium SA Self-assembled Systems and Gels

Organizers: Surita Bhatia and Kelly Schultz

Tuesday 1:30 Constellation E

SA6

### Permeability in fractal aggregates: Application to unstable colloidal gels

Alex Mertz<sup>1</sup>, Lev Gelb<sup>2</sup>, Alan Graham<sup>3</sup>, Marc Ingber<sup>1</sup>, and Redondo Antonio<sup>3</sup>

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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. However, in high-volume-fraction gels the "fractal" nature of the gel structure is questionable, and dependence of the permeability on finer structural details of the gel network is as yet unknown. We investigate permeability in model gel structures using coarse-grained numerical simulations. Our approach is based on assigning a "local" permeability to each point in the volume based on geometric considerations, in particular a geometrically defined local pore size and the distance to the nearest point on the gel network. The relationship between permeability and local pore size is established with supplementary finite-element simulations of pressure-driven flow past an array of cylinders. In calculations on model gel structures generated by diffusion-limited cluster aggregation (DLCA), this approach is found to be insensitive to the "coarse" grid size used, and reasonable agreement with available experimental data is obtained over a wide range of gel volume fraction. Subsequent calculations consider the effects of gel connectivity, polydispersity and pore size distribution on permeability, as investigated using model gel networks prepared using several different simulation algorithms.

Tuesday 1:55 Constellation E

SA7

### Phase behavior of aqueous suspension of Laponite: A rheological perspective

Shweta Jatav and Yogesh M. Joshi

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Laponite is a disk shaped nanoparticle. The scattering studies on Laponite suspension suggest that for concentrations between 1 and 2 weight % and up to 4 mM NaCl there exists an attractive gel state, while beyond 2 weight % and up to 4 mM NaCl suspension is in a repulsive 'Wigner' glass state. In this work we perform time resolved rheometry on Laponite suspensions over a concentration range of 1.4 to 4 weight % and NaCl concentration range of 0 to 7 mM, wherein suspension is subjected to cyclic frequency sweep as its structure evolves. We observe that the structural evolution of all the Laponite suspensions is accompanied by a decrease in  $\tan\delta$  with sharpness of decrease, increasing with decrease in frequency. Remarkably all the  $\tan\delta$  evolution curves pass through a single point demonstrating a presence of the critical gel state with a percolated space spanning network. Therefore, contrary to scattering studies, the present rheological work clearly suggests Laponite suspensions to be in attractive gel state over the studied concentration ranges. Interestingly we observe that the fractal dimension associated with the critical gel state is independent of concentration of salt but observe to increase with increase in Laponite concentration.

Tuesday 2:20 Constellation E

SA8

### Stabilization of the network structure induced by viscoelastic phase separation through self-assembly of nanorods: PS/PVME blend

Mohamad Ali Sanjari Shahrezaei<sup>1</sup>, Fatemeh Goharpey<sup>1</sup>, and Jafar Khademzadeh Yeganeh<sup>2</sup>

<sup>1</sup>Department of Polymer Engineering, Amirkabir University of Technology, Tehran, Iran; <sup>2</sup>Polymer Engineering Group, Faculty of Engineering, Qom University of Technology, Qom, Iran

The viscoelastic phase separation (VPS) can produce a network structure of the minor phase, which is useful to design heterogeneous structures with interesting mechanical and electrical functions. We investigate the stabilization of the percolated network structure induced by VPS in dynamically asymmetric PS/PVME blend by incorporation of nanowhiskers. Phase contrast optical microscopy is employed to investigate the time evolution of the phase-separating morphologies. The phase separation temperature and correlation length are evaluated from isochronal temperature scans in shear rheology. The addition of hydrophilic nanowhisker retards the volume shrinking process and slows down the kinetics of phase separation. The network structure of the minor phase is stabilized by the selective localization of nanorods in the PS-rich phase. The length scale of the cooperative rearranging region (?CRR) at  $T_g$ , assessed by calorimetric measurements, is observed to be higher in the case of blends with nanowhiskers.

Tuesday 2:45 Constellation E

SA9

### Relationship between rheology, calorimetry and structure properties in thermo-responsive laponite-Pluronic micellar solutions

Imane Boucenna<sup>1</sup>, Marie-Alice Guedeau-Boudeville<sup>1</sup>, Laurent Royon<sup>2</sup>, Ahmed Mourchid<sup>2</sup>, and Pierre Colinart<sup>2</sup>

<sup>1</sup>*Matière et Systèmes Complexes, CNRS-Université Paris Diderot, Paris 75205, France;* <sup>2</sup>*Matière et Systèmes Complexes, Université Paris Diderot - Laboratoire MSC, Paris 75205, France*

We investigate the microstructure of aqueous Pluronic triblock copolymer micellar solutions with embedded anisotropic colloidal nanoparticles and its connection to their rheological and thermal properties. The samples are formed of concentrated micelles solutions which exhibit a temperature induced phase transition from fluid to crystal. Addition of laponite nanoparticles is found to promote patterned microstructured samples with both a shift in the sol-to-gel transition temperature and a decrease of the viscoelastic moduli. In this presentation we will focus mainly on the connection between structure, studied by small angle neutron scattering and optical microscopy, and rheology results at the onset of gelation, on the one hand, and between calorimetry and rheology results, on the other hand. We will show that the solutions exhibit microscopic confinement of the nanoparticles triggered by increasing the temperature above the sol-to-gel transition point. The results strongly suggest that the elasticity of the copolymer solutions with added laponite nanoparticles is triggered by the formation of a networked solution of polycrystalline micelles forming grains of finite-size where laponite nanoparticles are in the interstices between them. These directed-assembly properties are governed by copolymer micelles-solvent interaction through temperature. We will also show that the appearance of the secondary endothermic peak, probed by  $\mu$ -differential scanning calorimetry, agrees with the transition point observed from rheology data. Further increase of laponite nanoparticles to the solutions induces a shift in the peak position, in agreement with the shift observed in the sol-to-gel transition temperature.

Tuesday 3:10 Constellation E

SA10

### Directed assembly of Janus rods in binary blends of polymers

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During the past two decades, addition of nano-particles in anisotropic shapes to polymers has been established as a common approach for developing new functional materials with engineered properties; however, the performance of these multi-component composites strictly depends on the morphology and microstructure of nano particles within the polymer matrix. Thus, controlled assembly of particles can provide a powerful tool for achieving desired properties in polymer nano-composites, although it still remains a challenging subject in the field of nanotechnology. Janus particles due to their amphiphilic nature show a strong affinity to the interfaces; therefore, by harnessing this interfacial activity, new routes for nano-particles directed assembly are being developed. In this work, using mesoscale computational methods, we show that mixtures of phase separating polymers can be exploited for engineering the spatial organization of Janus rods in nano-composites. Ordering Janus rods at the interface is directly influenced by their amphiphilicity (ratio between chemical compartments), aspect ratio and volume fraction whose effects will be investigated comprehensively. Additionally, the presence of Janus rods and their localization can affect the kinetic path of the morphology development in polymer blends, which is enhanced under flow conditions. Thus, the phase separation of these nano-composites is monitored under equilibrium, flow conditions and upon relaxation. We show that the nano-rod alignment at the interface plays an important role in controlling the stability of the morphology. The results of this study can be used for designing new approaches for directing nano-particles into desired morphologies, which will subsequently tune the final characteristics and properties of nano-composites.

Tuesday 4:00 Constellation E

SA11

### A comparison of linear and branched wormlike micelle solutions using LAOS and orthogonal superposition rheometry

Sunil Khandavalli<sup>1</sup>, Jan Hendricks<sup>2</sup>, Christian Clasen<sup>2</sup>, and Jonathan P. Rothstein<sup>1</sup>

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In this talk, we present the results of a series of non-linear oscillatory shear rheology measurements with the goal of discovering a clear difference in the response of linear and branched wormlike micelle solutions. We perform and compare the results of two different non-linear rheometry techniques: large amplitude oscillatory shear (LAOS) and orthogonal superposition rheometry. In the first, the applied strain of an oscillatory cycle is increased and the non-linear response of the fluid is observed. In the second, a small amplitude oscillatory shear flow is superimposed over a steady shear flow in a direction orthogonal to the applied shear rate. The experiments are performed using a series of linear and branched wormlike micelle solutions consisting of sodium oleate (NaOA) and octyl trimethyl ammonium bromide (C8TAB). The ratio of NaOA to C8TAB is varied from 85/15 to 70/30 while the total surfactant concentration is varied from 2% to 8%. The steady shear rheology of the wormlike micelle solutions is found to demonstrate a maximum in shear viscosity with increasing surfactant concentration or with increasing fraction of C8TAB. It has been shown through Cryo-TEM imaging that the maximum observed in the shear viscosity corresponds to the transition from linear entangled to branched micelles. Both the LAOS and the orthogonal superposition measurements show a loss of viscosity and elasticity for both the linear and branched wormlike micelles with increasing shear rate and applied strain. A clear distinction in the response of the linear and branched wormlike micelle solution is observed - the viscosity, relaxation time and elastic modulus of the branched systems are found to decay much more rapidly with increasing strain and shear rate. These results are most likely due to the additional stress relief mechanisms available to branched micelles; namely the fast and fluid sliding of branch points along the length of the micelle and the 'ghost-like' crossings of micelles at entanglement points.

Tuesday 4:25 Constellation E

SA12

**Effect of branching on shear banding in wormlike micelles (WLMs) under large amplitude oscillatory shear (LAOS)**Michelle A. Calabrese, Norman J. Wagner, and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States*

A model series of wormlike micelles (WLMs) with controlled levels of branching is studied to determine the effect of branching on the large amplitude oscillatory shear (LAOS) rheological response. The degree of branching in the mixed cationic/anionic surfactant (CTAT/SDBS) system is controlled via the addition of the hydrotropic salt sodium tosylate (Schubert et al., Langmuir, 2003) and is corroborated by cryo-TEM, SANS, and linear viscoelastic rheological measurements. Using 1-2 plane spatially resolved flow-SANS and rheo-SANS (Gurmon et al., JoVE, 2014), we identify different mechanisms of dynamic shear banding under LAOS that depend on the degree of micellar branching. In samples with low branching, shear bands consist of an inner band that flows in response to the applied strain rate coexisting with an outer band that responds in phase with the applied strain, consistent with recent observations (Fardin et al., Rheol Acta, 2014) and theoretical predictions (Stickel et al., JOR, 2013). For moderate levels of branching both bands flow and respond nearly in phase with applied strain rate. For higher levels of branching, no shear banding under LAOS is observed. This behavior under LAOS is consistent with reported observations under steady shear (Calabrese et al., submitted to JOR 2015; Calabrese et al., in preparation). This research quantitatively links micellar microstructure to the measured dynamic shear rheology of WLM solutions, providing insight into the formation of dynamic flow instabilities and shear-induced microstructures.

Tuesday 4:50 Constellation E

SA13

**Testing shear-induced breakage as the mechanism of shear banding for linear wormlike micelles**Peng Cheng, Gary Leal, and Matthew E. Helgeson*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

Shear banding of wormlike micelles (WLMs) involves spontaneous development of regions with distinct velocity gradient in geometries approximating simple shear flow, and is typically attributed to mechanical instability due to a non-monotonic constitutive curve. Unlike other contemporary models to predict shear banding of WLMs, the Vasquez-Cook-McKinley (VCM) constitutive model incorporates the unique physics of dynamic scission and reforming of WLM chains. Although fits of the VCM model to experimental data have shown agreement with rheological measurements and qualitatively predict experimentally observed behavior of shear banded flows, it has yet to be directly validated against independent experimental measurements (e.g., flow velocimetry, structural measurements, etc.). Here, we report a combination of rheology, flow velocimetry, and small angle neutron scattering (SANS) measurements in Taylor-Couette flow to rigorously test the ability of the VCM model to quantitatively describe shear banded flows of linear WLMs. We find that the VCM model successfully captures both the WLM rheology and flow kinematics at steady state. In particular, with increasing geometry curvature, the model successfully captures an expansion of the envelope of critical shear rates for banding. However, as with other models for shear banding, the predicted time scale to achieve steady state banding is at least an order of magnitude smaller than what is observed experimentally. We hypothesize that this is due to limitations of the model in capturing the spectrum of relaxation times reflected in the true length distribution of the micelles. To test this hypothesis, we carry out SANS measurements of the local length distribution of micelles with systematically varying average contour length, and compare this with coarse-grained distributions predicted by the VCM model. Finally, we propose adaptations to the model to better reflect the underlying equilibrium and non-equilibrium length distributions of micelles.

Tuesday 5:15 Constellation E

SA14

**Structural dynamics of lamellar surfactant solutions in planar extensional flow**Binbin Luo and Wesley R. Burghardt*Northwestern University, Evanston, IL, United States*

We report in situ x-ray scattering investigation of the structure of aqueous lamellar surfactant solutions in planar extensional flow. Samples were studied in a cross-slot stagnation flow cell fed by a syringe pump using a highly collimated synchrotron x-ray beam that provides for spatially resolved measurements of fluid structure in the stagnation region of the flow. Prior attempts to use planar stagnation flows for either x-ray or neutron scattering employed low-aspect ratio flow geometries in which the kinematics are dominated by parasitic velocity gradients along the incident beam direction. In contrast, our cross-slot flow cell employs an aspect ratio of 5:1, providing a much more ideal two-dimensional extensional flow field in the stagnation region. This device has been used to study two different lamellar surfactant systems. Both displayed induced alignment for the mesophase structure, but one being more persistent than the other and hardly relax after flow cessation. The impacts of flow upon degree of orientation and d-spacing are different in the two systems.

Tuesday 5:40 Constellation E

SA15

**Rheology of multilamellar vesicle (“onion”) formation and instability**Norman J. Wagner<sup>1</sup>, Luigi Gentile<sup>2</sup>, and Ulf Olsson<sup>2</sup><sup>1</sup>*University of Delaware, Newark, DE 19716, United States;* <sup>2</sup>*Division of Physical Chemistry,, Lund University, Lund SE-221 00, Sweden*

Soft matter often shows a complex rheological behavior with significant shear induced structural transformations on the colloidal length scale. A striking example can be found in surfactant lamellar phases with the reversible planar lamellae to multi-lamellar vesicle (MLV or "onion") transition. Here, we combine rheology, light and neutron scattering to develop a more fundamental understanding of how MLVs form during flow

start up from a lamellar phase (Gentile et al. Langmuir, 30 8316 (2014)). A critical strain and critical capillary number based on the MLV viscosity are demonstrated for MLV formation, criteria that are shown to be robust. MLV formation is shown to involve a buckling transition, but the instability is three-dimensional in simple shear flow. Unstable temporal viscosity behavior, with periodic oscillations, has recently been observed in a nonionic surfactant lamellar phase system under steady shear (Gentile et al. Soft Matter 9 1133 (2013)). Remarkable viscosity oscillations are observed at lower shear rates at the lamellar-to-MLV transition. A steady, alternance behavior evolves as a steady state at the applied shear rate of 2 s<sup>-1</sup>. Time-resolved and spatially-resolved rheo-small angle neutron scattering (SANS) experiments were performed to reveal a correlation between the periodic stress oscillations to a periodic fluctuation in the microstructure of the fluid. The stress oscillations are accompanied by oscillations in the MLV and planar lamellae fractions.

## Symposium BM

### Biological Macromolecules: Proteins, Cellulosic Biomass and other Biomaterials

Organizers: Jai A. Pathak and Patrick Underhill

Tuesday 1:30 Constellation F

BM21

#### Molecular-mechanical link in a shear-induced self-assembly of a functionalised biopolymeric fluid

Galina E. Pavlovskaya and Thomas Meersmann

*Sir Peter Mansfield Imaging Centre, University of Nottingham, Nottingham, Nottinghamshire NG7 2RD, United Kingdom*

$\kappa$ -carrageenan is a linear sulphated anionic polysaccharide extracted from edible red seaweeds. It is widely used in food sciences, pharmaceutical industry, biotechnology, tissue engineering, medical applications and is also used in some unconventional areas like marbling. Mechanical behavior of the 0.5% carrageenan fluid changes from Newtonian (313K) to shear-thinning (283K). This mechanics is presumably correlated with conformational changes experienced by these biomacromolecules upon cooling. Therefore novel <sup>23</sup>Na MQF rheo-NMR [1] methods were applied to establish this molecular-mechanical link.

The fluid was sheared in 1 mm gap at different flow rates in a Couette cell mounted inside 9.4T magnet. Temperature was varied from 285K to 313K with a range of flow rates sampled at each temperature. <sup>23</sup>Na nucleus frequency was used for the NMR signal detection in all experiments. We were able to demonstrate that <sup>23</sup>Na DQF MA and TQF signals were observed only in the presence of shear, however at 313K <sup>23</sup>Na MQF signals were absent with and without shear field. We have also shown a significant change in sodium dynamics under shear with the increase of flow rate and temperature. We also performed bulk rheological measurements of this fluid for all temperatures used in this study. We were able to correlate the detection of <sup>23</sup>Na MQF signals with the presence of flow-induced molecular alignment occurring only with macromolecules present in rod conformation.

Sodium is an important nucleus as it is naturally present in many biological systems including human bodies. The use of this methodology in vivo will better our understanding of mechanics of body fluids and their molecular behavior under shear. This could impact anti-cancer drug delivery and management of other life-threatening diseases.

[1] Pavlovskaya, GE; Meersmann, T, JPCL, 5(15), 2632-2636, (2014).

Tuesday 1:55 Constellation F

BM22

#### In-line rheological characterization of wood polymer composites

Valentina Mazzanti<sup>1</sup> and Francesco Mollica<sup>2</sup>

<sup>1</sup>Engineering, University of Ferrara, Ferrara, Italy; <sup>2</sup>University of Ferrara, Ferrara, Italy

Wood plastic composite (WPC) is a material composed of a thermoplastic matrix filled with wood flour. WPC is considered sustainable because it can be made using recycled plastics and waste products of the wood working industry. It is highly resistant to wet environment and the products can be manufactured rapidly and with freedom of shape using forming techniques that are typical of thermoplastics, such as extrusion or injection molding. In this study, commercial PP-based WPCs filled with various percentages of wood fibers (30 -70wt.%) have been investigated with a rheometer in oscillation mode at 170°C. This temperature is imposed by the requirement of performing the test within the linear viscoelasticity region, but the data that are measured are not directly useful for processing, as a convenient processing temperature should be in the range 180 - 195°C. In order to obtain the WPC viscosity at such temperatures, a model that uses the WPC viscosity measured at 170°C at different fibers quantity and of neat PP viscosity measured at various temperatures is proposed. The main hypothesis of this model is that the effects of temperature and filler content on the composite viscosity are disjoint. These measurements permit to obtain shift factors that allow to estimate the WPC viscosity using neat PP viscosity, temperature and fibers volume fraction. In order to validate the model, 30 and 70wt% WPC flow curves at 195°C have been measured with a process rheometer, in a setting that is similar to processing conditions. The slit die (50 x 105 mm) is directly connected to a single screw extruder. Three pressure transducers are flush mounted along the slit and three different slit heights are used for the Mooney procedure. The results show that the viscosity curve for the 30wt.% WPC validates the model with a reasonably good agreement while the agreement for the 70wt.% is questionable. The presence of an yield stress in the 70wt.% material appears to be the most probable cause and is studied in greater detail.

Tuesday 2:20 Constellation F

BM23

**Relative humidity as a new parameter in rheological testing**Joerg Laeuger and Gunther Arnold*Anton Paar Germany, Ostfildern, Germany*

In addition to temperature and pressure the water content of a sample as well as the relative humidity of the ambient air are important parameter influencing the rheological behavior of many complex fluids such as for example gels, biomaterials, polymeric systems, food products, and adhesives. A combination of a modified convection oven and an external humidity generator enables to work under defined relative humidity (RH) and temperature (T) in the ranges of RH = 5 to 95 % and T = 5 to 120°C. Traditional convection ovens are mainly equipped with electrical heaters. For lower temperatures a cold gas (e.g. LN<sub>2</sub>) is brought into the chamber and the oven heats against the cold gas. In the new humidity system the convection oven is based on Peltier elements allowing to set temperatures below ambient without the need of a cold gas as input to the oven chamber. In order to control the relative humidity a humidity sensor is located in the oven and the external humidity generator provides the needed moisture of the gas flowing into the chamber. The humidity sensor and the humidity generator are fully integrated into the operating software for the rheometer, allowing the programming of combinations of T and RH including ramps in RH at constant T or ramps in T at constant RH, respectively. Various standard geometries like parallel-plate, cone-and-plate, solid bar for torsional DMTA, extensional tools for DMTA and steady extensional rheological testing, a ball on three plate geometry for tribological investigations, as well as a newly designed modified ring geometry. The later consists of two broken rings in which the sample is placed on some small portions of the ring and has the advantage of a large surface to volume ratio, enabling an fast penetration of moisture into the sample. Applications examples in the different geometries show the importance of the relative humidity on the rheological behavior of many complex fluids.

Tuesday 2:45 Constellation F

BM24

**Study of the phase change behavior of food ingredients using rheo-microscopy**Tharanga D. Perera and Gina Paroline*Anton Paar USA, Ashland, VA 23005, United States*

Knowledge of the phase change behavior of food ingredients is critical to product formulation, storage properties, and consumer satisfaction. This is especially true of lipids and hydrocolloids used in food products. This paper focuses on identifying the phase change behavior of several food ingredients as impacted by temperature, accelerated aging, and pressure as well as visualization of the phase changes through combined rheological and microscopic characterization.

Tuesday 3:10 Constellation F

BM25

**Measuring adhesion between uropathogenic E. coli and bladder-epithelial cells**Emily C. Hollenbeck<sup>1</sup>, Lynette Cegelski<sup>2</sup>, and Gerald G. Fuller<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Stanford University, Stanford, CA, United States;* <sup>2</sup>*Department of Chemistry, Stanford University, Stanford, CA 94305, United States*

Bacterial adhesion to host cells is often a first step in the infection process. For example, uropathogenic Escherichia coli, the major causative agent of urinary tract infection, bind to host bladder-epithelial cells and initiate cell invasion. This triggers a subsequent pathogenic cascade characterized by recurrent infection. There is currently growing interest in developing new antimicrobials that, instead of targeting bacterial survival and placing high selective pressure for drug-resistant mutations, target mechanisms promoting infection such as binding to host cells. This new therapeutic strategy requires a detailed understanding of the factors that contribute to bacterial adhesion. To address this issue, we adapted a novel live cell monolayer rheometer recently developed in the Fuller lab to measure adhesion between a monolayer of bladder-epithelial cells and a layer of bacteria. The bacterial strain used in this study is UTI89, a uropathogenic strain of E. coli that is capable of expressing several different extracellular components such as type 1 pili, curli, and cellulose. Using our adapted device, we can quantitatively compare the extent to which these different extracellular components affect bacterial adhesion to the cell monolayer. Additionally, we can use these measurements to assess the effectiveness of various small molecules in preventing binding to host cells.

## Symposium SG

### Solids, Glasses, and Composites

Organizers: Lynden Archer and Anne Grillet

Tuesday 1:30 Baltimore/Annapolis

SG21

**Developing instruments to characterize and mimic building induced fatigue in polymers**Christopher C. White and Don Hunston*Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States*

Buildings Move. Our infrastructure is constructed from steel, concrete and glass, materials with very different thermal expansion coefficients. Every day, every season these massive structures heat and cool, with every expansion and contraction putting the materials holding the building together into complicated strain histories. Additionally, in the past fifty years significant effort and energy has been expended to distinguish the inside from the outside. Typically the most important component of the "seal" is a cured solid polymer, which is subjected to very complex

deformation history. Until recently, there was little effort to understand how this complex strain was affecting the performance of these materials. This work will describe experimental efforts to understand and then mimic how this constant movement affects the properties of the sealant. The characterization of the environmental movement, the characterization of the complex rheology of the sealant, will be presented. Additionally, a series of rheological instruments developed to meet the unique challenges of characterizing and mimicking the in-service conditions will be presented.

Tuesday 1:55 Baltimore/Annapolis

SG22

**The influence of viscoelasticity and surface energy on frictional behavior of elastomers**

Christopher J. Dimitriou

*Polymers R&D - IHM, Nike Inc., Beaverton, OR 97005, United States*

We conduct an in-depth characterization of the triborheological features of different elastomers in their rubbery regime. In particular, we measure some of the key rheological attributes of a thermoplastic polyurethane (TPU), and contrast them to those of a vulcanizate rubber. These bulk rheological measurements are then used to understand differences in how these materials behave from a tribological perspective. Using the universal testing platform of a strain controlled rheometer, several different experimental tests are conducted to rationalize these differences. Shift factors from time temperature superposition can be used to characterize the crosslinked and entangled network within the TPU as a function of temperature and frequency - this affects how the elastomer deforms at an interface with another solid. Pull off/tack tests are used to characterize deformation timescales and the work of adhesion between interfaces consisting of these elastomers. Finally, a triborheological fixture is used to measure the velocity dependence of the coefficient of friction for these materials. The results from this wide variety of tests allow us to account for the differences in the materials' frictional behavior; key insights are gained through a contrast of the materials' viscoelastic master curves and surface energies.

Tuesday 2:20 Baltimore/Annapolis

SG23

**Measuring and modeling the dimensional stability of high density polyurethane foams**

Kevin N. Long<sup>1</sup>, Lisa A. Mondy<sup>1</sup>, Christine C. Roberts<sup>1</sup>, Haoran Deng<sup>2</sup>, Mathew C. Celina<sup>3</sup>, and Rekha R. Rao<sup>1</sup>

<sup>1</sup>Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>2</sup>Materials Science and Engineering, Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>3</sup>Material Science Center, Sandia National Laboratories, Albuquerque, NM 87185-1411, United States

We are concerned with the shape stability of high-density polyurethane foams, both in the near term, to manufacture parts to tolerance, and in the long term, to maintain part shape and size during aging. We are creating a cradle-to-grave finite element modeling framework to predict the effects of process parameters during foam filling, cure, and aging on polyurethane foam dimensional stability over short and long time scales. The polyurethane foam of interest incompletely cures under most relevant processing conditions. To capture this behavior, the evolution of the glass transition temperature with the polymer extent-of-cure was modeled using a DiBenedetto relationship. To parameterize the vitrification model, experiments were performed on foam specimens in different states of cure, including absorbance infrared spectroscopy, digital scanning calorimetry, and oscillatory shear rheology measurements. The cure shrinkage of the matrix phase is also important to the residual stress state of the foamed component, and measurements of a model staple-shaped foam geometry are presented to determine this quantity. The dimensions of the foam are measured with high spatial resolution over months using a coordinate measuring machine. Experimental and simulation warpages are compared over time. Certain model parameter and manufacturing condition sensitivity studies are explored.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Tuesday 2:45 Baltimore/Annapolis

SG24

**The effect of polymer rheological behavior on the morphology and flame retardant behavior of co-extruded multi-layered PP/foamed PP structures**

Sangjin Lee and Joao Maia

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

Polypropylene (PP) foams are interesting for foam applications due to a number of desirable properties such as a comparably low density, relatively high service temperature, good impact strength, and excellent chemical resistance. Thus, PP is a potential candidate for interiors of trains, ships or airplanes, for example. However, PP is very flammable, so it should be improved with flame retardant (FR) particles. In addition, simple foamed polymers normally exhibit poor compressive moduli, which prevents them from being used in structural applications. Recently, however, we have developed a new type of continuously co-extruded multi-layered film/foam composites that possess much improved mechanical properties when compared with simple foams. Herein, the influence of rheological properties of PP/FR composites on the evenness of microcellular morphology of the foam/film structure, resulting in retention of good mechanical and flame retardancy properties is investigated. Two types of PP were used and named as PP1 and PP2, with the latter having a zero-shear viscosity double of the former. The nitrogen/phosphorous based FR particles play the dual role of nucleating agent and flame retardant. The transient extensional viscosity of both PPs and composites was also investigated, and both systems exhibited strong strain-hardening behavior with high Trouton ratio (>3) at all extensional rates. Moreover, PP1 exhibited stronger strain-hardening than PP2. Continuous multi-layered co-extruded sheets were produced with 16 layers, PP1 being used in the foam layers to maintain closed-cell integrity and PP2 in the film layers to contain the cell growth to the foamed layers. The final sheets showed very good and

well defined film/foam morphology with compressive moduli higher than 104 Pa and excellent flame retardancy, even better than simple sheets of solid PP reinforced with the FR particles.

Tuesday 3:10 Baltimore/Annapolis

SG25

### **Evaluating the performance of a stress model of long-fiber suspensions in simple flows**

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

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

Composite materials made of long (>1 mm) fibers in a thermoplastic matrix have been useful in automotive applications, primarily because of their light weight relative to metals and improved mechanical properties relative to short (<1 mm) fiber composites. The fibers' orientation is known to influence the property enhancement, and this makes controlling orientation an important factor in designing molds for injection molded parts.

Several models relating orientation to flow kinematics exist, but all of them make use of empirical parameters to account for fiber interactions. The current procedure for obtaining these parameters is to fit the orientation model to experimental orientation data at some point in the injection molded part. Doing so requires a significant amount of time and material.

Obtaining the orientation model parameters by fitting to the stress response of the composite under simple flows could streamline the process, but this requires coupling the orientation with a stress model. Although current stress models for fiber suspensions do incorporate orientation, few account for additional stress due to elastic bending of the fibers observed in injection molded parts.

The goal of this presentation is to evaluate the performance of a new stress model. This model is based on that proposed by Giesekus for dumbbell models but used in conjunction with the bead-rod fiber orientation model proposed by Strautins and Latz. This new model will be evaluated by comparing the predicted and experimental stress growth of a long-fiber suspension under startup of steady shear and startup of steady planar extensional flows.

Tuesday 4:00 Baltimore/Annapolis

SG26

### **Interaction between long flexible fibers in squeeze flow**

Gleb Meirson and Andrew N. Hrymak

*Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario, Canada*

The mechanical properties of fiber reinforced polymers are highly dependent on fiber orientation. There are many models for fiber orientation calculations available in the literature, however, most of them address the short and rigid fibers and the models which are developed for long flexible fibers are usually implemented in a simple shear flow case.

Long fiber thermoplastics (LFT) is processed both in compression and injection molding operations. In this case, we study the compression molding case through an idealized squeeze flow. The flow inside the mold is characterized as a squeeze flow and its process and material parameters are studied in the effects on fiber orientation. In LFT fibers can easily reach length of 70 mm and higher. Since Jeffery's model was developed for short fibers, models which are based on Jeffery's model can not describe correctly the behavior of LFT system.

In the present research, a long flexible fiber was simulated in a rheometric squeeze flow using a model with elements from the "Bead-Chain" model which treats the fiber as a collection of beads and the "Rod-Chain" model which unites several beads into rods to reduce calculations. In the literature these models are found to be implemented mostly in the simple shear flow case and for a single fiber. Interactions between long flexible fibers are added through incorporating elastic collisions between segments of different fibers into the overall momentum balance, thus allowing to simulate orientation and deformation of systems of fibers.

Tuesday 4:25 Baltimore/Annapolis

SG27

### **Mechanisms of natural fibre breakage during composite compounding: Rheo-optical observations and fibre size distribution study**

Romain Castellani, Erika Di Giuseppe, Tatiana Budtova, and Bruno Vergnes

*CEMEF, Mines ParisTech, Sophia Antipolis 06904, France*

Using natural fibres in composites has become a hot topic due to the gain in density (15-25%) as compared to glass fibres reinforced products, associated with "greener" materials needs. In order to obtain suitable mechanical performances, fibre distribution in the matrix, aspect ratio and adhesion with the polymer must be optimised. However, unlike many manmade fibres (e.g. from synthetic polymers or glass), lignocellulosic ones possess complex compositions (cellulose, lignin, pectin, waxes) and morphologies which depend on their botanical origin. Moreover, their diameters can be altered from thin semi-rigid elementary fibres to thick rigid bundles in which these elementary fibres are "glued" together. The breakage of such fibres during processing is thus much more complex and less understood than that of glass fibres.

In this work we prepared polypropylene-based composites with various lignocellulosic species: hemp (retted and not), flax, sisal and miscanthus. Their bio-chemical characteristics vary considerably from one to another leading to a large spectrum of breakage kinetics and mechanisms.

We used counter-rotating rheo-optical device to observe fibre behaviour under shear: dissociation of bundles, rotation, bending, peeling and breakage. These different mechanisms were correlated to the fibre cellulose and lignin contents. Composites with the same species were also prepared using an internal mixer; fibre size distribution was analysed as a function of specific mechanical energy. We demonstrate how and why

fibre behaviour under shear, breakage kinetics and final dimensions in the composite, are linked to fibre botanical origin and bio-chemical composition.

This work was performed in the frame of ANR (French National Research Agency) project DEFIBREX.

Tuesday 4:50 Baltimore/Annapolis

SG28

### **An ultrasonic approach to study the rheological behavior of raw Asian noodles**

Ali Salimi-Khorshidi<sup>1</sup>, Anatoliy Strybulevych<sup>2</sup>, Daiva Daugelaite<sup>1</sup>, Martin G. Scanlon<sup>1</sup>, John H. Page<sup>2</sup>, and Dave W. Hatcher<sup>3</sup>

<sup>1</sup>Food Science, University of Manitoba, Winnipeg, Manitoba R2N 3V1, Canada; <sup>2</sup>Physics and Astronomy, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada; <sup>3</sup>Grain Research Laboratory, Canadian Grain Commission, Winnipeg, Manitoba R3C 3G8, Canada

Rheological behavior of Asian noodles has been well correlated with the textural attributes of this widely consumed product which can be evaluated by sensory techniques and empirical tests in commercial noodle factories. Although useful for evaluating differences in noodle quality, sensory and empirical tests supply no useful information about the rheological parameters responsible for the viscoelastic behavior of raw Asian noodles. To address this need, a newly developed longitudinal ultrasound technique at 1.4 MHz was employed to determine the rheological characteristics of raw noodles including longitudinal storage modulus ( $M'$ ), longitudinal loss modulus ( $M''$ ), as well as loss tangent ( $M''/M'$ ). Using customized transducer assemblies attached to a commercial texture analyzer enabled stress relaxation measurements, for determination of Peleg's fundamental rheological parameters  $k_1$  and  $k_2$ , as well as stress relaxation and elastic index (EI), to be acquired concurrently with ultrasonic measurements. In subsequent additional tests, Young's modulus (E), apparent extensional viscosity (AEV) and apparent extension ratio (AER) were determined by Kieffer extensibility measurements. Ultrasonic velocity and attenuation, and the rheological parameters derived from them, were shown to be sensitive to the changes in viscoelastic behavior of raw Asian noodles caused by manipulating the protein network developed during the dough sheeting process. For example, more solid-like behavior of raw Asian noodles was apparent when a stronger protein network, with more cross-links between protein chains, was created by the work input during sheeting. Good correlations ( $r^2=0.71-0.85$ ) between parameters derived from ultrasonic measurements and those from conventional rheological tests were obtained, confirming the capability of the ultrasound technique as a reliable, fast and inexpensive means of evaluating the changes in rheological behavior of Asian noodles with the potential for measuring the properties of similar viscoelastic systems.

## **Symposium NF Non-Newtonian Fluid Mechanics**

Organizers: Paulo Arratia and R Sureshkumar

Tuesday 1:30 Frederick/Columbia

NF21

### **How elastic flow instabilities can induce motion in flexible solid structures**

Anita A. Dey and Jonathan P. Rothstein

*Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003, United States*

When a flexible object such as an elastic sheet is placed in a flow of a Newtonian fluid, the shedding of separated vortices at high Reynolds number can drive the motion of the structure. This phenomenon is known as Fluid Structure Interactions (FSI) and has been studied extensively for Newtonian fluids. If the same flexible object is placed in non-Newtonian flows, however, the structure's response is still unknown. Unlike Newtonian fluids, the flow of viscoelastic fluids can become unstable at infinitesimal Reynolds numbers due to a purely elastic flow instability. In this talk, we will investigate the fluid structure interaction between a wormlike micelle solution at high Weissenberg number and a flexible elastic sheet in cross flow. Elastic flow instabilities have been observed for wormlike micelle solutions in a number of flows including flow into a contraction and flow past a circular cylinder. Here we will study what happens when elastic flow instabilities occur in the vicinity of a thin flexible polymer sheet. We will show that the time varying fluid forces exerted on the structure can grow large enough to cause a structural motion which can in turn feed back into the flow to modify the flow instability. The static and time varying displacement of the flexible sheet including its oscillation frequency and amplitude will be presented for a series of flexible sheet oriented at different angles to the flow direction, for varying fluid flow rates, and for varying fluid compositions and properties. In addition, measurements of velocity profiles and flow induced birefringence will be presented in order to quantify the time variation of the flow field and the state of stress in the fluid.

Tuesday 1:55 Frederick/Columbia

NF22

### **Non-Newtonian swirling flow near an infinite stationary disk**

Bikash Sahoo<sup>1</sup>, Robert van Gorder<sup>2</sup>, and Helge Andersson<sup>3</sup>

<sup>1</sup>Mathematics, National Institute of Technology Rourkela, Rourkela, Odisha 769008, India; <sup>2</sup>Mathematics, University of Central Florida, Florida, FL, United States; <sup>3</sup>Energy and process engineering, Norwegian University of Science and Technology, Trondheim, Norway

The steady revolving flow of a non-Newtonian Reiner-Rivlin fluid near an infinite stationary disk is studied. The momentum equations give rise to a system of highly nonlinear boundary value problems. Attempt has been made to study the properties of the solution of the momentum equations analytically before proceeding for the numerical solution. The effects of non-Newtonian fluid characteristic on the velocity field have been discussed in detail and are shown graphically. It is interesting to find that the radial component of velocity is negative near the disk and reverses

direction away from the disk. It is clear that the increase in the values of  $K$  (non-Newtonian cross-viscous parameter) decreases the radial component of velocity in magnitude up to a significant distance from the disk and then increases and eventually reaches the asymptotic value zero. Moreover, it is observed that the magnitude of the transverse component of velocity decreases with increasing  $K$  near the disk and increases away from the disk. This accounts for a crossover of the velocity profiles.

Tuesday 2:20 Frederick/Columbia

NF23

### **Slow flow of a Boger fluid around a solitary cylinder**

David F. James, Terence Shiau, and Peter Aldridge

*Mechanical & Industrial Engineering, University of Toronto, Toronto, Canada*

The effect of elasticity on the flow around a solitary cylinder was investigated by measuring the drag on the cylinder and by mapping the flow field using PIV. The flow field was created by partially immersing a small vertical cylinder in a fluid contained in an open annular tank rotating on a turntable. The measurements were made with cylinders of various diameters and with both Newtonian and Boger fluids. To isolate the cylinders, the ratio of cylinder diameter to annular width was small, varying from 1/40 to 1/300. The Reynolds numbers were much less than unity so that the only relevant fluid properties were viscosity and elasticity. Corrections for end effects were made by varying the depth of immersion, and corrections for wall effects were made by using Faxen's formula. With the Newtonian fluids, the drag data and Kaplun's Stokes-flow prediction agree. The relaxation times of the Boger fluids were determined from N1 data. With all cylinders and both Boger fluids, the drag equalled Newtonian values for Deborah numbers up to about 0.6, and then rose above. At  $De \sim 3$ , the drag due to elasticity equalled that due to viscosity, and at  $De \sim 100$ , the elastic drag was several times the viscous drag. The PIV data revealed that the extensional rates and strains were so small that extensional stresses were negligible. The shear rates were high enough that the normal stresses generated by shearing likely caused the drag due to elasticity.

Tuesday 2:45 Frederick/Columbia

NF24

### **The effect of fluid rheology on slot die coating**

Sunil Khandavalli and Jonathan P. Rothstein

*Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003, United States*

Roll-to-roll coating of thin films and roll-to-roll patterning of small-scale features on a rapidly moving web is an industrially important process with a broad range of commercial applications both old and new. We will explore the effect of fluid rheology on slot die coating. In slot die coating fluid is extruded from a rectangular slit and applied continuously to a moving web. The focus of this talk will be the effect of shear thickening and shear thinning on the operating window of slot die coating. The shear thickening systems used in the study are colloidal dispersions of silica nanoparticles in PPG. We will present both shear and extensional rheology characterization for all fluids tested. For the slot die coating experiments, a home build slot die coating head was used. The flow rate and web speed were varied over a wide range so that the stable coating window could be observed and the flow instabilities at high rates could be characterized for the test fluids. The effect of shear-thickening and shear-thinning behavior on the operating window will be presented and compared the results for Newtonian fluids. Different coating defects observed outside the operating window based on the fluid rheology and their evolution during the coating process studied through high speed camera will be presented. The shape and stability of the coating bead in relation to different types of coating defect associated with the fluid rheology will also be discussed.

Tuesday 4:25 Frederick/Columbia

NF26

### **Flow instability in a micro-cavity swept by a visco-elastic fluid**

Hiroshi Suzuki<sup>1</sup>, Ruri Hidema<sup>2</sup>, and Yoshiyuki Komoda<sup>1</sup>

<sup>1</sup>*Department of Chemical Science and Engineering, Kobe University, Kobe, Hyogo 657-8501, Japan;* <sup>2</sup>*Organization of Advanced Science and Technology, Kobe University, Kobe, Hyogo 657-8501, Japan*

Instability of the visco-elastic fluid sweeping a micro-cavity mounded in one side between parallel plates has been investigated in order to develop a micro-mixing device using elastic instability of the visco-elastic fluid. The cavity depth were fixed at 0.2mm, whole the cavity length was changed from 0.25 to 1mm. As a visco-elastic fluid, a cationic surfactant system was used. The flow visualization experiments were performed under the condition where the Reynolds number based on the solvent viscosity and the cavity depth was ranged from 0.1 to 50. From the results, it was found that the tonguing motion instability of the separate bubble was formed in the downstream region of the cavity. It appeared at the same Reynolds number independently of the cavity length. The bulge instability also appeared in the upstream region of the cavity. It was found that the reattachment length and the separation bubble size don't depend on the cavity length. Then, the flow instability appearing in the downstream region approached to the upstream region when the cavity length decreases and the connected with the bulge instability observed in the upstream region. Thus, the effective micro-mixing region was expanded by the cavity length decrease under the present conditions.

Tuesday 4:50 Frederick/Columbia

NF27

**Numerical simulation of the flow of an asymmetric magnetic fluid in a driven cavity**Yuri D. Sobral<sup>1</sup>, Ataias P. Reis<sup>1</sup>, Camila O. Vieira<sup>1</sup>, and Francisco R. Cunha<sup>2</sup><sup>1</sup>*Departamento de Matematica, Universidade de Brasilia, Brasilia, DF 70910-900, Brazil;* <sup>2</sup>*Departamento de Engenharia Mecanica, Universidade de Brasilia, Brasilia, DF 70910-900, Brazil*

In this work, we perform a numerical study of the flow of a magnetic fluid in a lid-driven cavity under the influence of an external magnetic field. The governing equations of ferrohydrodynamics are presented and the relevant physical parameters, the hydrodynamic and the magnetic Reynolds numbers, are obtained. The magnetic fluid can be modelled both as a symmetrical as well as an asymmetrical fluid, for which we have to propose a constitutive equation for its magnetization. This constitutive equation will assume that the moment dipole is fixed on the particle, as  $t_{\text{Neel}} \gg t_{\text{flow}}$ . A definitive equation for the evolution of the magnetization is still an open problem, so we investigate some equations available on the literature. The governing equations are discretized using a second order finite difference scheme and are solved by a projection method adapted to take into account the coupled hydrodynamics - magnetostatic equations. Results concerning the stability of the flow as a function of the external magnetic field are presented, as well as an analysis of the bifurcations of the streamlines according to changes in the magnetic parameters.

Tuesday 5:15 Frederick/Columbia

NF28

**Investigation of nail enamel properties utilizing rheology, indentation, and scratch testing**Prajakta A. Kamerkar and Pierre Morel*Anton Paar USA, Ashland, VA 23005, United States*

Coatings are traditionally studied for industrial applications. More and more coatings and coating processes are found in personal care products. This paper focuses on characterization of nail enamel from the bottle to the final hard exterior coating on the nail. Rheological properties are used to characterize the coating and characteristics under varying temperature, humidity, and UV conditions. Nanoindentation is used to measure mechanical properties of the cured coating following various accelerated aging processes. Adhesion and scratch resistance of the coating are evaluated via scratch testing. Correlations between pre-cure rheology, curing behavior, mechanical properties and adhesion characteristics are analyzed.

Tuesday 5:40 Frederick/Columbia

NF29

**Nonlinear nanorheology of hydration layer**Wonho Jhe*Physics, Seoul National University, Seoul, Republic of Korea*

We present experimental and theoretical results on the nonlinear rheology of hydration water layer where the high shear rate is made up to  $10^7$  1/s by using the noncontact atomic dynamic force microscopy. In particular, we observe that the elasticity-induced instability produces the enhanced flow resistance. Our results provide a new insight to nonlinear rheology and give a deeper understanding on a viscoelastic fluid system where the hydration layer plays a key role.

## Wednesday Morning

### Symposium PL Plenary Lectures

Wednesday 8:30 Constellation D-F

PL3

#### **Flow in disordered systems: From simple fluids to athermal solids**

Mark O. Robbins<sup>1</sup>, Joel Clemmer<sup>1</sup>, Vikram Jadhao<sup>1</sup>, and K. M. Salerno<sup>2</sup>

<sup>1</sup>Physics, Johns Hopkins University, Baltimore, MD 21218, United States; <sup>2</sup>Sandia National Laboratory, Albuquerque, NM, United States

The talk will describe nonequilibrium molecular dynamics (MD) simulations of flow in disordered systems, following the evolution of stress-strain-rate curves, conformational changes, and spatial correlations as systems are quenched from simple fluids through the glass transition and to athermal solids. First the shear-thinning response of simple binary Lennard-Jones fluids, small molecules and the lubricant squalane are followed over more than 5 orders of magnitude in strain rate while the system is driven through the glass transition by varying temperature or pressure. When the full range of rates is considered, one finds inconsistencies with simple time-temperature superposition or power law shear-thinning. Theoretical and experimental stress-strain-rate curves for squalane are compared at room temperature for pressures from ambient to 1 GPa as the Newtonian viscosity rises from  $10^{-2}$  to  $10^4$  Pa·s. Results for strain rates from 10 to  $10^{10}$  s<sup>-1</sup> fit an Eyring model with a constant shear stress. The implications for models of elastohydrodynamic lubrication will be discussed. The second part of the talk will describe the extreme athermal limit where the system evolves through mechanical instability rather than thermal activation. In the thermodynamic limit, there is a yield stress followed by a power law rise in shear stress with strain rate. The power law is related to critical exponents describing a diverging correlation length and a power law distribution of avalanches as the system approaches the quasistatic limit. The connection to the high rate response near the glass transition will be discussed as well as anomalous diffusion due to power law spatial correlations.

### Symposium SC Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Wednesday 10:00 Constellation C

SC31

#### **Transient yield in reversible colloidal gels: A micro-mechanical perspective**

Lilian C. Johnson, Benjamin J. Landrum, and Roseanna N. Zia

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

We study the nonlinear rheology of colloidal gels via large-scale dynamic simulation, with a view toward understanding the micro-mechanical origins of the transition from solid-like to liquid-like behavior during flow startup, and post-cessation relaxation, and its connection to energy storage and viscous dissipation. Such materials often exhibit an overshoot in the stress during startup, but the underlying microstructural origins of this behavior remain unclear. To understand this behavior, a fixed strain rate is imposed on a reversible colloidal gel, where thermal fluctuations enable quiescent gel aging. It has been suggested flow occurs only after clusters first break free from the network and then disintegrate, leading to two stress peaks that vary with age, flow strength, volume fraction, bond strength, and pre-strain history. However, our detailed studies of the microstructural evolution during startup challenge this view. We present a new model of stress development, relaxation, and microstructural evolution in reversible colloidal gels in which the ongoing age-coarsening process plays a central role.

Wednesday 10:25 Constellation C

SC32

#### **The mechanics of particle bonds and the elastic modulus of cluster gels**

Eric M. Furst and Kathryn A. Whitaker

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

The rheology and stability of colloidal depletion gels affects the applications and shelf-life of materials and products ranging from paints, foods, and personal care products to pharmaceuticals and agrochemicals. Processes occur over multiple length scales that contribute to the rheology of gels, including their elastic modulus and yield stress. These processes include the nanometer-scale colloidal interactions of "bonds" that stretch and rupture to the formation, deformation, and break-up of percolating micro-structures throughout the material. In this talk, I will discuss the direct measurement of the colloidal forces that constitute the rupturing of the physical bonds between particles in a gel. Thermal rupture force distributions are measured by averaging many approach and retraction bond rupturing cycles between pairs of particles [1]. By connecting these bond-level mechanics to the bulk rheology to in a single model depletion gel material [2], we gain unique insight into the relationship between non-equilibrium gel states, the underlying phase behavior of colloidal suspensions, and the mesoscale mechanics that ultimately govern the elasticity and breakup of colloidal depletion gels.

[1] Swan, J.; Shindel, M.; Furst, E. M. Measuring Thermal Rupture Force Distributions from an Ensemble of Trajectories. *Phys. Rev. Lett.* 2012, 109, 198302. [2] Hsiao, L. C.; Solomon, M. J.; Whitaker, K. A.; Furst, E. M. A Model Colloidal Gel for Coordinated Measurements of Force, Structure, and Rheology. *J. Rheology*, 2014, 58, 1485-1504.

Wednesday 10:50 Constellation C

SC33

### **Aging and nonlinear rheology of thermoreversible colloidal gels**

Melissa B. Gordon, Christopher J. Kloxin, and Norman J. Wagner

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

Colloidal dispersions are found in a wide variety of consumer products such as paint, food and pharmaceuticals. Despite their abundance, the behavior of these systems is often complex and further study of colloidal dispersions is vital to establish processing conditions as well as to determine and predict stability and shelf-life. As a model system, we are investigating gel formation and aging in a thermoreversible gel consisting of octadecyl-coated silica nanoparticles suspended in n-tetradecane. In this system, the octadecyl brush can undergo a phase change allowing the attractions between particles to be tuned by temperature (1,2). By probing the system with steady shear and large amplitude oscillatory shear, we have studied the effect of thermal history and shear history on gel formation and gel mechanical properties during aging. Gels were formed by approaching a common temperature from above and below to determine a reference state from which creep tests were conducted. Creep ringing was observed as expected for the viscoelastic gel. The rheological aging is interpreted in terms of the gel microstructure formed with differing thermal and shear histories to determine how processing affects structure. Recently proposed scaling laws for the rheology and structure under flow are explored within the context of gel aging (3). Through rheological and microstructural measurements, we will further the understanding of gel formation and aging in this model system which may be applied to processing conditions in an industrial setting.

1. Eberle, A.P.R., Wagner, N. J., Akgun, B. & Satija, S. K. *Langmuir* 26, 3003-3007 (2010). 2. Eberle, A.P.R., Castañeda-Priego, R., Kim, J. M. & Wagner, N. J. *Langmuir* 28, 1866-1878 (2012). 3. Eberle, A.P.R., et al., *Physical Review E*, 89, 050302 (2014).

Wednesday 11:15 Constellation C

SC34

### **The formation of structures in anisotropic colloidal glasses and gels containing weakly adsorbing polymers**

Suhagini Kishore<sup>1</sup> and Surita R. Bhatia<sup>2</sup>

<sup>1</sup>*Chemical Engineering, University of Massachusetts-Amherst, Amherst, MA 01003, United States;* <sup>2</sup>*Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY 11973, United States*

The aim of this work is to understand the formation of large-scale structures in an anisotropic colloidal system with weakly adsorbing polymers and its influence on the macroscopic properties of the system. Techniques like rheology, ultra-small angle neutron and x-ray scattering (USANS and USAXS) were combined to study systems containing Laponite RD and polyethylene oxide (PEO). Aqueous dispersions of Laponite form a repulsive colloidal glass with time. Nanometer to micron-sized aggregates form with the addition of PEO chains larger than the minimum required for polymer-clay bridging. Below this critical molecular weight, the addition of smaller chains result in the melting of the repulsive colloidal glass and no large-scale structure is observed. Additionally when the polymer chain number density increases we observe non-monotonic changes in the density of the structures, thus indicating that in these aging systems the characteristic nature of these structures is not only dependent on polymeric interactions but they also depend on the transient cluster re-arrangements that take place more frequently during the early aging phase of these systems. Through rheology, we observe the variations in the viscoelastic moduli ( $G'$  and  $G''$ ) which can be correlated with the changes in the low- $q$  power law exponent extracted from an x-ray and neutron scattering experiment.

Wednesday 11:40 Constellation C

SC35

### **Reversible structure formation in aluminum trihydroxide/PDMS dispersions**

Christopher J. Cox<sup>1</sup>, Timothy D. Fornes<sup>1</sup>, and Saad A. Khan<sup>2</sup>

<sup>1</sup>*Chemical Research, Lord Corporation, Cary, NC 27511, United States;* <sup>2</sup>*Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

Filled polymer systems based on thermally conductive particles are commonly employed in industry to greatly improve the efficiency and reliability of electronic devices. One such filled polymer system used in high performance applications consists of a thermosetting silicone fluid filled with aluminum trihydroxide (ATH). To better understand the flow behavior of this system during processing, a model system consisting of ATH and polydimethylsiloxane (PDMS) has been investigated using dynamic oscillatory rheometry. We observe that miniscule amounts of water when present in this system can dramatically cause the once readily flowable material to immediately exhibit strong gel-like behavior. At intermediate ATH loadings of ~20 vol%, and in the absence of water, the ATH/PDMS system exhibits some flocculation. The weak gel-like behavior can likely be attributed to van der Waals interactions and hydrogen bonding between the dispersed ATH particles. However, upon addition of low concentrations of water, a transition to a strong physical gel is observed indicating a fully flocculated network structure. The observed transition is accompanied by a five orders of magnitude increase in elastic modulus ( $G'$ ) and is thought to be the result of strong hydrogen bonding between hydration layers present at the ATH particle interfaces. This presentation will review the aforementioned results and provide detailed insight into the possible structure-property mechanism responsible for the observed behavior. Additional discussion will be dedicated to materials, e.g., molecular sieves (zeolites), which greatly influence hydrogen bonding in this system and contribute to the reversibility of the observed structure formation.

## Symposium SM Polymer Solutions and Melts

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Wednesday 10:00 Constellation D

SM31

### **Nonequilibrium thermodynamic modeling of semi-dilute polymer solutions**

Soroush Hooshyar and Natalie Germann

*Fluid Dynamics of Complex Biosystems, TUM, Freising 85354, Germany*

Although shear banding is a ubiquitous phenomenon observed in soft materials, the mechanisms that induce the formation of a shear band are not always the same. In this talk, we present a thermodynamically consistent two-fluid model for semi-dilute polymer solutions. A recently developed two-fluid approach (1-2) was adopted to account for the Fickian diffusion and the stress-induced migration. Because the polymeric constituents are allowed to diffuse locally, it is possible to predict the shear band formation realistically. Within the developed model, the Giesekus model was used to describe the conformational dynamics of the polymers. An additional relaxation term was added in an ad hoc fashion to predict the upturn of the flow curve at high shear rates. Sample calculations performed in the cylindrical Couette geometry are discussed here. As a result of the calculations, we found that the steady-state solution is unique for different initial conditions and independent of the deformation history. Furthermore, we observed that the stress-induced migration is responsible for the shear band formation. Because of its simplicity, the developed model is a good candidate for future benchmark simulations.

1) N. Germann, L.P. Cook, and A.N. Beris, JNNFM, (207):21-31, 2014. 2) N. Germann, L.P. Cook, and A.N. Beris, JNNFM, in preparation.

Wednesday 10:25 Constellation D

SM32

### **Towards a better understanding of shear flow cessation from experimental and slip-link model comparison**

Thomas B. Schweizer<sup>1</sup>, Maria Katzarova<sup>2</sup>, and Jay D. Schieber<sup>2</sup>

<sup>1</sup>*Institute of Polymers, ETH Zurich, Zurich CH-8093, Switzerland;* <sup>2</sup>*Center for molecular study of condensed soft matter, IIT, Chicago, IL 60616, United States*

The understanding of flow phenomena following cessation of shear flow is important to gauge rheological models and to understand processing. 70 years after Weissenberg presented his rheogoniometer, these measurements are still a challenge to the rheologist. Normal forces distort the sample's edge and open the rheometer gap. This induces a small radial flow and adds an additional time scale to the experiment, the axial response time. The shape of the sample's edge is a critical factor in the course of an experiment. Any deviation from the ideal spherical shape leads to an inhomogeneous flow profile. Even worse, the non-sphericity of the edge is augmented by normal stresses. Based on data from a monodisperse polystyrene melt and a solution of monodisperse polystyrene in DEP, this presentation elucidates which rheometric parameters are most affected by experimental deficiencies. The discussion is founded on a comparison with an ideal experiment, namely predictions with the slip-link model. This data is free of the aforementioned experimental errors since the only two model parameters are obtained from the dynamic modulus of the monodisperse fluid.

To reduce the impact of edge fracture on the rheological data, the cone partitioned-plate technique has been used. The melt data has been acquired on the two-partitions MTR25 rheometer. In spite of its high stiffness, comparison with the slip-link model shows the data still suffer from compliance effects. The solution has been tested on the triple-partitioned CPP3 cell mounted on a commercial MCR502. In spite of the lower stiffness of this rheometer, the results appear reasonable. This could be explained by the fact that the ratio of the reptation time of the fluid to the axial response time of the rheometer is proportional to the entanglement molecular weight of the fluid.

From the comparison of the experiments with the slip-link model, a recommendation is given on how the best non-linear experiments can be obtained for a given stiffness of the rheometer.

Wednesday 10:50 Constellation D

SM33

### **Influence of chain stiffness on the thermal and rheological properties of polycarbonate copolymers**

Manojkumar Chellamuthu

*Materials Science, SABIC, Mt. Vernon, IN 47630, United States*

The current market trends in automotive lighting require materials with superior thermal resistance and optimal flow properties. Therefore, a detailed structure-property analysis is critical to meet these challenging requirements. In this talk, the thermal and rheological properties of a novel PC copolymer resins will be discussed. The main goal of this talk is to address the role of molecular modification on the entanglement density of polycarbonate copolymers and their consequences for the rheological and thermal properties. In particular, the relationship between glass transition temperature ( $T_g$ ) and entanglement density as a function of co-polymer content will be evaluated.

Wednesday 11:15 Constellation D

SM34

**Effect of hydration on the mechanical performance of anion exchange membranes**Benjamin R. Caire, Melissa A. Vandiver, Andrew M. Herring, and Matthew W. Liberatore*Chemical and Biological Engineering, Colorado School of Mines, USA, Golden, CO 80401, United States*

Anion exchange membranes facilitate ion transport in polymer electrolyte membrane fuel cells. An AEM must have a high ionic conductivity, low gas/fuel crossover, and be chemically and mechanically stable over the lifetime of the fuel cell. The sorption and desorption of water can cause pin hole cracks, which lead to fuel crossover and stack failure. As membrane thickness is decreased to reduce resistance, maintaining membrane integrity becomes increasingly difficult. A modified Sentmanat Extensional Rheometer (SER) was used to perform tensile-like testing using <5% of material needed for a traditional tensile tester on films 10-100 microns thick. A humidity delivery system was developed for the TA Instruments ARES-G2 rheometer to allow for testing at a range of temperatures (30-100°C) and relative humidity conditions (0-95% RH). The humidity oven was built to use with all other rheometer accessories. Dynamic mechanical analysis is used to investigate moduli changes while ramping humidity at constant temperature and while ramping temperature at saturated gas conditions. These tools established metrics for a robust membrane through mechanical characterization across temperatures and humidities. A series of block, random, and crosslinked polymers have been characterized with these tools. Complementing destructive tensile testing, a "water stress" test was explored to measure the tension and durability under hygral cycles. Membranes with a low (<5 MPa) and near constant water stress absorb and desorb water reversibly. Membranes performing well in the water stress test had an elongation to break 10 times that of its in-plane swelling in liquid water. Ion exchange membranes need to be able to mechanically stretch in the elastic region well above the in-plane swelling with water to withstand hygral stresses in an electrochemical device. Identifying a relationship between the mechanical and hygral stretching to predict durability in a working device is critical to the development of durable anion exchange membranes.

Wednesday 11:40 Constellation D

SM35

**Effects of nanographene on rheological properties of polyamide 6/acrylonitrile-butadiene-styrene nanocomposites**Alireza Mojarad<sup>1</sup> and Maryam Zarghami Dehaghani<sup>2</sup><sup>1</sup>*Azad University of Shiraz, Tehran, Iran;* <sup>2</sup>*Sahand Petroplastic, Tehran, Iran*

Abstract The influence of nanographene (NGO) on the rheological properties of polyamide6/acrylonitrile butadiene styrene (PA6/ABS) blends with different compositions was investigated by using rheometry. The results showed that the, decrement in dispersed domain size, recognized in the increased viscosity and elasticity at low frequencies. Also, the results indicate that the enhancement of elasticity and existence of plateau at low frequencies occurs by increasing NGO content. Consequently, in all blends by raising the NGO loading, storage modulus  $G'$  and complex viscosity  $\eta^*$  increase and also crossover points close together which cause to expansion of plateau elasticity. On the other hand, Cole-Cole plot and Van Gurp-Palmen plot confirm the compatibilization effect of NGO, which enhances the elasticity and non-linearity behavior of molten blends.

**Symposium SA****Self-assembled Systems and Gels**

Organizers: Surita Bhatia and Kelly Schultz

Wednesday 10:00 Constellation E

SA16

**Soft solid rheology near the gel point**H. Henning Winter*Chemical Engineering and Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003-3110, United States*

Physical and chemical gelation are between the most common ways of inducing a liquid-to-solid transition in amorphous materials. The transition requires that small-scale constituents of the material establish long-range internal connectivity and form a first sample-spanning cluster at the gel point (GP). While the internal connectivity mechanism may differ greatly from material to material, their GP structure always seems to exhibit a powerlaw relaxation time spectrum with negative exponent,  $H(\tau)/H_0 = [\tau/\tau_{\min}]^{-n}$  for  $\tau_{\min} < \tau < 8 \cdot \tau_{\min}$ . (Winter and Chambon 1986; Chambon and Winter 1987) While the powerlaw format appears to be universal, material differences express themselves in the material-specific property values,  $n$ ,  $H_0$ , and the lower time limit of the powerlaw spectrum,  $\tau_{\min}$ . The negative exponent value indicates gelation as opposed to the soft glass transition, which would have a positive exponent (Winter et al. 2009, 2013) and is not discussed here. This rheological study focuses on the soft solid states just beyond GP. Interestingly, the apparent universality of the distribution of relaxation modes at GP is limited to a very narrow region near GP. Soon beyond GP, universality gets lost: the diversity of material connectivity expresses itself in a diversity of evolving material states with their own evolution of rheological properties. Here we address the question whether there are rheological properties or patterns that soft solids might share even if their way of internal connecting differs fundamentally.

References: Chambon F, Winter HH (1987) *J Rheology* 31:683-697; Winter HH (2013) *Macromol* 46:2425-2432; Winter HH, Chambon F (1986) *J Rheology* 30:367-382; Winter HH, Siebenbürger M, Hajnal D, Henrich O, Fuchs M, Ballauff M (2009) *Rheol Acta* 48:747-753

Wednesday 10:25 Constellation E

SA17

**Critical-gel-like response and fractional dynamics of an A-B-A thermoplastic elastomer near  $T_{g,A}$** Luca Martinetti, Frank S. Bates, and Christopher W. Macosko*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455-0132, United States*

We report on the linear behavior of an undiluted PLA-PI-PLA thermoplastic elastomer (TPE) subjected to uniaxial extension, at a service temperature approaching the  $T_g$  of the endblock. The analysis herein is independent from the specific choice of the constituent blocks and thus applies to any microphase-segregated TPE of the A-B-A type. The material exhibited a critical-gel-like response that we associated with arm retraction dynamics of entangled dangling structures coupled with augmented motional freedom of the B block ends at the B/A interfaces. This critical-gel-like behavior was first analyzed in terms of a power-law distribution of relaxation times (derived from the wedge distribution), shown to be equivalent to Chambon-Winter's critical gel model and to the mechanical behavior of a fractional element. A relation between the observed power-law exponent and molecular structure was established. Understanding the measured material parameters inherently led to fractional calculus and to the concept of quasi-properties, which are intimately related to the stochastic behavior on a microscopic level. The measured low-frequency response, originating from the incipient glass transition of the A domains, was exploited and extrapolated to lower frequencies via a sequential application of the fractional Maxwell model (FMM) and the fractional Zener model (FZM). This allowed us to estimate the dynamics of the A block glass-rubber transition, and a secondary pseudo-plateau region consistent with the entanglement network of the system. With only a few, physically meaningful material parameters we obtained a realistic description of the A-B-A self-similar relaxation over a frequency range (12 decades) much broader than the experimental window (5 decades) and not accessible via time-temperature superposition.

Wednesday 10:50 Constellation E

SA18

**Normal force controlled rheology for thermoreversible gels**Bosi Mao, Patrick Snabre, and Thibaut Divoux*Centre de Recherche Paul Pascal - CNRS, Pessac 33600, France*

A wide range of biopolymer gels made of polysaccharides and/or proteins are prepared by cooling down to ambient temperature hot aqueous solutions of polymers. Spontaneous contraction of the polymer network near the sol-gel transition or non controlled solvent losses through evaporation at gel interfaces can lead to numerous experimental issues regarding rheological measurements, such as the contact loss between the gel and the shear cell, the stress-induced release of solvent and wall slip. In this talk we discuss the experimental issues associated with the temperature variations involved in the formation of thermoreversible gels. In a benchmark series of experiments conducted in a plate-plate geometry on agar gels, we show that the sample contraction during the gelation results in negative normal forces and leads to an artificial drift in the measurements of the gel elastic modulus  $G'$ . We demonstrate that imposing a constant normal force equals to zero instead of a constant gap during the gelation makes it possible to determine accurately the linear properties of the thermoreversible gel, even with smooth boundary conditions. We further illustrate the relevance of the zero normal force protocol by revisiting the influence of the thermal history on the mechanical properties of agar gels. Finally, we discuss the impact of the oil layer traditionally added at the sample periphery to prevent solvent evaporation. We show that if the anti-evaporation layer indeed has no effect upon the steady state values of the viscoelastic moduli, the oil may impact the early stage of the gelation by triggering an artificial and premature increase of  $G'$ . Our results highlight the relevance of normal force controlled rheology for the study of gelation transitions and offer a review of the experimental artifacts encountered during such studies.

Wednesday 11:15 Constellation E

SA19

**Laponite and laponite-PEO hydrogels with enhanced elasticity in phosphate-buffered saline**Xiao Liu<sup>1</sup> and Surita R. Bhatia<sup>2</sup><sup>1</sup>*Chemistry, SUNY Stony Brook University, Stony Brook, NY 11794, United States;* <sup>2</sup>*Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY 11973, United States*

Hydrogels of the synthetic clay laponite® and laponite®-poly (ethylene oxide) (PEO) have long been studied as model systems to understand fundamental aspects of colloidal disks and colloid-polymer systems. More recently, these systems have been explored for a variety of biomedical applications. However, there is limited information in the literature on the fundamental properties of laponite® and laponite®-polymer gels at pH < 9 under biological relevant conditions. Here, we explored the rheological behavior of laponite® and laponite®-PEO systems at biologically relevant conditions (e.g., physiological pH and ionic strength) and examine the effect of phosphate buffered saline (PBS) on the properties of the gel. Hydrogels with different polymer molecular weights and laponite concentrations were evaluated with oscillatory rheology experiments. Our results show that the elastic modulus of both laponite® and laponite®-PEO gels increases dramatically, in some cases by one order of magnitude or more, after immersing gels in PBS. We attribute this phenomenon to an enhanced edge-face attractive interaction between laponite® particles in buffered solutions at physiological pH, which would promote a long-lasting "house of cards" network structure of clay particles. These results are encouraging for future design of clay-polymer gels and nanocomposites hydrogels for biomaterials applications, such as scaffolds for tissue engineering.

Wednesday 11:40 Constellation E

SA20

**Polymer gelants for repair of leaky wellbores in CO<sub>2</sub> storage formations**Mohammadreza Shafiei<sup>1</sup>, Steve Bryant<sup>2</sup>, Roger T. Bonnecaze<sup>3</sup>, Mathew Balhoff<sup>4</sup>, Chun Huh<sup>4</sup>, Paul Bommer<sup>4</sup>, Fei Ho<sup>4</sup>, Valeriy Shakenov<sup>4</sup>, and Das Paulami<sup>4</sup><sup>1</sup>*McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712-1589, United States;* <sup>2</sup>*University of Calgary, Calgary, Alberta, Canada;* <sup>3</sup>*University of Texas at Austin, Austin, TX 78712, United States;* <sup>4</sup>*Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

Many prospective storage formations for anthropogenic CO<sub>2</sub> already have wellbores in place, constructed to explore for or produce hydrocarbons from deeper formations. A major concern with this technology is the possible leakage of the buoyant supercritical gas along existing wellbores which are difficult to treat with current technologies. This could release millions of tons of CO<sub>2</sub> to the atmosphere. The ability to block such pathways will be valuable when implementing large-scale geologic CO<sub>2</sub> storage. Polymer gelants consisting of pH-sensitive particles suspended in an aqueous phase can increase their viscosity by orders of magnitude in response to changes in the pH. Moreover at higher pH, the gels exhibit a significant yield stress. These pH-sensitive gelants can seal the leakage pathways along wellbores which are difficult to repair with oilfield cement. Here we report experiments on different grades of Carbopol to find the optimal gelant composition for the ease of injection as well as for stopping the flow of saline water, brine containing dissolved CO<sub>2</sub> or bulk phase CO<sub>2</sub>. Effect of pH on yield stress is reported for a range of concentrations of gelant. The effects of salt concentration, salt valance, and temperature on yield stress are presented as well. Yield stress, consistency index and power law index are obtained from flow curves which are used to model the transport behavior of the gel formation in the cement fracture. We present the correlation between power law index and consistency index as a function of polymer concentration. We show how the stress versus shear rate flow curves can be represented as a single universal flow curve.

## Symposium CR Computational Rheology

Organizers: Jay Schieber and Roland Winkler

Wednesday 10:00 Constellation F

CR1

**Dissipative Particle Dynamics with diffusion and reaction: Application to blood clotting**Alireza Yazdani<sup>1</sup>, Li Zhen<sup>1</sup>, Bruce Caswell<sup>2</sup>, and George E. Karniadakis<sup>1</sup><sup>1</sup>*Division of Applied Mathematics, Brown University, Providence, RI 02912, United States;* <sup>2</sup>*School of Engineering, Brown University, Providence, RI 02912, United States*

Dissipative Particle Dynamics (DPD) is well-understood to be appropriate for the simulation of flow phenomena of complex fluids at the mesoscopic level. Frequently these are strongly affected by events at much smaller scales, e.g. oxygen transport to red blood cells (RBCs). To account for these smaller scale processes we have incorporated diffusion and reaction of multiple species into an extended version of DPD. At the continuum level this is equivalent to the Navier-Stokes equation plus one diffusion-convection equation for each species. Clot initiation and growth at a damage site on a blood vessel wall involves a number of simultaneous processes including: multiple chemical reactions, species diffusion and flow. The chemistry of clot initiation and growth is now understood to be determined by mechanisms involving many reactions among some two-dozen species in dilute solution. Approximate diffusion coefficients in plasma can be estimated from correlations, while bulk and surface reaction-rate constants are available from the literature. Here the extended DPD is used to simulate the initiation and growth of a clot on a vessel wall. The role of blood particulates, i.e. RBCs and platelets, in the clotting process is being studied by including them separately and together in the simulations.

Wednesday 10:25 Constellation F

CR2

**Non-equilibrium properties of sheets in shear flow**Anoop Varghese, Gerhard Gompper, and Roland G. Winkler*Institute of Complex Systems, Forschungszentrum Jülich, Jülich, NRW 52425, Germany*

Soft matter objects in solution exhibits a remarkably rich structural and dynamical behavior in external flow fields. Polymers, membranes, cells, vesicles etc. are deformed and alignment by the flow. Moreover, shear flow induces a tumbling motion with a power-law dependence of the tumbling frequency and relaxation times on the shear rate. These microscopic conformational and dynamical properties are tightly linked to the macroscopic rheological behavior of the solution and give rise to phenomena such as shear rate dependent normal stress differences and shear thinning. Using mesoscale hydrodynamic simulations, we study the non-equilibrium properties of two-dimensional sheets in shear flow by combining the multiparticle collision dynamics approach for the fluid with molecular dynamics simulations for the sheet. We find a preferred alignment of a sheet in the flow, where the alignment angle decays in a power-law manner with the shear rate for small rates, and saturates at high shear rates in contrast to, e.g., flexible polymers and rods. Similar, the tumbling frequency, relaxation times, and viscosity exhibit a power-law dependence on the shear rate. Thereby, some of the exponents are different from those obtained for rodlike or flexible polymers in shear flow. We will discuss the various results and compare them with those of polymer systems.

Wednesday 10:50 Constellation F

CR3

**Numerical simulations of the rheology of suspensions of rigid spheres in a viscoelastic fluid under shear**Eric S. Shaqfeh<sup>1</sup>, Mengfei Yang<sup>1</sup>, and Gianluca Iaccarino<sup>2</sup><sup>1</sup>Chemical Engineering, Stanford University, Stanford, CA, CA 94305, United States; <sup>2</sup>Mechanical Engineering, Stanford University, Stanford, CA, CA 94305, United States

The effective rheology of rigid particles suspended in viscoelastic fluids is of considerable interest because of the frequent occurrence of such materials in commercial processing operations and the design of polymeric fluids with better particle transport properties for applications such as oil recovery and microfluidics. We present 3D simulations of neutrally buoyant, non-Brownian rigid spheres freely suspended in a viscoelastic fluid matrix under imposed shear flow using the Giesekus constitutive model. In the dilute particle concentration limit, we study the particle contribution to the bulk stress for Weissenberg numbers ranging from 0 to 5 and discuss the competing effects between the particle stresslet and the particle-induced polymer stress in the fluid domain in determining the viscometric functions of the suspension. At low Weissenberg number, we compare our simulation results with prior theoretical and experimental results for a dilute suspension of spheres in a weakly non-Newtonian fluid matrix. In this context, we discuss the apparent contradictory results in the literature regarding the second normal stress difference. We then examine fluid suspensions at higher volume fraction using an immersed boundary framework to study particle-particle interactions. Thus we calculate the effect of particle-particle interactions on the particle stresslet and again compare simulation results with experimental measurements.

Wednesday 11:15 Constellation F

CR4

**Accelerated Stokesian Dynamics simulations of active microrheology: Microviscosity, microdiffusivity and suspension stress**Yu Su<sup>1</sup>, Kevin L. Gu<sup>2</sup>, Henry C. Chu<sup>1</sup>, Nicholas J. Hoh<sup>1</sup>, and Roseanna N. Zia<sup>1</sup><sup>1</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States; <sup>2</sup>Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States

The non-equilibrium rheological response of colloidal suspensions is studied via active microrheology utilizing Accelerated Stokesian Dynamics simulations. In our recent work, we derived the theory for micro-diffusivity and suspension stress in dilute suspensions of hydrodynamically interacting colloids. This work revealed that force-induced diffusion is anisotropic, with qualitative differences between diffusion along the line of the external force and that transverse to it, and connected these effects to the role of hydrodynamic, interparticle, and Brownian forces. This work also revealed that these forces play a similar qualitative role in the anisotropy of the stress and in the evolution of the non-equilibrium osmotic pressure. Here, we show that theoretical predictions hold for suspensions ranging from dilute to near maximum packing, and for a range of flow strengths from near-equilibrium to the pure-hydrodynamic limit.

Wednesday 11:40 Constellation F

CR5

**A "matrix-free" Brownian dynamics approach for hi-fidelity simulation of semi-dilute polymeric solutions**Amir Saadat and Bamin Khomami

Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996-2200, United States

Evaluating the concentration dependence of static and dynamic properties of macromolecules in semi-dilute polymer solutions requires accurate calculations of long-range hydrodynamic interaction (HI) and short range excluded volume (EV) forces in these systems. In the conventional Brownian dynamics simulation (BDS), computation of HI necessitates construction of a dense diffusion tensor based on Ewald summation. This tensor is in turn decomposed to calculate the Brownian displacements using Krylov subspace based technique and the computational cost scales as  $O(N^2)$ , where  $N$  is the total number of monomers (beads in bead-spring representation of macromolecules) inside the periodic simulation box.

In this work, a matrix-free approach is implemented which leads to  $O(N \log N)$  scaling of computational expense. The advantages of the matrix-free algorithm over the conventional BDS arises due to the fact that all matrices involved in BDS are treated as sparse matrices, which in turn result in considerable speed-up. Moreover, the matrix-free implementation benefits from using the smooth particle mesh Ewald (SPME) method in construction of diffusion tensor along with block Krylov for computation of Brownian displacements. The fidelity and computational efficiency of the algorithm is demonstrated by evaluating the static and dynamic properties of the semi-dilute polymer solutions. Subsequently, the extension of the method to the systems under shear flow will be discussed.

## Symposium PM Probe Microrheology

Organizers: Eric Furst and Roseanna Zia

Wednesday 10:00 Baltimore/Annapolis

PM1

**The influence of compressibility on a probe translating through a fluid-fluid interface**Joseph R. Samaniuk<sup>1</sup>, Mathias Nagel<sup>1</sup>, Anna Leth-Espensen<sup>2</sup>, and Jan Vermant<sup>1</sup><sup>1</sup>Materials Science, ETH Zürich, Zürich 8093, Switzerland; <sup>2</sup>Technical University of Denmark, Kgs. Lyngby, Denmark

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 for the study of biological membranes, especially lipid bilayers, where viscoelastic properties affect the transport of molecules through the membrane, and mechanical properties provide biological cells with requisite structural integrity. Unlike most bulk fluids, fluid-fluid interfaces of this type are highly compressible and display a rich variety of viscoelastic behavior that depends strongly on the area-density of the interfacial molecules. Although these interfaces are quite clearly compressible, the most successful hydrodynamic models of probes translating through a fluid-fluid interface make the simplifying assumption that the interface is incompressible on the time scale of the movement of the probe. Recent experimental work has indicated that in certain interfaces the validity of this assumption is questionable. Understanding the role that dilatational effects play in fluid-fluid interfaces is especially important for the implementation of interfacial microrheological methods, and the movement of molecules within biological membranes. We will present our findings from simulation and experiment on the influence of compressibility on a probe translating through a fluid-fluid interface.

Wednesday 10:25 Baltimore/Annapolis

PM2

### **Probing microrheology with and without probes by differential dynamic microscopy**

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

*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106-5080, United States*

Differential dynamic microscopy (DDM) is emerging as a powerful characterization technique to measure the ensemble dynamics of colloidal and complex fluid motion using simple optical microscopy methods. By correlating the intensity fluctuations of a video micrograph in Fourier space, it is possible to quantify dynamics (and therefore viscoelasticity) in systems that would otherwise be difficult to measure using traditional photocorrelation spectroscopy or probe microrheology. Here, we present two examples in which DDM can be used as a powerful tool to measure the microdynamics of fluids that would be otherwise difficult to interpret using traditional probe microrheology. In one example, we show for the first time how DDM analysis can be extended to dark-field imaging by accounting for scatterers with a non-homogeneous intensity distribution as they move within the imaging plane. This allows us to characterize the dynamics of simple and complex fluids using spherical probes as small as 10 nm in size, giving access to dynamics at length scales inaccessible by larger probes. In another example, we show how DDM can be used to make microrheology measurements of a phase separating colloidal gel using direct imaging of the fluid structure without probe particles. From this, we are able to deconvolute fast diffusive motions within dense domains and slow superdiffusive modes of the domains themselves that would be difficult to interpret through traditional probe microrheology. The superdiffusive motions quantified by DDM are further compared with real-space tracking of domains to elucidate mechanisms of coarsening and aging in the fluid. Ultimately, we show how this information can be used to better understand the macroscopic rheology and aging of heterogeneous colloidal gels.

Wednesday 10:50 Baltimore/Annapolis

PM3

### **The impact of hydrodynamics on stress formation, relaxation, and memory in colloidal dispersions: Transient, non-linear microrheology**

Ritesh P. Mohanty and Roseanna N. Zia

*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

In active Microrheology, a Brownian "probe" particle is driven through a suspension, and its motion is tracked in order to infer rheological properties of the surrounding material. Most studies thus far have focused on steady-state behavior to establish the relationship between the microstructure, probe motion, and rheology. However, microstructural development and relaxation can be captured by the transient response of the material during startup and cessation of flow. Here, we develop a theoretical model for the rate of stress formation and relaxation, and their dependence on microstructural evolution under strongly non-linear microrheological forcing of a probe through a suspension of hydrodynamically interacting particles. The transient microstructure is governed by the Smoluchowski equation, which we solve to obtain the microstructure and rheological properties of the suspension are computed by combining the microstructure with statistical mechanical theory. Here we focus on understanding the influence of hydrodynamic interactions between particles on stress buildup during flow startup and relaxation after flow cessation. We study the behavior analytically in the dual limits of weak / strong probe forcing, and weak / strong hydrodynamic interactions; and numerically for the full range of forcing and hydrodynamics. We employ an excluded annulus model to systematically tune the strength of hydrodynamics in order to elucidate the relative contributions of hydrodynamic, Brownian, and interparticle forces to stress formation and relaxation. The recovery of entropically stored energy is studied.

Wednesday 11:15 Baltimore/Annapolis

PM4

### **Non-continuum intermolecular correlated displacements in complex fluids**

Zachary E. Dell<sup>1</sup>, Boyce Tsang<sup>2</sup>, Lingxiang Jiang<sup>2</sup>, Steve Granick<sup>3</sup>, and Kenneth S. Schweizer<sup>4</sup>

*<sup>1</sup>Department of Physics, University of Illinois, Urbana, IL, United States; <sup>2</sup>Materials Research Laboratory, University of Illinois, Urbana, IL, United States; <sup>3</sup>Center for Soft and Living Matter, Institute for Basic Science, Ulsan, Republic of Korea; <sup>4</sup>Materials Science, University of Illinois, Urbana, IL, United States*

There is intense interest in microrheology that uses probe particles to elucidate mechanical properties of soft materials, but one can go beyond this by directly probing the constituent unit of complex liquids, free of invasive particles. Here we present a microscopic theory for intermolecular correlated displacements in dense colloidal suspensions and entangled biopolymer solutions. Augmenting and testing the theory by recent experimental advances that measure, in real space, the correlated dynamical displacements of two tagged colloids, or labeled parts of biopolymers respectively, we predict the dynamic displacement cross correlations at relatively short times where diffusion is Fickian. Our approach is based on a recent force-level theory [1] for the separation-dependent non-hydrodynamic relative friction that relates transport to structure. In dense colloidal suspensions, at small enough separations of the tagged particles we find that non-hydrodynamic diffusion dominates and the cross

correlation depends on interparticle separation in a manner related to fluid structural pair correlations. These cross-correlations decrease faster with interparticle separation than the continuum behavior, but the crossover to macroscopic behavior is delayed to surprisingly large distances. The approach for spherical colloids can be extended to entangled rigid-rod-like polymer solutions. Distinctive, non-continuum cross correlations are predicted to extend up to length scales of many microns; on the order of the rod length. We propose that the physical origin is a significant contribution from the intermolecular spatial correlation hole. The theoretical results are favorably compared with new measurements on dense 2D hard sphere colloidal suspensions and heavily entangled F-actin solutions.

[1] U. Yamamoto and K.S. Schweizer, *J. Chem. Phys.* 139, 064907 (2013).

Wednesday 11:40 Baltimore/Annapolis

PM5

### **Passive microrheological characterization of the degradation of covalently adaptable hydrogel scaffolds**

Francisco S. Escobar IV<sup>1</sup>, Daniel D. McKinnon<sup>2</sup>, Kristi S. Anseth<sup>2</sup>, and Kelly M. Schultz<sup>1</sup>

<sup>1</sup>*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States;* <sup>2</sup>*Department of Chemical and Biological Engineering, HHMI, University of Colorado, Boulder, CO 80303, United States*

Covalently adaptable hydrogels (CAH) are responsive polymer networks that mimic certain aspects of the native extracellular matrix in vivo where cells apply traction, shear, and degrade to move freely. Understanding information about the network structure would lead to improvements in wound healing and drug delivery applications. Incubating the CAH in a pH buffer shifts the reaction equilibrium and causes breakage and reformation of bonds in the hydrogel until complete degradation. A mixture of 8-arm 10kDa polyethylene glycol (PEG)-hydrazine and 8-arm 10kDa PEG-aldehyde self-assemble to form the network. In this work, we incubate the CAH in pH buffers at native acidic, pH 4.3, physiological, pH 7.1, and basic pH 10.27. Degradation of the CAH's scaffold is measured using multiple particle tracking (MPT). This technique tracks micron sized particle movement to characterize the state, connectivity of the network, and spatial homogeneity. MPT measures complete dissolution of the CAH scaffold to be hours to months at these different pH values. A smooth transition from gel to sol is measured over 2 days during incubation in pH 4.3 buffer. When the CAH is incubated in a pH 7.1 buffer, bonds are broken and reformed over 24 hours and this cycle is repeated over several days until complete dissolution of the matrix. Reverse time-cure superposition (RTCS) is used to identify the critical relaxation exponent and critical degradation time, time when the last-spanning cluster is broken in the gel network. CAH incubated in a pH 4.3 buffer has a critical relaxation exponent of 0.44, representative of a tightly cross-linked network, and the CAH placed in a pH 7.1 buffer has a value of 0.9, indicative of a loosely cross-linked network. This analysis has quantified the time scales for degradation and microstructure of the CAH in biologically relevant environments. This work aims to determine the material applicability in enhancing drug delivery in relevant disease environments.

## **Symposium MN Micro and Nanofluidics**

Organizers: Charles Schroeder and Siva Vanapalli

Wednesday 10:00 Frederick/Columbia

MN1

### **Massive elasticity-driven particle accumulation of confined suspensions in kinked and tortuous geometries**

Alexander C. Barbati<sup>1</sup>, Agathe Robisson<sup>2</sup>, and Gareth H. McKinley<sup>1</sup>

<sup>1</sup>*Massachusetts Institute of Technology, Cambridge, MA 02139, United States;* <sup>2</sup>*Schlumberger-Doll Research Center, Schlumberger, Cambridge, MA 02139, United States*

Particles, inertia, elasticity, and irregular geometries can collude to exhibit unanticipated and dramatic flow behavior. Industrial systems, like hydraulic fracturing, regularly subject viscoelastic suspensions to strong and fast flows. Predictable and reliable particle transport is essential to flow control and successful overall system performance; however, these systems are difficult to analyze. Standard rheometric instruments fail for a variety of reasons, including poor scaling of flow/particle dimensions and kinematics which are inappropriate mimics of many industrial flows. Further, large imposed Weissenberg numbers, ambiguity in the relevant non-linear constitutive law, and irregular geometries often preclude analytical and computational interrogations of the flow field and fluid-particle interactions. To address these limitations, we construct novel microscale replicas of irregular geometries (chiefly expansion-contraction and tortuous channels) to directly interrogate the flow and quantify particle transport across several decades of Reynolds ( $0.1 < Re < 100$ ) and Weissenberg ( $0 < Wi < 20,000$ ) number. Particles used are non-colloidal and isodense, and the device is composed of a rigid, optically transparent epoxy to minimize hydraulic capacitance and enable interrogation using micro-PIV, streakline, and high-speed imaging of particle transport. We employ high molecular weight poly(ethylene oxide) solutions as the carrier fluid, and characterize both shear and extensional properties off-device to accurately characterize  $Re$  and  $Wi$ . We identify three regimes of particle transport, corresponding to the successive appearances of three-dimensional elastic secondary flows and elastic streamline tightening as  $Wi$  is increased. The interaction of elasticity and geometry with the embedded particles gives rise to a sudden and massive accumulation of particles away from the primary flow within cavities of the irregular geometries.

Wednesday 10:25 Frederick/Columbia

MN2

**Size-selective collection of particles using vortical flows in inertial microfluidics**Hamed Haddadi and Dino Di Carlo*Bioengineering, University of California Los Angeles, Los Angeles, CA 90024, United States*

Liquid Biopsy of Circulating Tumor Cells (CTCs) from relatively non-invasive blood draws can provide a low cost alternative for CT and PET imaging, providing up-to-date information on cancer progression. For this purpose, a technology based on inertial focusing of particles in microchannels combined with micro-vortices has been developed to collect CTCs from blood samples. The important design objective is to maximize the number of entrapped CTCs in micro-vortices while rejecting smaller blood cells, which necessitates understanding the physical aspects of particle-laden flow over micro-cavities. In the present work, we utilize lattice-Boltzmann simulations and micro-fluidics experiments to understand particle interactions with recirculating wakes and to address the underlying mechanisms of particle entrapment and maximum device efficiency.

Wednesday 10:50 Frederick/Columbia

MN3

**Towards producing and characterizing vesicle suspensions for studies of cross stream migration in channel flow**Kari J. Storslett and Susan J. Muller*Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States*

The migration of suspended particles lateral to the flow direction in a channel is not yet well understood. Understanding this phenomenon, particularly in vesicle suspensions, will provide insight into the physics and rheology of blood flow as well as the design of drug delivery vehicles and lab-on-a-chip diagnostic tools. Ultimately, we are interested in determining the effect of parameters such as vesicle size, deformability, and suspension volume fraction on the collective migration behavior of vesicles in channel flow in the vanishing Reynolds number limit. This requires developing a protocol for producing well-controlled vesicle suspensions. However, controlling vesicle size, polydispersity, and membrane properties is extremely challenging. We have examined varying electroformation protocols as well as size separation via microfluidic devices to generate monodisperse vesicle suspensions of different sizes and deformabilities. Separation devices show promise in reducing polydispersity of electroformed vesicles. We will report comparisons for a range of electroformation and separation strategies. In addition, preliminary experiments using fluorescence microscopy to quantify the migration behavior of vesicles in channel flow in terms of entry length and focusing position in the channel will be discussed.

Wednesday 11:15 Frederick/Columbia

MN4

**Capsule dynamics in microfluidic junctions**Panagiotis Dimitrakopoulos*Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111, United States*

Cross and T-junctions are commonly used in microfluidic devices for manipulation and characterization of soft particles, such as droplets, artificial capsules and cells. Our interest for this work is concentrated on the interfacial dynamics of capsules (i.e. membrane-enclosed fluid volumes) in Stokes flow which has seen an increased interest during the last few decades due to their numerous engineering and biomedical applications. In this talk we will present our investigation of the membrane dynamics in microfluidic junctions, including large deformations, tensile and compressive tensions, wall effects and non-linear membrane dynamics.

Wednesday 11:40 Frederick/Columbia

MN5

**Stokes trap: Multiplexed particle trapping and manipulation using precision microfluidics**Charles M. Schroeder and Anish Shenoy*Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

The ability to trap and control single particles in free solution has led to major advances in science and engineering. In this talk, we report the development of the Stokes Trap, which is a multiplexed microfluidic trap for control over an arbitrary number of small particles in a microfluidic device. Our work involves the design and implementation of 'smart' flow-based devices by coupling feedback control with microfluidics, thereby enabling new routes for the fluidic-directed assembly of particles or the development of precise methods for single particle rheology. Here, we discuss the development of a new method to achieve multiplexed microfluidic trapping of an arbitrary number of particles using the sole action of fluid flow. In particular, we use a Hele-Shaw microfluidic cell to generate hydrodynamic forces on particles in a viscous-dominated flow defined by the microdevice geometry and imposed peripheral flow rates. Addition of multiple inlets to the cell increases the degrees of freedom for trapping additional particles. We employ a model-predictive controller for the non-linear system and solve a constrained optimal control problem in real-time. This platform allows for a high degree of flow control over individual particles and can be used (for example) for fluidic-directed assembly by bringing two particles together in time and space. From a broader perspective, our work provides a solid framework for guiding the design of automated on-chip experiments for conducting single particle and single molecule rheology under controlled conditions and environments.

## Wednesday Afternoon

### Symposium SC Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Wednesday 1:30 Constellation C

SC36

#### Experiments to characterize particle flotation in a curing epoxy

Lisa A. Mondy<sup>1</sup>, Stephen A. Altobelli<sup>2</sup>, Anne M. Grillet<sup>1</sup>, Haoran Deng<sup>3</sup>, Christine C. Roberts<sup>1</sup>, Melissa M. Soehnel<sup>1</sup>, Rekha R. Rao<sup>1</sup>, John E. Bower<sup>4</sup>, Carlton F. Brooks<sup>1</sup>, and Amy K. Kaczmarowski<sup>5</sup>

<sup>1</sup>Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>2</sup>New Mexico Resonance, Albuquerque, NM 87106, United States; <sup>3</sup>Materials Science and Engineering, Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>4</sup>Microsystems Science and Technology, Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>5</sup>Neutron Generator Enterprise, Sandia National Laboratories, Albuquerque, NM 87185, United States

We are developing engineering models to help design encapsulation of electronic parts by epoxies embedded with high concentrations of glass microbubbles. The epoxy composite begins as a two-part liquid, with one part a curative and the other a mixture of the resin and particles, which are used to control the coefficient of thermal expansion. The combined liquid is injected into a mold surrounding the electronics and then cured in an oven. The curing time is long enough that particle migration can occur due to density differences. To populate the parameters of the model, experiments are needed to determine the rate of the curing reaction and the migration of the particles. Complicating the process are the facts that the particles have a bimodal size distribution with a significant fraction of "fines," the particles are difficult to mix into the liquid uniformly, the curing reaction is exothermic, and both the curing rate and viscosity are temperature-dependent. We will discuss experiments to determine the rheology and hindered settling behavior of the system as functions of cure/time/temperature. Independent tests using rheometry, differential scanning calorimetry, and nuclear magnetic resonance imaging are performed. The latter is used to obtain vertical profiles of the fluid fraction in batch flotation experiments in order to determine the hindrance function. X-ray computed tomography of final material molded in simple geometries is used for validation. These images also show the effects of entrapped air bubbles, which can lead to density gradients not presently accounted for in the model.

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Wednesday 1:55 Constellation C

SC37

#### Silica nanoparticles in cocontinuous blends

Huang Sijia<sup>1</sup>, Bai Lian<sup>1</sup>, Xiang Cheng<sup>1</sup>, Christopher W. Macosko<sup>1</sup>, and Milana Trifkovic<sup>2</sup>

<sup>1</sup>Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States; <sup>2</sup>Chemical Engineering and Petroleum Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada

Cocontinuous blends of immiscible polymers can produce mechanically strong blends of conductive polymers. When one phase is extracted they yield porous polymer sheets, which can be used as filters and membrane supports. However, because the polymers are immiscible cocontinuous blend morphology is unstable, coarsening if held at high temperature. In this study, we show that silica nanoparticles can stabilize the morphology of polyethylene (PE)/poly(ethylene oxide) (PEO) polymer blends via interfacial localization. Two commercial (Cabot) 100nm silica nanoparticles with different surface treatments were melt compounded into these blends and their morphology and characteristic pore size were analyzed by laser confocal microscopy. Scanning electron micrographs revealed that silica particles with octyltriethoxysilane surface groups were trapped at the PE/PEO interfaces. With 4 wt% nanoparticles, the interface was fully covered and coarsening was completely suppressed due to interfacial jamming. The viscoelastic storage modulus,  $G'$ , continued to increase long after the domain size stabilized. We speculate that this was due to particle rearrangement and densification in the interface.

Wednesday 2:20 Constellation C

SC38

#### Experiments and modelling of the thinning and breaking of particle suspension filaments

Christian Clasen<sup>1</sup>, Oliver G. Harlen<sup>2</sup>, Claire McIlroy<sup>2</sup>, Wouter Mathues<sup>1</sup>, Mariano Rubio<sup>3</sup>, and Alejandro Sevilla<sup>3</sup>

<sup>1</sup>Chemical Engineering, KU Leuven, Leuven, Belgium; <sup>2</sup>University of Leeds, Leeds, United Kingdom; <sup>3</sup>Universidad Carlos III de Madrid, Madrid, Spain

The physics of liquid bridges has been widely studied in the past, including their equilibrium shapes and the linear and nonlinear dynamics of natural and forced oscillations, among many other aspects. In this paper we investigate how the presence of particles modifies the thinning behavior and capillary break-up of a liquid bridge. While the presence of particles increases the bulk viscosity, experimental measurements suggest that eventually the thinning no longer follows the behavior predicted by the bulk viscosity; thinning is 'accelerated' due to effects of finite particle size, but decelerates again during final stages of thinning and approaches the behavior of the matrix fluid prior to break-up. Our hypothesis is that

accelerated thinning arises from variations in local particle density. As the filament thins, variations are amplified, leading ultimately to sections of the filament containing no particles. Sections of the filament that have a low particle density have a lower viscosity and can therefore thin more easily. To test this hypothesis, we have constructed a simple one-dimensional model in which the viscosity is determined from the local particle density, found by tracking individual particles within the suspension. Particles only contribute to the dynamics through the local viscosity, so the direct effects of hydrodynamic interactions and effects of the individual particles on the free surface are not included. Nevertheless, the model is able to reproduce the accelerated thinning found in experiments. Finally, we calculate the final thinning stages of the liquid trapped between two particles of finite diameter as a stretching Newtonian liquid bridge with a non-uniform prescribed movement of the confining particles. We show that this second model, based on the one-dimensional mass and momentum conservation equations, shows quantitative agreement with the experimentally observed deceleration and final pinching behavior of the medium between individually monitored particles in the suspension.

Wednesday 2:45 Constellation C

SC39

### **Rheology of cellulose nanofibers suspensions**

Behzad Nazari and Douglas W. Bousfield

*Department of Chemical and Biological Engineering, University of Maine, Orono, ME 04469, United States*

Cellulose nanofibers (CNF) are processed at low solids contents (< 4 wt%) in water. Even at low solids content, CNF/water suspensions tend to have shear-thinning behavior and yield stress due to the structures that seem to form at rest. In the rheology of CNF suspensions, the measurement method may influence the results due to wall-slippage. The suspensions violated the Cox-Merz rule in a significant manner as a sign of containing weak gel structures and wall-slippage. Parallel-plate and vane geometries were utilized to compare yielding and flow of CNF suspensions obtained by steady-state shear and oscillatory rheological measurements. For suspensions lower than 3% solids, the yield stress measured different procedures were within 20%, but for high solids suspensions, differences between the methods could be as large as 100%, due to wall-slippage. A pipe rheometer was used to obtain flow curves at higher shear rates and compare them with data collected by the parallel-plate geometry. It turned out the pipe rheometry data agreed with the power-law line fitted to the parallel-plate ones.

Wednesday 3:10 Constellation C

SC40

### **Structure and rheological properties of rod-shaped cellulose nanocrystal suspensions in aqueous dilute polymer solutions**

Yaman Boluk, Hale Oguzlu, and Zahra Khalili

*Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta T6G 2W2, Canada*

Rod-shaped cellulose nanocrystal(CNC)particles with uniform particle size distribution are typically prepared by careful hydrolysis with concentrated sulfuric acid. This process generates cellulose nanocrystal whiskers which are typically 6-8 nm wide and 100-150 nm long. In addition, rod-shaped NCC particles in aqueous solutions carry negative electrical charges due to the formation of sulfate groups on surfaces. As expected, aqueous suspensions of dilute to semi-dilute CNC particles (less than 1%) does not have any thickening characteristics. However, such suspensions in dilute hydroxyethyl cellulose and carboxymethyl cellulose solutions show extreme non Newtonian shear thickening characteristics. The rheological behavior of dilute to semi-dilute rod shaped cellulose nanocrystalline suspensions in dilute hydroxyethyl cellulose and carboxymethyl cellulose solutions were determined by oscillatory rheology and steady state shear rheology. The threshold of cellulose nanocrystalline particle concentration is 0.2% that exhibits viscoelastic structure. The formation of liquid crystal pockets of cellulose nanocrystals is due to the depletion by non adsorbing polymers in solution. The critical threshold of thickening is 0.2% is also coincides the transition concentration from dilute to semi-dilute concentration.

Wednesday 4:00 Constellation C

SC41

### **Inkjet printing of carbon nanotube suspensions**

Yang Guo<sup>1</sup>, Brice Bognet<sup>1</sup>, Huseini Patanwala<sup>1</sup>, Sahil Vora<sup>2</sup>, and Anson Ma<sup>1</sup>

<sup>1</sup>*Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States;* <sup>2</sup>*Chemical Engineering, University of Connecticut, Storrs, CT 06269, United States*

Inkjet printing is capable of depositing a wide range of materials (e.g., metals, polymers, and ceramics) onto different substrates, such as paper, plastics, and fabrics, to produce flexible electronics and 3-D objects. Inkjet printing is typically characterized by high shear rate ( $> 10^4 \text{ s}^{-1}$ ), short residence time (5 - 250  $\mu\text{s}$ ), and high actuation frequencies ( $> 100 \text{ kHz}$ ) that are orders of magnitude larger than what is accessible using conventional rheometers ( $\sim 15 \text{ Hz}$ ). In this presentation, we will report the development of a stroboscopic imaging platform coupled with a custom-built print chamber, where acoustic waves of arbitrary waveforms can be applied to drive an ink fluid out of a nozzle. We have combined this imaging platform with digital image correlation to investigate the jetting behavior of fluids containing carbon nanotubes (CNTs) — rolled graphene cylinders with a diameter of ca. 150 nm and an aspect ratio exceeding 40. Of particular interest is how the inclusion of CNTs with different states of aggregation affects the classical Plateau-Rayleigh instability, which further influences the jet breakup and CNT drop size distribution. The findings may have broader impact on understanding the reliability and resolution of inkjet printing high-aspect ratio particles like CNTs.

Wednesday 4:25 Constellation C

SC42

**The mechanobiology of construction and operation of traffic networks in interstitial swarms of bacteria**Ranganathan Prabhakar<sup>1</sup>, Amarender Nagilla<sup>2</sup>, Cynthia B. Whitchurch<sup>3</sup>, and Sameer Jadhav<sup>4</sup><sup>1</sup>*Mechanical and Aerospace Engineering, Monash University, Clayton, Victoria 3800, Australia;* <sup>2</sup>*IITB-Monash Research Academy, Powai, Maharashtra, India;* <sup>3</sup>*The ithree Institute, University of Technology Sydney, Ultimo, NSW, Australia;* <sup>4</sup>*Chemical Engineering, Indian Institute of Technology Bombay, Powai, Maharashtra, India*

Many pathogenic bacteria such as *Pseudomonas aeruginosa* colonise interstitial spaces between tissue surfaces. When cells reach a sufficient density, they appear to use a range of collective strategies to spread quickly as a monolayer to lay the foundations for a mature biofilm. It has been recently shown (Gloag et al., PNAS, 110, 11541-11546, 2013) that, in *P. aeruginosa* colonies growing at an agar-glass interface, cells at the edge of advancing colonies self-organize into distinctive networks of trenches as they plough through the soft agar. Cells behind these bulldozer rafts secrete extracellular DNA (eDNA) that through an as-yet-unknown mechanism appears to regulate traffic to ensure a smooth supply of cells from the colony interior to the advancing edge. Incorporating DNA-degrading enzymes in the substrate results in traffic grid-lock and considerably slows down the speed of surface colonization. A model is proposed to explore the mechanobiological interplay between cell motility, active forcing, and mechanical interactions of the bacterial colony with the substrate. A fingering instability of the edge of the bacterial monolayer as it ploughs its way through the soft substrate appears to explain the emergence of cell rafts. The merging of rafts and the prevention of cells from aligning perpendicular to trench walls in the colony interior leads to colony morphologies similar to those observed in the experiments.

Wednesday 4:50 Constellation C

SC43

**Using a stochastic field theory to understand active colloidal suspensions**Yuzhou Qian<sup>1</sup>, Peter R. Kramer<sup>2</sup>, and Patrick T. Underhill<sup>1</sup><sup>1</sup>*Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States;* <sup>2</sup>*Mathematical Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

Active colloidal suspensions are an important class of materials that appear both in natural biological systems (e.g. bacteria or algae) and in synthetic systems. Even without external forcing they are out of equilibrium, which gives rise to interesting properties in both small and large concentrations of the particles. These properties have been observed in experiments as well as simulation/modeling approaches. It is important to understand how hydrodynamic interactions between active colloids cause and/or alter the suspension properties including enhanced transport and mixing. One of the most successful approaches has been a mean field theory. However, in some situations the mean field theory makes predictions that differ significantly from experiments and direct (agent or particle based) simulations. There are also some quantities that cannot be calculated by the mean field theory. In this talk, we will describe our new approach which uses a stochastic field to overcome the limitations of the mean field assumption. It allows us to calculate how interactions between organisms alter the correlations and mixing even in conditions where there is no large-scale group behavior.

Wednesday 5:15 Constellation C

SC44

**Diffusion of an ellipsoid in bacterial suspensions**Xiang Cheng and Yi Peng*Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States*

Active matter such as swarming bacteria and motile colloids exhibits exotic properties different from conventional equilibrium materials. Among these features, the enhanced diffusion of tracer particles is generally deemed as a hallmark of active matter. Here, rather than spherical tracers, we investigate the diffusion of isolated ellipsoids in quasi-two-dimensional bacterial bath. Our study reveals a nonlinear enhancement of both translational and rotational diffusion. More importantly, we uncover an anomalous mode of coupling between translation and rotation that is strictly prohibited in normal Brownian diffusion. Combining experiments with theoretical analysis, we show that this anomaly arises from stretching flows created by complex bacteria-particle interactions. Our work sheds new light on fundamental transport processes in microbiological systems and provides important insights into organizing principles of active matter.

Wednesday 5:40 Constellation C

SC45

**Effect of hematocrit and dextran on human blood viscoelasticity**Giovanna Tomaiuolo, Antonio Carciati, Sergio Caserta, and Stefano Guido*DICMAPI, Università di Napoli Federico II, Napoli 80125, Italy*

The study of the rheological properties of blood is an important issue for both the scientific point of view, in research and clinic, and for industrial biotechnologies, in the formulation of fluids of biological interest. Blood is a complex fluid with non-Newtonian characteristics, and consists primarily of a concentrated suspension of deformable red blood cells (RBCs), which tend to aggregate reversibly in microstructures. This tendency is the major contributor to the viscoelastic flow behavior of blood. The big majority of both research and clinical investigation in the field of hemorheology is based on steady shear measurements aimed to the knowledge of blood viscosity as a function of shear rate. Although the rheological behavior in steady-state conditions can elucidate the mechanism at the base of the non-Newtonian, shear-thinning and viscoplastic behaviour of blood, transient conditions are often encountered in vivo, such as in going from larger to smaller vessels or in vascular bifurcations, and pulsations and unsteady flow are natural in the cardiovascular system. Despite the study of the transient behaviour of blood could provide valuable information about its microstructure, investigations on blood under oscillatory flow are sparse in the literature and currently limited. Here, we present a systematic experimental investigation of human blood transient behavior in the linear viscoelastic regime, by performing

oscillatory shear measurements by conventional bulk rheology. The storage ( $G'$ ) and loss ( $G''$ ) moduli of whole normal human blood have been measured over a wide range of frequencies. In order to elucidate the mechanism at the base of the transient flow behavior of blood, the change in the viscoelastic response has been recorded for the case of increased RBC volume fraction and for suspension of RBC in aggregating media (i.e. dextran solution in two different concentration of dextran).

## Symposium SM Polymer Solutions and Melts

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Wednesday 1:30 Constellation D

SM36

### **SAXS/WAXS measurements of HDPE crystallization during uniaxial extensional flow**

Erica M. McCready and Wesley R. Burghardt

*Northwestern University, Evanston, IL, United States*

We report studies of flow-induced crystallization of high density polyethylene during uniaxial extensional flow. Flow was applied using an SER extensional fixture housed in a custom built oven designed to facilitate in situ synchrotron x-ray experiments. Samples were loaded onto the fixture, heated to well above the melting temperature, and then cooled to the desired crystallization temperature. Extent of crystallization, orientation of crystallites, and extensional viscosity were determined throughout the entire uniaxial extensional flow, using simultaneous small- and wide-angle x-ray scattering (SAXS and WAXS) and torque measurements. Both temperature and extension rate were varied. SAXS patterns show distinct shapes characteristic of shish kebab morphology formation. WAXS peaks indicate high alignment of unit cell structure along the flow direction. Evolution of features within both SAXS and WAXS patterns can be correlated to each other and to extensional viscosity features during the crystallization process.

Wednesday 1:55 Constellation D

SM37

### **Transient shear rheology of a thermotropic liquid crystalline polymer below the melting point**

Chen Qian, Craig D. Mansfield, and Donald G. Baird

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

Thermotropic liquid crystalline polymers (TLCPs) are high performance thermoplastics, which are known for their outstanding mechanical, barrier and thermal properties. However, the inherently low melt viscosity of TLCPs is detrimental to processes requiring high melt strength, such as extrusion blow molding, film blowing and thermoforming. We have developed a method to enhance the viscosity of TLCPs by first raising the temperature above the melting point ( $T_m$ ) to exclude all solid crystalline structure and then lowering the temperature below the  $T_m$  to supercool the materials. Therefore, the rheology of TLCPs below  $T_m$  plays a critical role in processing. The transient rheology of TLCPs is also of fundamental importance in elucidating the microstructure evolution of these complex structured fluids. Although the rheology of TLCPs above the  $T_m$  has been well documented and discussed, few have explored the transient rheology of TLCPs below  $T_m$ .

In this study a commercial TLCP, Zenite HX-8000 ( $T_m=280$  °C), is used. The solidification behavior of HX-8000 is investigated by small amplitude oscillatory shear measurements in both the temperature ramp and time sweep modes. The dynamic tests determine the temperature and time windows below  $T_m$  in which the transient measurements can be performed. Different transient experimental protocols (shear inception, relaxation after preshear, interrupted shear and flow reversal) are applied to monitoring the shear stress growth. The effect of temperature on the transient behavior as well as the microstructure evolution will be discussed. Additionally, a comparison is made on the degree of shear-induced molecular orientation above and below  $T_m$ .

Wednesday 2:20 Constellation D

SM38

### **Flow and thermal profiles of fused deposition modeling extrusion**

Jonathan E. Seppala<sup>1</sup>, Kaitlyn E. Hillgartner<sup>2</sup>, Aaron M. Forster<sup>3</sup>, and Kalman B. 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>*Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO 80401, United States;* <sup>3</sup>*Materials and Structural Systems Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8615, United States*

Fused deposition modeling (FDM), a now common and inexpensive additive manufacturing method, produces 3D objects by extruding molten polymer layer-by-layer. Commercial systems utilize inexpensive dies to deposit material with control limited to temperature and flow rate. Understanding the flow through the die will aid the development of advanced materials for additive manufacturing. To better understand the FDM process the flow through the extrusion die was characterized using tracer loaded filament sections. Acrylonitrile butadiene styrene (ABS), one of the most common FDM polymers, was used for the study. Tracer segments were prepared by including commercially available black ABS filament. The flow is characterized over a range of temperatures and extrusion rates. Discussion of the stream lines and onset of melt fracture is supplemented with rheological measurements of the ABS, thermal imaging of the FDM build process, and mechanical tests on FDM welds.

Wednesday 2:45 Constellation D

SM39

**Simultaneous rheology and Raman spectroscopic measurements during polyethylene crystallization**Anthony P. Kotula<sup>1</sup>, Matthew W. Meyer<sup>2</sup>, Francesca De Vito<sup>3</sup>, Jan P. Plog<sup>4</sup>, Angela R. Hight Walker<sup>5</sup>, and Kalman B. Migler<sup>1</sup><sup>1</sup>Materials Science and Engineering, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States;<sup>2</sup>Thermo Fisher Scientific, Madison, WI, United States; <sup>3</sup>Thermo Fisher Scientific, Tewksbury, MA 01876, United States; <sup>4</sup>Thermo Fisher Scientific, Karlsruhe, Germany; <sup>5</sup>National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

The structure and rheology of polyolefins during crystallization is of critical importance to the polymer processing industry. Optical, thermal, and mechanical properties of semi-crystalline polymer products are directly related to the composition of amorphous and crystalline material in the final product, which depends on flow history during crystallization. Here, we present simultaneous rheological and Raman spectroscopic characterization of high density polyethylene samples during isothermal crystallization in a parallel-plate geometry. Experiments are performed at a low undercooling in order to clearly resolve the shear modulus and Raman spectra on timescales much shorter than the total crystallization time. Analysis of the Raman spectra allows for the quantification of the mass fractions of crystalline and amorphous chains, as well as chain segments in a consecutive trans conformation that are not part of the orthorhombic crystal. The optical system allows for Raman as well as bright field images to be taken at various radial positions along the sample to observe spatial variation in the polymer composition. These results provide a direct correlation between average molecular conformation and measurable rheological quantities.

Wednesday 3:10 Constellation D

SM40

**Qualitative and quantitative SAXS/WAXS studies of shear-induced crystallization of poly(1-butene)**Mu Sung Kweon, Binbin Luo, and Wesley R. Burghardt*Northwestern University, Evanston, IL, United States*

Flow-induced crystallization of poly(1-butene) was studied in shear flow. Flow was produced using a Linkam shear cell that has been modified to allow x-ray access for in situ studies of polymer structure using synchrotron x-ray scattering techniques. After loading in the shear cell, samples were first heated well into the melt, and then cooled to a crystallization temperature selected such that negligible quiescent crystallization would occur on reasonable time scales. A short burst of shear flow was then applied at various rates, after which simultaneous wide- and small-angle x-ray scattering (WAXS and SAXS, respectively) data were collected to study the impact of both deformation rate and total applied strain on accelerated crystallization kinetics as well as the morphology of the resulting crystallites (e.g. degree of crystallite orientation). SAXS and WAXS data generally showed qualitative agreement in measures of the extent of crystallization and the degree of crystallite orientation. Average crystallite orientation was found to decrease over the course of crystallization. The crystalline volume fraction in the sample was calculated from the (i) SAXS invariant and (ii) integrated WAXS intensity profile to quantify the extent to which the sample crystallized at various flow conditions. Qualitative and quantitative analyses demonstrate that it is indeed the growth of crystal lattices in the atomic scale and well-ordered regions at larger length scales that gives rise to crystallinity.

Wednesday 4:00 Constellation D

SM41

**Understanding and modelling the dynamics of entangled linear associative polymer melts**Evelyne van Ruymbeke<sup>1</sup>, Laurence Hawke<sup>1</sup>, Ashwinikumar Sharma<sup>2</sup>, and Hadi Goldansaz<sup>1</sup><sup>1</sup>Bio and Soft Matter, Université catholique de Louvain, Louvain-La-Neuve, Belgium; <sup>2</sup>DSM Ahead, DSM, Geleen, The Netherlands

Associating polymers consist of polymer chains that carry functional groups. These functional groups are capable of forming transient interactions/bonds, which provide a convenient control of the physical properties of this class of polymeric systems. For example, depending on the temperature or/and the concentration of functional groups, the rheological behaviour of associative polymers ranges from rubber-like to liquid-like. We focus on melts of entangled, linear associative polymers. In order to model their viscoelastic properties, we extend our TMA tube based model that successfully predicts the linear viscoelasticity of ordinary, i.e. non-associative, polymer melts, in order to account for the stickers along the chains. These last ones give rise to a slow stress relaxation process, which is impossible to capture by ordinary reptation. To describe the dynamics of the system at intermediate frequencies (timescales), we show that tension equilibration must be considered, which is a slow Rouse-like relaxation process along the entangled chains, due to the blinking nature of the mobile polymer fraction. A detailed comparison between experimental data and model predictions is performed on different supramolecular systems.

Wednesday 4:25 Constellation D

SM42

**New insight into structure healing ability of polylactic acid-graphene nanocomposites by rheological investigations**Mohammad Sabzi<sup>1</sup>, Long Jiang<sup>2</sup>, and Florian J. Stadler<sup>1</sup><sup>1</sup>College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China; <sup>2</sup>Mechanical Engineering, North Dakota State University, Fargo, ND 58108, United States

Two types of graphene were used to make polylactic acid (PLA)-graphene nanocomposites with various concentrations of graphene through a solution casting method. Due to the differences in surface area, thickness, and aspect ratio between the two types of graphene, the graphene-graphene and graphene-polymer interactions were different in these two nanocomposites. As a result, the two types of graphene nanoplatelets assembled into different interconnected structures in the matrix. Steady state shear, stepwise small-amplitude oscillatory shear (SAOS) and large-

amplitude oscillatory shear (LAOS), and frequency sweep tests immediately after the stepwise shear were used to determine and study the two different graphene aggregate structures. The disruption (under LAOS) and recovery (under SAOS) of the structures were monitored and the great disparities between the two types of graphene were ascribed to their structural roots. The formation of a percolated graphene network structure in the matrix significantly altered the structural evolution under the stepwise shear. This multi-step shear process was found to be a very sensitive tool to differentiate sample microstructures while traditional linear viscoelastic tests (i.e. SAOS) failed.

Wednesday 4:50 Constellation D

SM43

### **Application of polymer concepts to dynamics of short-chain hydrogen-bonded liquids: Tests of the minimal model of associating polymers**

Yangyang Wang

*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

Recent intensive studies of the supramolecular relaxation mode - the so-called Debye-like relaxation in hydrogen-bonded liquids have highlighted the importance of polymer concepts in explaining their dynamic properties. Nevertheless, a detailed analogy is yet to be drawn between these hydrogen-bonded liquids and traditional associating polymers such as wormlike micelles. Here we apply the minimal model for associating polymers [J. Chem. Phys. 125, 184905 (2006)] to understand the dynamic features of short-chain hydrogen-bonded liquids including monohydroxy alcohols and imidazoles. At first glance, by combining Rouse dynamics with parallel-channel relaxation coupling mechanism, the model seems to be able to describe the emergence of a Debye-like relaxation in dielectric spectroscopy, as well as the overall shape of the experimental viscoelastic spectra. However, a closer examination of the model reveals that the appearance of the "slower-than-structural" supramolecular relaxation mode requires a long hydrogen-bonding lifetime and this would be inconsistent with the existing near infrared temperature-jump experiments. The implications of our analysis will be discussed in this talk.

This work was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

Wednesday 5:15 Constellation D

SM44

### **Linear and circular DNA dynamics in semi-dilute solutions**

Kai-Wen Hsiao<sup>1</sup>, Yanfei Li<sup>2</sup>, Gregory B. McKenna<sup>2</sup>, and Charles M. Schroeder<sup>1</sup>

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

<sup>2</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

In this work, we study the dynamics of ring polymers in semi-dilute solutions of linear DNA using single molecule techniques. Using this approach, we first determined the molecular weight scaling behavior for the longest relaxation times of ring polymers in semi-dilute linear polymer solutions. In addition, we performed a series of step-strain experiments on polymer molecules in planar extensional flow using an automated hydrodynamic trap. In this way, we are able to precisely control the flow strength (Weissenberg number) and the amount of strain applied to single polymer chains, thereby allow for the direct observation of the full stretching and relaxation process of ring polymers in semidilute polymer solutions. We also compare the results for ring polymer stretching to our previous work on linear polymer dynamics in a semi-dilute linear background, which reveals the contribution of polymer chain architecture on polymer dynamics. Overall, our work aims to provide a molecular-level understanding of the role of polymer architecture on the stretching dynamics in non-dilute polymer solutions via direct observation of single chain dynamics in strong flows.

Wednesday 5:40 Constellation D

SM45

### **Investigating the behavior of bead-spring chains in dilute and semi-dilute regimes: A hi-fidelity Brownian dynamics approach**

Amir Saadat and Bamin Khomami

*Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996-2200, United States*

In the first part of this work, a highly efficient Brownian dynamics algorithm for simulation of bead-spring chain micromechanical models that utilizes the Krylov framework and the semi-implicit predictor-corrector scheme is used to study the behavior of dilute solutions of high molecular weight polystyrene in uniaxial extensional flow. The influence of key parameters, namely appropriate inclusion of hydrodynamic interactions (HI), the level of fine-graining, and the flow strength on the observed extensional hardening of the dilute solutions over a broad molecular weight range is considered. Specifically, it is demonstrated that the combination of HI and successive fine-graining (SFG) method [Sunthar et al., *Macromolecules*, 2005, **38**, 10200] results in very good predictions of rheological properties of solutions of high molecular weight polystyrene. Furthermore, it is shown that the results of Brownian dynamics simulation (BDS) are in disagreement with the extension thinning of experimentally measured steady state elongational viscosity of polystyrene solutions.

The second part of the work is concerned with the application of a "matrix-free" BDS, recently developed in our group, to study the static and dynamic material properties of semi-dilute polymer solutions. The asymptotic value of center of mass diffusivity of polymer molecules at very low concentrations and their radius of gyration scaling as a function of number of beads in the dilute and semi-dilute concentration regime are used to demonstrate the fidelity of the algorithm. In turn, a favorable comparison between our results and the blob theory is shown. The matrix-free method is then applied to study the material properties of the semi-dilute polymer solution under shear flow.

## Symposium SA Self-assembled Systems and Gels

Organizers: Surita Bhatia and Kelly Schultz

Wednesday 1:30 Constellation E

SA21

### The sequencing of dynamic rheological measurement

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

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

A new quantitative analysis scheme is presented that is commensurate with recent studies [S. A. Rogers et al., *J. Rheol.* (2011), C. R. Lopez-Barron et al., *Phys. Rev. Lett.* (2012)] suggesting that nonlinear responses to large amplitude oscillatory shear (LAOS) are due to sequences of physical processes. In addition to two 'regular' viscoelastic material parameters (moduli, viscosities, compliances, or fluidities), the new scheme includes two new terms that account for the apparent shifting of the strain equilibrium and the apparent yield stress. This work represents the first material-agnostic analysis in which the strain equilibrium is allowed to shift. We are therefore able to distinguish between the strain in the lab frame and the strain a material responds to. The new technique is used to analyze the nonlinear rheological response to LAOS of a series of mixed cationic/anionic surfactant (CTAT/SDBS) WLMs in which the level of branching is controlled via the addition of the hydrotropic salt sodium tosylate [B. A. Schubert et al., *Langmuir* (2003)]. It is shown that the position from which strain is meaningfully acquired during LAOS shifts dramatically during a period, spending much of an oscillation near the lab frame strain extremities. By providing temporal resolution to the analysis of viscoelastic responses, this research provides both a rational pathway toward a more complete understanding of results from all time-dependent tests as well as guiding the next generation of model development.

Wednesday 1:55 Constellation E

SA22

### Nonlinear shear rheology of a supramolecular organogelator

Ameur Louhichi<sup>1</sup>, Alan R. Jacob<sup>1</sup>, Laurent Bouteiller<sup>2</sup>, and Dimitris Vlassopoulos<sup>1</sup>

<sup>1</sup>*Institute of Electronic Structure and Laser, Foundation for Research and Technology, Heraklion, Crete 70013, Greece;* <sup>2</sup>*Chimie des Polymeres, Universite Paris 6-CNRS, Institut Parisien de Chimie Moleculaire, Ivry sur Seine, France*

We investigate the transient and steady state shear rheological properties of an organogel formed by association of a bi-functional monomer 2,4 bis(2-ethyl hexyl ureido)toluene[EHTU], with Hydrogen bonds, in a non polar organic solvent<sup>[1]</sup>. The linear viscoelasticity of this supramolecular polymer has studied using rheology<sup>[2]</sup> and microrheology<sup>[3]</sup> whereas recent work has addressed the potential link of microstructural evolution and large amplitude oscillatory shear<sup>[4]</sup>. Here, we present a systematic investigation of the nonlinear rheology at different concentrations in order to probe the relevant mechanisms prevalent in this organogelator under shear. We show evidence of shear banding, whereas stress relaxation after cessation of steady state shear flow is shown to provide insights into the two characteristic timescales present in these living systems. These are attributed to the breakage and reformation of Hydrogen bonds (fast time) and the overall motion (reptation-like) of the supramolecular polymer.

[1] *Solvents with similar bulk properties induce distinct supramolecular architectures*, T. Pinault et al., *Chem. Phys. Chem.*, **7**,816 (2006). [2] *Rheological characterisation of bis-urea based viscoelastic solutions in an apolar solvent*, G. Ducouret et al., *Journal of Colloid and Interface Science*, **310**, 624,(2007). [3] *Brownian particles in supramolecular polymer solutions*, van der Gucht et al., *Phys. Rev. E.*,**67**, 051106 (2003). [4] *Large amplitude oscillatory shear of supramolecular materials*, A.R. Jacob et al., *Journal of Non-Newtonian Fluid Mechanics*, **206**, 40 (2014).

Wednesday 2:20 Constellation E

SA23

### Nonlinear rheology and cavitation of a triblock copolymer gel

Santanu Kundu<sup>1</sup>, Seyed Meysam Hashemnejad<sup>1</sup>, Mahla Zabet<sup>1</sup>, Satish Mishra<sup>1</sup>, and Madhu Namani<sup>2</sup>

<sup>1</sup>*Dave C. Swalm School of Chemical Engineering, Mississippi State University, MS State, MS, United States;* <sup>2</sup>*TA Instruments, MS State, MS, United States*

Polymer gels are subjected to large-strain deformation during their applications. Here, we report the large-strain deformation behavior of a physically cross-linked, swollen polymer gel, which was obtained by dissolving a triblock copolymer poly (methyl methacrylate) - poly (n-butyl acrylate) - poly (methyl methacrylate) [PMMA-PnBA-PMMA] in 2-ethyl 1-hexanol, a midblock selective solvent. Investigations were performed using large amplitude oscillatory shear (LAOS) and custom developed cavitation rheology techniques. The gel displays unique strain-stiffening response at large-strain. The stress vs strain responses have been captured using Gent constitutive model. In cavitation experiments a syringe-needle was inserted into the gel and a growth of cavity at the tip of the needle was captured. The critical pressure for cavitation scales with the local modulus of the gel. Both analytical method and finite-element based modeling have been implemented to capture the pressure response in cavitation experiments. Our results provide new understanding of gel failure mechanism at large-strain.

Wednesday 2:45 Constellation E

SA24

**Stochastic modeling of networked fluids**Lin Zhou<sup>1</sup> and L.Pamela Cook<sup>2</sup><sup>1</sup>*Mathematics Department, New York City College of Technology, CUNY, Brooklyn, NY 11201, United States;* <sup>2</sup>*Department of Mathematical Sciences, University of Delaware, Newark, DE 19716, United States*

Networked fluids, such as wormlike micellar solutions and physically cross-linked gels, are studied either through macroscopic (closure) models or through direct mesoscopic simulation. Each approach has advantages and disadvantages. In this work we model and simulate a networked system at the mesoscale level, the results of which are then integrated to the macro scale. One distinct advantage of this method is that there is no need of a closure approximation.

This work builds on earlier work of van den Brule and Hoogerbrugge (JNNFM 1995) in which a mesoscale network is simulated with clear physical rules using stochastic simulations. In those simulations the network topology was tracked. As opposed to mesoscale dumbbell models in which the topology is not tracked. This modeling approach allows the network to weaken/relax globally due to local disentanglements and allows a direct relationship between a network connector's length and its stress. In that simulation the lifetimes of the network connections are governed by Poisson distributions. We extend those results to a nonlinear framework in which we consider network node lifetimes dependent on local stresses. These results are compared with those of macroscopic two species models which have been successful in prediction wormlike micellar solution flows. We analyze the network connector length distributions in equilibrium and compare with the predictions of the Cates model (Macromolecules 1987). Simulation results with varying parameters (network node lifetimes, node attractive distance) are presented.

Wednesday 3:10 Constellation E

SA25

**The fluidity model for the mechanical description of thixotropic elasto-viscoplastic materials**Paulo R. de Souza Mendes<sup>1</sup>, Roney L. Thompson<sup>2</sup>, Behbood Abedi<sup>1</sup>, and Luiz R. Sica<sup>1</sup><sup>1</sup>*Mechanical Engineering, Pontifícia Universidade Católica-RJ, Rio de Janeiro, RJ 22453-900, Brazil;* <sup>2</sup>*Mechanical Engineering, Universidade Federal Fluminense, Niterói, RJ, Brazil*

A constitutive model that accounts for thixotropy, viscoelasticity and yielding behavior is presented. It uses the fluidity to specify the microscopic state. The model is composed of two differential equations, one tensorial equation that relates the stress to the rate of strain and one scalar evolution equation for the fluidity. The equation for stress is a modified version of the Oldroyd-B model in which the relaxation and retardation times are functions of the fluidity. In contrast to the existing phenomenological models for thixotropic elasto-viscoplastic materials, the present one relies only on a few material functions that are directly measurable by means of three standard rheological tests. No fitting parameters are involved. The model predictions were compared with transient shear flow data pertaining to a laponite aqueous suspension, and the agreement turned out to be quite remarkable.

Wednesday 4:00 Constellation E

SA26

**Structure and rheology of Pluronic® tri-block copolymer binary mixtures self-assembled micelles in the protic ionic liquid ethylammonium nitrate**Ru Chen<sup>1</sup>, Carlos R. López-Barrón<sup>2</sup>, and Norman J. Wagner<sup>1</sup><sup>1</sup>*Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States;*<sup>2</sup>*ExxonMobil Chemical Company, Baytown, TX, United States*

The structural and rheological properties of a model series of binary Pluronic block copolymer mixtures that self-assemble in a protic ionic liquid are studied as a strategy to modulate and control the soft solid behavior of amphiphilic block copolymers in ionic liquids. The properties of the soft solids are controlled via tuning the mixture composition of Pluronic block copolymers P123 and F127 in deuterated ethylammonium nitrate (dEAN). [López-Barrón et al, 2014, 2015] Equilibrium microstructures are studied by linear viscoelasticity and small angle neutron scattering (SANS), while the shear induced microstructures are probed by in situ rheo-SANS in the radial direction (1-3 plane of flow) under steady and oscillatory shear flow using recently developed time resolved methods [López-Barrón et al, 2012]. Mixing properties are shown to systematically affect the self-assembly into micelles, which further exhibit crystalline structure at higher concentrations with an inverse melting transition. Solutions with total Pluronic composition of 27.5 wt% and 50/50 mass ratio of P123/F127 in dEAN form closed packed micellar phases similar to those formed in parent homopolymers. [Newby et al, 2009] The application of shear flow in a Couette geometry leads to layering of the closed packed phases. It was also observed that relatively low amplitude oscillations induces slightly different ordering than steady shear. This study points out a strategy for modification of the structural, and hence rheological, properties of Pluronic block copolymers in ionic liquid solvent, providing insights useful for comparing the properties of self-assembled amphiphilic block copolymers in molecular versus ionic liquid solvents under rest as well as steady and dynamic oscillatory shear flows.

Wednesday 4:25 Constellation E

SA27

**Effect of dispersed nanoparticles on the static structure and flow behavior of block copolymer soft solids**Melissa M. Dao and Lynn M. Walker*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

Block copolymer soft solids are formed by driving a disordered triblock copolymer solution through a thermoreversible phase transition to close packed micelles. For certain chain architectures, the crystal structure of the soft solid further undergoes an order-order transition (OOT) from

spherical micelles packed in a cubic crystal structure to close packed cylindrical micelles. In this work, we characterize the impact of nanoparticles dispersed in the soft solids on the nanoscale structure and flow behavior of the micellar phase. An aqueous block copolymer solution with hydrophilic particles, specifically globular proteins, segregated into the interstitial spaces between micelles provides a system with a wide variety of structures; including BCC and FCC phases as well as hexagonally packed cylinders. The soft solids can be aligned to near single crystals with high amplitude, high frequency, oscillatory shear. The crystal structure is characterized using small angle neutron scattering (SANS) with contrast variation while mechanical properties are probed with rheology. Changes in structure of the cubic and cylindrical micellar crystals are observed with dispersed protein size being a primary variable of importance. The flow behavior of both phases is also observed and quantified. The observations and connection to macroscopic rheology are discussed.

Wednesday 4:50 Constellation E

SA28

### **Structure and tensile properties of cross-linked Pluronic-diacrylate copolymers /ethylammonium nitrate ionoelastomers**

Carlos R. López-Barrón<sup>1</sup>, Ru Chen<sup>2</sup>, and Norman J. Wagner<sup>2</sup>

<sup>1</sup>*ExxonMobil Chemical Company, Baytown, TX, United States;* <sup>2</sup>*Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States*

The self-assembly of Pluronic-diacrylate block copolymers F127DA and L121DA in deuterated ethylammonium nitrate (dEAN) is studied via small-angle neutron scattering. Analogous to the non-acrylated Pluronics [1] (F127, L121), F127DA/dEAN and L121DA/dEAN solutions form spherical and wormlike micelles, respectively. We found that these morphologies remain unchanged upon crosslinking the solutions in presence of a UV-curing initiator. Crosslinking of concentrated F127DA/dEAN solutions produces soft elastomers (ionoelastomers) with remarkable large elongation at break and high ionic conductivity, whereas the cross-linked L121/dEAN solutions are much more brittle. This difference can be explained as the highest crosslinking density in L121DA, compared to F127DA. The tensile properties and in-situ microstructure evolution during uniaxial extension of the ionoelastomers are measured using the Sentmanat extensional rheometer (SER) mounted in the SANS instrument NG-7 at the NIST Center for Neutron Research (NCNR). Uniaxial deformation induces micelle alignment in the L121DA/dEAN solutions and a transition from isotropic face-centered cubic lattice grains to a hexagonal close packed crystal structure in the F121DA/dEAN. Both transitions are reversible after unloading.

[1] C. R. López-Barrón, D. Li, N. J. Wagner, J. L. Caplan. *Macromolecules*, 2014, 4 (47), 7484-7495.

Wednesday 5:15 Constellation E

SA29

### **SAXS studies of the structure of a BCC-ordered block copolymer melt subjected to uniaxial extensional flow**

Wesley R. Burghardt and Erica M. McCready

*Northwestern University, Evanston, IL, United States*

We report in situ small-angle x-ray scattering (SAXS) investigations of a spherically-ordered block copolymer melt with a low styrene content (13 %) resulting in spherical polystyrene microdomains ordered in BCC lattice. Melt annealing after clearing above the ODT produces ordered samples that have a macroscopically random orientation distribution of BCC 'grains'. Melt samples are subjected to uniaxial extensional flow in a counter-rotating drum extensional flow fixture housed in an oven with synchrotron x-ray access. During flow, initially isotropic diffraction rings in SAXS patterns become deformed, reflecting distortion of the BCC lattice. Diffracted intensity also concentrates azimuthally, indicating macroscopic alignment of the BCC lattice. There is evidence that extensional flow leads to progressive disordering of the BCC structure, with loss of higher order peaks and the emergence of a diffuse 'halo' of scattering. While the primary diffraction peak is visible in directions parallel and perpendicular to the stretching direction, the deformation of the lattice d-spacing follows affine deformation. Indications of ordering persist to higher strains in samples stretched at higher extension rates, and evidence of affine lattice deformation persists to very high strains (Hencky strains of 1 - 2) under these conditions. The azimuthal distribution of intensity provides evidence that the BCC lattice orients with the 100 direction along the flow direction, although the lattice deformation and simultaneous degradation of long range ordering complicates interpretation of the orientation state. Vestiges of oriented BCC diffraction persist throughout the flow, specifically diffraction peaks attributed to 110 planes oriented with normals at 45° to the stretching direction. We speculate that these features are the most long-lived because lattice planes with this orientation are subjected to neither extreme compression nor dilation by the extensional flow.

Wednesday 5:40 Constellation E

SA30

### **Enhanced gelling properties of gelatin and xanthan mixtures due to synergistic interactions**

Changsheng Wang, Giovannantonio Natale, Nick Virgilio, and Marie-Claude Heuzey

*Chemical Engineering, Ecole Polytechnique Montreal, Montreal, Quebec, Canada*

Studying the rheological properties of polysaccharides and protein aqueous mixtures is of great importance for the development of efficient and novel low-cost thickeners and/or gelling agents. In this work, we show that the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) of gelatin B (GB) and xanthan gum (XG) mixed aqueous solutions (GB/XG) can be significantly superior to those of the pure compounds solutions alone, indicating a synergistic interaction between GB and XG. For mixed GB/XG (5:1, 1.2 wt%), the rheological properties are maximized at a pH of 5.5 when no salt is added. Under this value, insoluble complexes are formed, resulting in a fast decrease of the rheological properties; over pH 5.5, the rheological properties gradually decreases. Zeta potential measurements and dynamic rheological probing as function of pH indicate that a delicate balance between electrostatic attraction and repulsion between GB and XG is needed to achieve the highest rheological properties. This is further supported by the effect of salt addition, which leads to a significant drop of  $G'$  and  $G''$  due to a charge screening effect. The time-resolved dynamic

rheological results and heat-reversible properties of the solutions also suggest the involvement of hydrogen bonding. Confocal laser scanning microscopy (CLSM) analysis reveals that the solution microstructure is sensitive to pH and salt concentration, in accordance with the rheological results, and evolves with time. After 24h, large discontinuous and isolated aggregates are observed at pHs below 5.5, while a network-like structure appears at pH 5.5; further increase of pH results in subtle modifications of the network microstructure, most probably due to the increasing repulsion between the two biopolymers. In order to ultimately understand the mechanism giving rise to these synergistic properties, micro-spectroscopy analysis experiments are currently in progress to obtain the distributions of GB and XG in the mixed solutions.

## Symposium CR Computational Rheology

Organizers: Jay Schieber and Roland Winkler

Wednesday 1:30 Constellation F

CR6

### **Using the discrete sliplink model to predict flows in complex geometries**

Jay D. Schieber<sup>1</sup>, Hualong Feng<sup>1</sup>, and Andreev Marat<sup>2</sup>

<sup>1</sup>*Center for molecular study of condensed soft matter, IIT, Chicago, IL 60616, United States;* <sup>2</sup>*Institute for Molecular Engineering, University of Chicago, Chicago, IL, United States*

The discrete slip-link model (DSM) is combined with smoothed-particle hydrodynamics (SPH) to predict flows of entangled polymers in complex geometries. The continuum equations, conservation of mass and momentum, are handled by SPH, whereas stresses are determined by DSM. By using recent advances in coarse graining, hierarchical modeling, and graphics processors, simulations of moderately entangled polymers in 2D flows can be simulated to steady state on a small cluster in less than two hours. The code is verified by comparing with analytic, asymptotic solutions of Newtonian flow, and by the method of manufactured solutions. The technique is applied to a journal bearing, which exhibits elastically induced vortices at zero Reynolds number, and Weissenberg number order one.

Wednesday 1:55 Constellation F

CR7

### **Self-organization of end-functionalized semiflexible polymer suspensions at equilibrium and under shear flow**

Jin Suk Myung, Roland G. Winkler, and Gerhard Gompper

*Institute of Complex Systems, Forschungszentrum Jülich, Jülich, NRW 52425, Germany*

Functionalized polymers are able to self-organize into complex structures covering a broad-range of length scales and thus provide the building blocks for novel complex materials. Examples are suspensions of end-functionalized rodlike polymers, which exhibit a novel scaffold-like structure above a certain adhesive strength and concentration. The complex structure affects the dynamics and rheological behavior of these systems. We investigate the equilibrium and non-equilibrium dynamical behavior of such end-functionalized semiflexible polymer suspensions by using mesoscale hydrodynamic simulations. The hybrid simulation approach combines the multiparticle collision dynamics (MPC) method for the fluid, which accounts for hydrodynamic interactions, with molecular dynamics simulations (MD) for the semiflexible polymers. Scaffold-like network structures of the polymers are observed in equilibrium, which are governed by polymer flexibility and end-attraction strength. The structural properties are discussed for various adhesive strengths and polymer stiffnesses. In addition, we investigate the flow behavior of the polymer network under shear and analyze the non-equilibrium structural and rheological properties. The scaffold structure breaks up and densified aggregates are formed at low shear rates, while the structural integrity is completely lost at high shear rates. We provide a detailed analysis of the flow-induced structures on various length scales with the respective changes of shear stress and the flow profile. These studies provide a deeper understanding of the formation and deformation of network structures in complex materials.

Wednesday 2:20 Constellation F

CR8

### **Entanglement loss during crazing of glassy polymers is not geometrically necessary**

Robert S. Hoy<sup>1</sup>, Ting Ge<sup>2</sup>, Stefanos Anogiannakis<sup>3</sup>, Christos Tzoumanekas<sup>3</sup>, and Mark O. Robbins<sup>4</sup>

<sup>1</sup>*Physics, University of South Florida, Tampa, FL 33620, United States;* <sup>2</sup>*Chemistry, University of North Carolina, Chapel Hill, NC 27599, United States;* <sup>3</sup>*Mat. Sci. & Chem. Eng., National Technical University of Athens, Athens 15780, Greece;* <sup>4</sup>*Physics, Johns Hopkins University, Baltimore, MD 21218, United States*

Using molecular dynamics simulations and topological analyses, we examine the evolution of entanglements during crazing in model polymer glasses. By tracking individual topological constraints (TCs) over the course of deformation, we show how the evolution of their statistical properties can be used - in conjunction with characterization of the complex, nonaffine lateral displacements that occur during fibrillation - to provide insights not available from previous studies. Our findings directly contradict the conventional assumptions that entanglements act like chemical crosslinks and that therefore a large fraction must be lost during interfibril void formation and expansion. Instead, the number of TCs remains nearly constant throughout the craze drawing process; about 1/3 of TCs are ultimately replaced by other TCs associated with the same rheological tubes. By combining this key result with extensive measurements of the distributions of entanglement spacings and stretches, the evolution of these during deformation, and end-constrained melt-dynamics simulations that relate processes in crazes to processes familiar from tube theory, we formulate a new molecular-scale picture of entanglement evolution during crazing.

Wednesday 2:45 Constellation F

CR9

**Viscoelastic properties of an entangled polymer melt by probe rheology simulation**Mir Karim<sup>1</sup>, Tsutomu Indei<sup>2</sup>, Jay D. Schieber<sup>2</sup>, and Rajesh Khare<sup>1</sup><sup>1</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States;* <sup>2</sup>*Center for molecular study of condensed soft matter, IIT, Chicago, IL 60616, United States*

The linear viscoelastic (LVE) properties of an entangled polymer melt are extracted from probe rheology simulations. The model polymer melt consists of bead-spring chains of length  $N = 80$  containing a single, embedded model nanoparticle. Following the approach proposed in our previous work [Karim et al., Phys. Rev. E, 86, 051501 (2012)], both active and passive particle rheology modes are applied to study the melt viscoelasticity. As was previously observed for the unentangled melt, the probe particle and medium inertial effects need to be incorporated into the generalized Stokes-Einstein relation (GSER) to determine the viscoelasticity. The inertial generalized Stokes-Einstein relation (IGSER) so obtained is applied to determine the melt viscoelasticity from the analysis of the probe particle motion. Our probe rheology simulation results are compared with those from other simulation techniques such as Green-Kubo and Non-Equilibrium Molecular Dynamics (NEMD). We elucidate the important role played by the long-range hydrodynamic interactions between the particle images in governing the frequency range of applicability of the technique. Furthermore, the strength of the IGSER is demonstrated by its ability to calculate the particle mean squared displacement from the knowledge of the medium viscoelasticity. Such an ability should be of great interest for biomedical applications of targeted drug delivery using nanoparticles.

Wednesday 3:10 Constellation F

CR10

**Molecular dynamics of polymer melt crystallization**Triandafylidi Vasilii<sup>1</sup>, Joerg Rottler<sup>2</sup>, and Savvas G. Hatzikiriakos<sup>1</sup><sup>1</sup>*Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia V6T1Z3, Canada;*<sup>2</sup>*Department of Physics and Astronomy, The University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada*

Large scale molecular dynamics simulations were carried out to study the kinetics of polymer melt crystallization. A coarse-grained model CG-PVA developed by Meyer and Muller-Plathe is applied (Meyer 2001). A new algorithm for analyzing crystallization is proposed. It is based on the alignment of individual chains which speeds up previous similar calculation by about 10 times. Moreover, it is found to be more suitable for investigating chain crystallinity in polydisperse systems. Different thermodynamic protocols of polymer crystallization are studied: deep quench, shallow quench and cooling. The cooling with the slowest rate was shown to exhibit the highest final crystallinity. For the case of deep quench, crystallization studies of polydisperse systems were carried out. Short chains were shown to exhibit only one-folded lamellae and therefore have faster crystallization rate, comparing to longer chains. The resulting crystallinity evolution was fitted using the Avrami equation. The crystallization rate is shown to be independent of chain length, whereas the saturation value is found to depend strongly on chain length. The numerical results are found to be in qualitative agreement with experiments.

H. Meyer and F. Müller-Plathe, J. Chem. Phys. 115, 7807 (2001).

Wednesday 4:00 Constellation F

CR11

**Hydrodynamically interacting particles confined by a spherical cavity via dynamic simulations**Christian Aponte-Rivera, Yu Su, and Roseanna N. Zia*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

We study the diffusion in and rheology of hydrodynamically interacting colloids confined by a spherical cavity via dynamic simulation, as a model of intracellular and other confined biophysical transport. Previous attempts to model such behavior have been limited primarily to a single particle inside a spherical cavity. Although attempts have been made to extend such models to more than one confined particle, none has yet successfully accounted for the effects of hydrodynamics, owing to the difficulties of modeling many-body long-ranged interactions. In some such studies, attempts have been made to circumvent this difficulty by modeling all particle interactions as pairwise additive, and accounting only for leading-order far-field interactions (neglecting near-field lubrication interactions entirely). In the present study, we utilize a Stokesian-dynamics like approach, implementing our newly derived mobility functions to fully account for all many-body far-field interactions between the particles themselves, and between particles and the enclosing cavity. Together with the appropriate near-field resistance functions, these form a complete model for simulation of the motion of an arbitrary number of particles enclosed by a cavity of arbitrary size relative to the particles. Here we report the short- and long- time self-diffusion at equilibrium, with a focus on the dependence of the former on particle positions relative to the cavity, and of both on volume fraction and size ratio. Comparison to recent experimental results is discussed.

Wednesday 4:25 Constellation F

CR12

**Boundary integral simulations of dissolving drops in circular tubes**Thomas Leary and Arun Ramachandran*Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada*

Recent years have seen an upsurge in the literature reporting the microfluidic measurement of the kinetics of 'fast' gas-liquid reactions (e.g. CO<sub>2</sub> and switchable solvents), by recording the shrinkage of bubbles in segmented flows of these gas-liquid combinations in microfluidic channels. A critical aspect of the deconvolution of bubble shrinkage data to deduce dissolution and kinetic constants is the knowledge of how dissolution

influences the velocity field in the liquid slug, and hence, the mass transport characteristics. While there have been extensive studies of the flow characteristics in liquid slugs segmented by undissolving bubbles, there is no literature on the corresponding problem with dissolving ones.

This research examines the dissolution of drops confined in a tube using a boundary integral method (a bubble, which is a drop with low viscosity, would be a special case of this study). Drop dissolution is modeled as a discontinuity of the normal components of the inner and outer fluid velocities at the drop interface. The effects of the dissolution rate on the film thickness and the inter-drop separation distance are examined as a function of the capillary number and the viscosity ratio. The results demonstrate that depending on the dissolution rate, the degree of mixing can change appreciably from one slug to the next. A curious result is that the film thickness and the droplet separation distance can change significantly beyond a critical capillary number, producing flow patterns within a liquid slug that are completely different from those known for the undissolving bubble case. These flow patterns have the potential to reduce the length scale for diffusion within a slug and improve mixing, but at the same time, they also induce cross-talk between adjacent liquid slugs. These results will ultimately guide the selection of operating regimes that enable convenient interpretation of data from reacting gas-liquid segmented flows to obtain kinetic constants.

Wednesday 4:50 Constellation F

CR13

### **Deformation of a viscoelastic drop in periodic planar extensional flows**

Abhilash Reddy Malipeddi and Kausik Sarkar

*The George Washington University, Washington, DC 20052, United States*

The deformation of a viscoelastic (modified FENE–CR) drop suspended in a Newtonian fluid subjected to time-periodic planar extensional flows is numerically investigated. Motivation for this study stems from the simplicity of the flow which can be an effective tool for understanding how viscoelasticity affects drop dynamics. A front-tracking finite difference method is used to simulate the system varying various parameters (inertia, interfacial tension, viscosity and viscoelasticity). The drop deformation exhibits a complex dependence on Weissenberg number—depending on the other non-dimensional parameters, drop deformation may increase, decrease or show a non-monotonic variation. A simple ordinary differential equation based on a lumped parameter approximation is developed that qualitatively describes and explains the behavior (amplitude and phase) observed in the simulated drop deformation. It shows that the complex drop dynamics results from a subtle competition between the different forces present in the system.

Wednesday 5:15 Constellation F

CR14

### **Effects of polymer additives on the structural, dynamic and rheological properties of asphalt: A molecular simulation study**

Fardin Khabaz and Rajesh Khare

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States*

Asphalt rheology is important for designing asphalt formulations for road construction in a given environmental zone. Asphalt is a mixture of organic molecules of many different types, which makes the modeling and prediction of its viscoelastic properties a challenging task. The main constituents of asphalt are low to medium molecular weight hydrocarbons. Polymer additives are expected to enhance the mechanical properties of these asphalt systems. In this work, we will use molecular simulations to study the effect of polymer additives on the mechanical properties of these systems. The polymer additives studied are styrene-butadiene rubber (SBR) and atactic polypropylene (a-PP). The volumetric and structural properties of modified asphalt systems are characterized by determining the density and the radial distribution function, respectively. Nonequilibrium molecular dynamics (NEMD) method is used to determine the shear viscosity and the complex modulus. Simulation results are used to elucidate the molecular mechanisms underlying the mechanical property changes on addition of the polymeric chain.

Wednesday 5:40 Constellation F

CR15

### **Inferring structure from rheology: Parameter uncertainties in fitting asymptotically-nonlinear rheology**

Piyush K. Singh<sup>1</sup> and Randy H. Ewoldt<sup>2</sup>

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

It is a common practice in rheology to infer material structure information by fitting constitutive model parameters to experimental data. Appropriate estimation of parameter uncertainty is critical to our confidence in the estimated parameter value. Our objective here is to identify best practices for honest quantitative uncertainty predictions in model fit parameters, motivated by the end goal of inferring molecular/structural information from such parameters. We consider data from both linear and nonlinear oscillatory measurements. Specifically, nonlinear rheological information is from asymptotically-nonlinear large-amplitude oscillatory shear (LAOS), which is highly relevant for inferring molecular information; it probes the nonlinear response across a range of timescales (Deborah numbers), yet is accessible to analytical solutions of nonlinear constitutive models. To illustrate model parameter uncertainty calculations, we consider a multimode Giesekus model (which includes the anisotropic polymer drag coefficient as a fit parameter) fit to the linear and asymptotically-nonlinear LAOS data of a 1,4-polyisoprene melt. We emphasize key sources of parameter uncertainty, including (i) experimental measurement uncertainty, (ii) the insensitivity of model predictions to a parameter, and (iii) model parameter correlations. For the cases considered, parameter correlations tend to dominate leading to potentially large uncertainties in fit parameters, especially in over-parameterized models. Importantly, these findings suggest that the common practice of fitting linear data first, and nonlinear data second, does not account for the true uncertainty in parameters, since many parameter correlations are neglected. This is in contrast to fitting the overall dataset simultaneously, which produces the true parameter uncertainties. This is of key

importance for inferring material structure from any combination of rheological measurements, be they linear, asymptotically-nonlinear, or fully nonlinear.

## Symposium PM Probe Microrheology

Organizers: Eric Furst and Roseanna Zia

Wednesday 1:30 Baltimore/Annapolis

PM6

### **Towards probe-free microviscometry of cells**

Zeina S. Khan, Nabiollah Kamyabi, and Siva A. Vanapalli

*Chemical Engineering, Texas Tech University, Lubbock, TX 79415, United States*

Intracellular or cytosol viscosity is a key determinant of rates of biochemical reactions in living cells as well as their physiological functions. Intracellular viscosity is currently measured using nanoscale probe rheology. Although significant advances have been made in both chemical probe design and imaging modalities, measurements can be difficult because of their sensitivity to probe shape, concentration and binding as well as solvent polarity. In this study, we explore the potential of microfluidics to characterize intracellular viscosity by building on the recent understanding that at millisecond time scales cell rheology is dominated by the cytosol viscosity. We expose cells to rapid strain deformation by flowing them through a constricted microchannel. Simultaneously, we record the corresponding excess pressure drop induced by the cell as a measure of stress. To ascertain if indeed this stress-strain data encodes intracellular viscosity, we conducted experiments with emulsion droplets of varying internal viscosity and interfacial tension, as well as soft elastic particles of varying elastic modulus. We find that the excess pressure drop shows no apparent dependence on elastic modulus or drop interfacial tension, but depends significantly on drop internal viscosity. Strikingly, the excess pressure drop for different cell types lies between two universal bounds determined by the viscous drop and elastic particle limit respectively, allowing us to quantify an effective intracellular viscosity. Moreover, our intracellular viscosity estimates are closer to the values reported from probe rheology than whole cell viscosity methods (e.g. AFM) suggesting that our millisecond microfluidic deformation experiments are exciting intracellular fluid flows. In conclusion, our microfluidic viscometry method is simple, probe-free, high throughput, and compatible with all cell types making it attractive for biomedical applications.

Wednesday 1:55 Baltimore/Annapolis

PM7

### **Multi particle tracking microrheology probing structure and flow of turbid, concentrated colloidal dispersions**

Norbert Willenbacher and Clara Weis

*Institut für Mechanische Verfahrenstechnik und Mechanik, Karlsruher Institut für Technologie, Karlsruhe 76131, Germany*

Multi particle tracking (MPT) optical microrheology using fluorescent tracer particles with diameters between 100 nm and 1000 nm is a versatile tool to study the structure and dynamics of heterogeneous complex fluids. The particle size and also the inter-particle distance are the length scales on which structural information is obtained. Surprisingly, the method is especially useful to study turbid, highly concentrated colloidal dispersions. Commercial aqueous colloidal dispersions have been studied systematically covering the full range of the phase diagram including the fluid, the crystalline and the glassy state. Fluid suspensions with short range repulsive interactions at particle loading  $f < 0.5$  exhibit perfect agreement between viscosity from bulk rheometry and microrheology. Hard sphere type crystallizing dispersions in the liquid/crystalline coexistence regime show a large variation in MSD of different tracer particles with slopes  $\Delta \text{MSD} / \Delta t$  between 0 and 1. The heterogeneity of the samples can be directly imaged based on this rheological contrast using Voronoi triangulation. The broadening of the fluid/crystalline coexistence region due to weak attractive depletion forces induced by added polymer is directly proven by MPT and the change in crystallite size is imaged. Tracer particle mobility strongly decreases as the colloidal glass transition  $f_g = 0.58$  is approached. The change of particle mobility and the variation of sample heterogeneity is also discussed in the so-called re-entry regime at  $f > f_g$  where the system transitions from glassy to fluid and from fluid to gel-like when attractive interaction controlled by non-adsorbing polymer increases from 0 to a few kT.

Wednesday 2:20 Baltimore/Annapolis

PM8

### **Quantitative imaging of fluid systems under flow: Novel 3D rheoscope option for rotational rheometers**

Aloyse J. Franck

*R&D, TA Instruments - Waters LLC, New Castle, DE 19720, United States*

Microscopy options have been used in conjunction with rotational rheometers for many years to study structural changes under flow in complex materials such as emulsions, blends, suspensions, etc. Quantitative imaging in 3D, combining a scanning microscope and a rheometer for simultaneous rheological characterization and micro-structural analysis is a new technique that can be used to measure the rheological material properties resulting from changes in microstructure imposed by the flow. The 3D microscope presented here has been developed for the rotational rheometer DHR from TA Instruments. The microscope assembly is mounted below an optical stage, attached to smart swap base of the rheometer. The objective is mounted on a piezo stage for precise vertical positioning over a distance of 100 micron and can be positioned in any horizontal location underneath the rotating glass plate (to allow counter-rotation experiments) of the optical stage. The compact microscope assembly consists of objective, piezo element, LED light source, filter block and camera and mounts directly to the rheometer base. The rigid coupling to the rheometer facilitates setup and reduces vibrations during image capturing. The microscopy option has been designed for versatile applications and lends itself for wide field and fluorescence microscopy; camera, objectives, light source and filter blocks can be easily exchanged and adapted to the application requirements. Connection to an external confocal microscopy is possible. In this presentation the microscope option is used to

measure the velocity profile across the gap in the cone-plate/plate-plate geometry as a function of the shear rate to determine wall slip or flow non-uniformities such as shear banding. 1.5 micrometer stabilized PS spheres, dyed with fluorescein were added as markers. The recorded video clips were analyzed using 2D correlation and particle tracking algorithms to determine velocity as a function of the gap position.

Wednesday 2:45 Baltimore/Annapolis

PM9

### **Combined DLS-optical microrheology and Raman spectroscopy: A novel tool for probing self-assembly and gelation in complex fluids**

Samiul Amin, Steven Blake, Stacy Kenyon, Madhabi Majumdar, and E.Neil Lewis  
*Malvern Biosciences Inc, Columbia, MD, United States*

Soft matter / complex fluid systems are ubiquitous across a range of industrial and consumer sectors with common examples being inks, paints, drilling fluids, cosmetics, personal care products and foodstuffs. In many instances, the final product format of these complex fluids are gels or soft solids and the processing and product functionality attributes of such materials are often dependent on their rheological response and viscosity. The rheology evolution in such complex fluid systems as a function of formulation parameters (e.g. pH, ionic strength) is intimately connected to corresponding changes in the micro- and mesostructure and intermolecular and intramolecular associations and interactions. Most insights developed into understanding the self-assembly and rheology evolution process in such systems has primarily focused on elucidating the associated micro- and mesostructural changes through various scattering and imaging techniques. Furthermore detailed insights into the associated chemical conformational/structural changes and various non-covalent interactions (e.g. H-bonds, hydrophobic interactions) leading to the self-assembly process have been very limited. This talk will illustrate the utility of the combination of mesoscale structure-property elucidation techniques such as DLS/microrheology with the high resolution chemical structure/conformation elucidation techniques such as Raman spectroscopy in generating novel mechanistic insights that will allow the performance engineering of complex fluids and soft matter systems. This will be exemplified through studies into the self-assembly/gelation mechanisms in three very different complex fluids-mixed anionic/zwitterionic surfactant wormlike micelles, polyvinyl alcohol and a thermo-reversible, gel-forming agarose biopolymer.

## **Symposium MN Micro and Nanofluidics**

Organizers: Charles Schroeder and Siva Vanapalli

Wednesday 1:30 Frederick/Columbia

MN6

### **Shape controllable wax microparticle generation using microfluidics and droplet impact**

Doojin Lee<sup>1</sup>, Shilpa Beesabathuni<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>*Mechanical engineering, University of Washington, Seattle, WA, United States*

Microfluidics has become an versatile and emerging tool for the generation of particles and droplets, providing fine tuning over the size and shape of particles, porosity, internal structure, chemical functionality, and chemical anisotropy. A number of recent studies have investigated the use of non-spherical particles in biotechnology, pharmaceutical, optics, cosmetics, and image enhancement due to their unique properties such as anisotropic responses to external fields, large surface areas, and high packing density. Here, we present the formation of spherical and non-spherical wax microparticles by employing a facile two-step process which consists of the generation of molten wax microdroplets in a flow-focusing channel and their subsequent off-chip solidification via microdroplet impingement on an immiscible liquid interface. The size of wax microdroplets in a microfluidic platform is controlled by temperature and the effect of the temperature on the droplet sizes is theoretically estimated. A cursory phase diagram of morphology transition is depicted depending on the Capillary number and the Stefan number. Numerical calculations of the heat transfer and crystallization of molten wax microdroplets are carried out to understand the physics behind the deformation and solidification process. The results reveal that key parameters on the formation of wax microdroplets in a microfluidic channel are the viscosity of continuous fluid and the interfacial tension between continuous and discontinuous fluids. The deformation of wax microparticles is crucially governed by the viscous and thermal effects rather than the gravitational and buoyancy effects. Non-isothermal crystallization kinetics explains the time-dependent thermal effects on the droplet deformation and solidification.

Wednesday 1:55 Frederick/Columbia

MN7

### **Diamagnetic-levitation viscometer based on electro-magnetically spinning system**

Yuji Shimokawa, Yusuke Matsuura, Taichi Hirano, and Keiji Sakai

*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, Japan*

Low viscosity fluids play important roles in advanced technologies in recent years. For example, the viscosity of biofluids such as blood is almost the same as that of water, and accurate methods to measure the viscosity of these fluids attract attention in biology and medical science. However, the measurement of the viscosity lower than 1 mPa·s is very difficult even if a high-end rheometer is used, because the effect of inertia and mechanical friction exceeds that of the viscosity. The capillary tube viscometer is accurate and reliable for low viscosity fluids, however, the principle is based on the Hagen-Poiseuille's law, and the analysis of the flow in the capillary is simplified under the approximation of incompressible fluids; the approximation is not valid for compressible fluids such as gases. Therefore, the standard method to measure the fluid viscosity, in the range

from  $\mu\text{Pa}\cdot\text{s}$  to  $1\text{ mPa}\cdot\text{s}$ , has not been established at present. The purpose of this study is to develop an accurate and convenient method to measure the viscosity in the order of  $\mu\text{Pa}\cdot\text{s}$ .

The viscometer we developed in this study avoids mechanical friction by means of the diamagnetic levitation. We used a graphite disk attached with an aluminum disk as a probe. The graphite has a large diamagnetic susceptibility enough to lift the probe in the air. The rotation of the probe is driven by the Lorentz force, and laminar shear flow is formed in the gap between the probe and the base magnet. Their torque is balanced during the steady rotation, and the viscosity coefficient is obtained from the rotation speed of the probe. In this presentation, we introduce the measurement principle in detail, and report the result of quite low viscosity measurement ( $\sim 10^{-8}\text{ Pa}\cdot\text{s}$ ) in the low pressure region.

Wednesday 2:20 Frederick/Columbia

MN8

### **Continuous shear-rate and disposable microfluidic viscometers for complex fluid rheology**

Siddhartha Gupta and Siva A. Vanapalli

*Chemical Engineering, Texas Tech University, Lubbock, TX 79415, United States*

Microfluidic viscometry is transforming into a complementary approach to conventional rheometry. It offers distinct advantages such as high shear rates, small sample volumes and precise control of geometry and flow conditions. Currently, two unmet needs exist in microfluidic viscometry. First, to obtain a viscosity versus shear rate curve, current approaches require that the flow rate on the pump be varied after acquiring each readout to cover a range of shear rates. Since pump flow rates require long stabilization times, generation of viscosity curves can be tedious. Second, the viscosity is often measured by incorporating pressure sensors on the channel floor, which may not be ideal for handling biological samples where use-and-throw capability may be desired to avoid cross-contamination. Moreover, repeated handling of particulate fluids in these devices may lead to particle adhesion on sensor surfaces, unless washing protocols are implemented. In this study, we propose a microfluidic viscometer that addresses these two limitations of current approaches. Our approach involves using a tapered microchannel in combination with co-flowing laminar streams. The taper in the microchannel allows the shear rate to be varied continuously in the streamwise direction of flow, while the location of the fluid-fluid interface determines the viscosity of the fluid. Thus, from a single snapshot of the interface, one can obtain the viscosity versus shear rate curve without actively manipulating the flow rate. Moreover, since the sensor (camera) is not located in the device, our approach lends to disposable viscometers. We test this methodology both experimentally and numerically. We use lubrication analysis to investigate the viscosity and shear rate range that can be obtained with such a device for both Newtonian and powerlaw fluids. Our results show that tapered microchannels are capable of yielding viscosity curves with two orders of magnitude variation in the shear rates from a single flow rate condition at the inlet.

Wednesday 2:45 Frederick/Columbia

MN9

### **Effects of contraction ratio on elastic instability of sodium hyaluronate solution in a micro channel**

Ruri Hidema<sup>1</sup>, Taiki Oka<sup>2</sup>, Hiroshi Suzuki<sup>2</sup>, and Yoshiyuki Komoda<sup>2</sup>

<sup>1</sup>*Organization of Advanced Science and Technology, Kobe University, Kobe, Hyogo 657-8501, Japan;* <sup>2</sup>*Department of Chemical Science and Engineering, Kobe University, Kobe, Hyogo 657-8501, Japan*

High deformations of viscoelastic fluids in an abrupt contraction or expansion channel induce unstable behaviors of the fluids. This happens especially in a micro scale of the channel, which order is 50 microns or less, even when Reynolds number is low. In micro-channels, since a characteristic length scale is small, Reynolds number that determines the flow stability becomes lower. Therefore, the ratio, called elasticity number, of Weissenberg number to Reynolds number becomes high in micro-channels. The elasticity number represents elasticity effects to inertia. When the elasticity number becomes high, the flow induces unstable flows due to the elasticity. Although elastic instability is important for the micro-fluidity, such as techniques of 3D printing and lab-on-a-chip etc., the phenomena have been just started to study.

Here, we focus on elastic instability of hyaluronate solution in micro-channels. Hyaluronan is essential biopolymers for human body. Lack of hyaluronan in the synovial fluids induces joint pain. Flow behaviors of sodium hyaluronate in water solution and in phosphate buffered saline solution as viscoelastic fluids in planer abrupt contraction-expansion channels have been observed. Especially, the effect of the geometry of the flow path on the flow behavior was focused on. The corner vortices in the corner of the upper region in the abrupt contraction-expansion channels were also analyzed to quantify the flow characteristics. The elasticity numbers of the solution had a big influence on the fluidity, that is, stable or unstable, when the concentration of the solution in lower. It was concluded that such stable and unstable flows are categorized on Weissenberg-Reynolds number space. Such a technique can be also used to determine the concentration of hyaluronan in solution as an application of diagnosis of synovial fluids.

Wednesday 3:10 Frederick/Columbia

MN10

### **Polymer solution flow in porous media: Pore and macro scale analyses**

Nicolle Lima, Ricardo Dias, and Marcio S. Carvalho

*Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, RJ 22451-900, Brazil*

Water flooding is the most commonly used oil recovery method. However, the high mobility ratio between the water and oil phases limits the amount of oil displaced. The addition of polymer molecules to the injected water increases its viscosity, leading to a better mobility ratio and consequently larger volumes of produced oil. Despite recent progress, the fundamental understanding on how elastic properties of a polymer solution improve oil recovery is still not complete. Because of the complexity of the flow, different mechanisms for residual oil mobilization have been proposed. The relative importance of each of these mechanisms is not clear. In this work, oil displacement by viscoelastic liquids in a porous

media is studied in pore and macroscopic scales using a microchannel network and sandpacks. A glass microfluidic chip is used as a 2-D model of a porous space to visualize the evolution of the water phase saturation as it displaces oil. Above a critical flow rate, the converging-diverging flow of the polymer solution leads to a higher pressure gradient acting on trapped oil ganglia, mobilizing them. The results clearly show the reduction of the residual oil saturation after the polymer solution injection. The macroscopic behavior is studied by injecting different polymer solutions in an oil-saturated sandpack. The amount of oil displaced is determined as a function of the rheological properties of the solution and flow rate.

Wednesday 4:00 Frederick/Columbia

MN11

### **Microfluidic valve based on the light-activated self-assembly of a biopolymer**

Srinivasa Raghavan and Hyuntaek Oh

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

Fluids with light-responsive rheology (i.e., photorheological or PR fluids) have been studied by many research groups. One advantage of light over other stimuli is in its spatial selectivity, i.e., its ability to be directed at a precise location, and an application that leverages this feature is for flow control within microfluidic devices. However, existing PR fluids are not suitable for this purpose. Here, we report a PR fluid based on the biopolymer, alginate that can be used for microfluidic flow control. The fluid is composed entirely of commercially available components: alginate, a photoacid generator (PAG), and a chelated complex of divalent cations. Upon exposure to UV, the PAG dissociates, which releases free divalent ions from the chelate. These ions self-assemble with the alginate chains to give a stiff gel (modulus  $\sim 1000$  Pa). We flow the above fluid through a network of microchannels and expose a specific channel to UV light. At that point, a gel is formed that blocks the flow. When the UV light is removed, the gel is gradually diluted by the flow and the channel reopens. We have thus demonstrated a new kind of light-activated fluidic valve; note that the above concept relies on physical bonds, i.e., on self-assembly, rather than on covalent crosslinking of monomers.

Wednesday 4:25 Frederick/Columbia

MN12

### **Domain expansion dynamics in stratifying foam films**

Yiran Zhang, Subinuer Yilixiati, and Vivek Sharma

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

The stability, rheology and applications of foams, emulsions and colloidal sols depend on the hydrodynamics and thermodynamics of thin liquid films that separate bubbles, drops and particles respectively. Thin liquid films containing micelles, colloidal particles, liquid crystals or polyelectrolyte-surfactant mixtures exhibit step-wise thinning or stratification, often attributed to the layer-by-layer removal of the aforementioned supramolecular structures. Stratification proceeds through emergence and growth of thinner circular domains within a thicker film, and the domain expansion dynamics are the focus of this study. Domain and associated thickness variation in foam films made from sodium dodecyl sulfate (SDS) micellar solutions are examined using a Scheludko-type cell with a novel technique we call Interferometry Digital Imaging Optical Microscopy (IDIOM). Below 100 nm, stratification and drainage cause a thickness-dependent variation in reflected light intensity, visualized as progressively darker shades of gray. We show that the domain expansion dynamics exhibit two distinct growth regimes with characteristic scaling laws. Initially, the radius of the isolated domains grows with square root time, and the expansion rate can be characterized by an apparent diffusion constant. In contrast, after a section of the expanding domain coalesces with the Plateau border, the contact line between domain and the surrounding thicker region moves a constant velocity. We show that a similar transition from a constant diffusivity to a constant velocity regime is also realized when a topological instability occurs at the contact line between the growing thinner isolated domain and the surrounding thicker film. Though several studies have focused on the expansion dynamics of isolated domains that exhibit a diffusion-like scaling, the change in expansion kinetics observed after domains contact with the Plateau border has not been reported and analyzed before.

## Thursday Morning

### Symposium AP Award Presentations

#### *Metzner Award Presentation*

Thursday 8:00 Constellation A

AP1

#### **The rheology and microstructure of carbon nanotube suspensions**

Anson Ma

*Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States*

Carbon nanotubes (CNTs) are rolled cylinders of graphene sheets with an aspect ratio on the order of hundreds or larger. In this presentation, the rheology of suspensions containing aggregating and non-aggregating CNTs will be compared and contrasted. The aggregating and non-aggregating CNT suspensions both exhibited shear-thinning behavior in steady shear flow, but they showed remarkably different breakup behavior in capillary thinning experiments. In the case of a non-aggregating CNT suspension, the shear rheology was successfully modeled using an orientation model, where the shear-thinning behavior was attributed to the progressive alignment of CNTs in the shear direction. Such model, however, failed to capture the stronger shear-thinning behavior associated with aggregating CNT suspensions. Inspired by the associative polymer literature, an aggregation-orientation model has been developed to connect the rheology data with not only the orientation, but also the aggregation state of CNTs. In the second part of this presentation, latest findings on the microstructure and the apparent surface pressure of CNTs adsorbed at an air-water interface will be reported. Using CNTs as a model system, we aim to explore and understand how the particle shape fundamentally influences the interfacial transport phenomena. The findings may offer a general and yet relatively simple strategy to improve the stability of foams and emulsions widely used in pharmaceutical, agricultural, and personal care products.

### Symposium SC Suspensions and Colloids

Organizers: Ali Mohraz and Nina Shapley

Thursday 8:40 Constellation C

SC46

#### **The electrorheological effect for polyhedral silsesquioxane cage structures with cyanopropyl functional groups**

Carl McIntyre and Mishaun Sturm

*Chemical Engineering, University of Louisiana, Lafayette, LA 70503, United States*

Previous research has shown that sulfonated polyhedral silsesquioxane (s-POSS) material when mixed with silicone oil (PDMS) exhibits a significant ER effect. Here we show that cyanopropyl POSS (c-POSS) particles in silicone oil also show significant ER activity. The effects of the functional group attached to the nanocages (POSS) on the rheological properties of the suspension is demonstrated through steady flow and oscillatory tests. Furthermore the electrorheological properties of these mixtures is also shown in these tests. The yield stress,  $(\tau)_y$ , scales with the electric field,  $E$ , as  $(\tau)_y \sim E^{1.15}$ . The elastic storage modulus of the suspension at small strains ( $\gamma=0.10$ ) scales with the electric field  $E$  as  $G' \sim E^{0.99-1.76}$ . The research also contributed answers to the effects of changing the concentration of c-POSS particles. The preyield, yield and postyield characteristics of the ER fluid were determined using the flow curves, small amplitude oscillatory tests, and thixotropic stress loop tests.

Thursday 9:05 Constellation C

SC47

#### **In-situ simultaneous rheo-conductivity and rheo-impedance spectroscopy measurements of strongly conductive complex fluids**

Ahmed Helal<sup>1</sup>, Xin Wei Chen<sup>1</sup>, Thibaut Divoux<sup>2</sup>, Yet-Ming Chiang<sup>1</sup>, and Gareth H. McKinley<sup>1</sup>

<sup>1</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>Centre de Recherche Paul Pascal - CNRS, Pessac 33600, France

Ionically & electronically conductive complex fluids represent an important class of materials with applications in flow battery technologies. For example, electrolyte suspensions containing carbon black nanoconductor networks show promise for novel semi-solid flow cell designs. As the conductive semi-solid suspension is pumped, the attractive colloidal network in the suspension is prone to rupture leading to a decrease of conductivity and, consequently, cell performance. Characterizing the conductivity of the semi-solid suspension under flow is therefore crucial for cell modeling and design. On controlled-stress rheometers, measuring simultaneously the viscometric & electrical properties of a complex fluids is challenging due to the friction associated with electrical connections to the rotating shaft. Our new approach utilizes liquid metal (eutectic Gallium/eGal) as a safe and stable low-friction & low-resistance electrical connection to the rotating shaft. Using gold-plated parallel plates as

electrodes, this new setup allows us to perform in-situ simultaneous rheo-conductivity (DC) and rheo-impedance spectroscopy (AC) measurements to extend our understanding of electro-chemical measurements in complex fluids and soft solids from a static viewpoint to a dynamic one. We present measurements using this new setup on different carbon black suspensions and demonstrate the importance of corrections for shear-inhomogeneity & contact resistance on the accuracy of the conductivity measurement. In addition, we will show how simultaneous measurements of viscometric and electrical properties can give valuable insight into the evolution of the microstructure of a dense conductive flow battery material under shear.

Thursday 9:30 Constellation C

SC48

### **Alignment dynamics of magnetic microdisks in rotating magnetic field**

Mingyang Tan<sup>1</sup>, Han Song<sup>2</sup>, Albrecht Jander<sup>2</sup>, Pallavi Dhagat<sup>2</sup>, and Travis W. Walker<sup>1</sup>

<sup>1</sup>*Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States;* <sup>2</sup>*Electrical Engineering and Computer Science, Oregon State University, Corvallis, OR 97331, United States*

Next generation wireless communication devices require inductors and antennae to function at high frequencies. Composites with fine metallic magnetic particles embedded in a polymer matrix are promising materials for high-frequency application. Materials with magnetic anisotropy (i.e., rod-like or disk-shaped particles) are gaining increased attention, as they exhibit enhanced high-frequency permeability in comparison to materials with spherical particles. Moreover, magnetic alignment of these anisotropic particles further increases the high-frequency permeability and ferromagnetic resonance frequency. Alignment can be achieved by applying an external magnetic field, prior to freezing the configuration in the composite. In this study, we show that the application of a rotating magnetic field can bi-axially align disk-shaped particles, producing planar anisotropy in the composite. The dynamics of alignment are investigated, and the timescales associated with the alignment process as a function of the properties of the composite and the conditions of external magnetic field are studied. We introduce a theoretical Stokes-flow model to describe the dynamic process. This model guides the process control conditions to achieve highly aligned planar anisotropy. Experimentally, Ni and NiFe microdisks embedded within a composite are observed under bright-field optical microscopy. Comparisons between experiments and model time scales are made.

Thursday 10:25 Constellation C

SC49

### **Rheology of cubic particles suspended in both a Newtonian fluid and a concentrated colloidal dispersion**

Colin D. Cwalina and Norman J. Wagner

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

We investigate the flow behavior of concentrated suspensions of cubic zeolite particles suspended in a Newtonian fluid (glycerol) under both steady and large amplitude oscillatory shear (LAOS). Under steady shear, at low shear stresses, the rheology is Newtonian. Shear thickening is observed beyond a critical value of the shear stress. The relative viscosity of these suspensions of cubic particles in the shear-thickened state is significantly larger than that for suspensions of spherical particles at comparable volume fractions which can be understood in terms of the lubrication hydrodynamics interactions between spheres and cubes. In oscillatory flow, Newtonian behavior and dynamic shear thickening are observed but the magnitude of the complex viscosity in the low stress amplitude Newtonian regime is consistently reduced below its steady shear value. We find the steady shear viscosity of these cubic particles in the Newtonian regime diverges around a volume fraction of 0.67, above random close packing for spheres (0.63) and below that for perfect cubes (0.78). In contrast, the complex viscosity in the Newtonian regime diverges at a volume fraction of 0.86. We postulate that this increase in the maximum packing fraction is due to a degree of ordering imparted to the cubic particles by the oscillatory nature of the flow. We also explore the rheological consequences of adding the cubic particles to a concentrated colloidal dispersion of near hard-spheres. At low volume fractions, the flow curves of these suspensions reflect that of the underlying colloidal dispersion suspending medium. When plotted against the shear stress, the flow curves can be made to superimpose with a single shift factor. This simple shifting procedure is violated at higher volume fractions of cubic particles as the shear thinning becomes more pronounced. We show that the increase in the low shear viscosity can be understood through a depletion attraction resulting from overlap of the zeolites' excluded volume.

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

Organizers: Randy Ewoldt and Dimitris Vlassopoulos

Thursday 8:40 Constellation D

SM46

### **Single molecule dynamics of DNA comb polymers**

Charles M. Schroeder and Danielle J. Mai

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

We report the synthesis and direct observation of branched DNA polymers. We developed a two-step synthesis method to generate branched polymers for single molecule visualization. Here, we use a graft-onto synthesis method by linking side branches onto DNA backbones, thereby producing star, H-shaped, and comb-shaped polymers. In these experiments, DNA-based branched polymers are designed to contain short branches (1-10 kilobase pairs) and long backbones (10-30 kilobase pairs), where the branches and backbones are monodisperse and the branch distribution can be controlled in an average sense. Following synthesis, we utilize single-color or dual-color single molecule fluorescence

microscopy (SMFM) to observe the dynamics of these molecules, in particular by tracking the side branches and backbones independently. In this way, our imaging method allows for characterization of these materials at the single molecule level, including quantification of polymer contour length and branch distributions for varying synthetic conditions. Moving beyond characterization, we study the dynamics of single branched polymers in flow using a molecular rheology approach. In one experiment, we utilize precision microfluidics to study the relaxation of branched DNA from high stretch. Here, we directly observe conformational relaxation dynamics of single chains by characterizing backbone relaxation from high stretch, and we find that the relaxation of branched polymers is a strong function of the number of branches and position of branch points along the main chain backbone. In a second experiment, we also observe the transient and steady-state dynamics of single branched polymers in planar extensional flow. Overall, our work aims to probe the impact of branching on the dynamics of polymers in dilute and concentrated solutions, thereby providing a molecular-level understanding of the dynamics of topologically complex polymers in flow.

Thursday 9:05 Constellation D

SM47

### **Constraint release leads to size-dependent diffusivity of nanoparticles in solutions of unentangled polyelectrolytes**

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

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

Using a polyelectrolyte model system, we show that polymer mobility controls the size-dependent deviations from Stokes-Einstein behavior for nanoparticles diffusing in unentangled polymer solutions. We measure the long-time diffusivity of fluorescent polystyrene nanoparticles ranging in diameter from 300 nm to 2  $\mu\text{m}$  in dilute and semidilute solutions of partially hydrolyzed polyacrylamide. At short time scales, the particles exhibit subdiffusive behavior characterized by  $\text{MSD} \sim t^a$  where  $a < 1$ . On long time scales, the particles exhibit Fickian diffusion ( $a=1$ ) from which the diffusivities are extracted. Whereas diffusivities of the large particle agree with predictions using the Stokes-Einstein equation and bulk zero-shear viscosity, the smaller particles diffuse much faster than predicted. To capture the particle- and polymer-size dependence of the long-time diffusivity, we propose a model in which particles diffuse in a matrix with relaxing constraints caused by the diffusion of polymer segments. We derive an effective length scale that collapses the long-time diffusivities onto a single curve and cleanly captures a smooth crossover to bulk behavior when the particles are much larger than the polymer chains. Furthermore, the effective length scale controls the crossover time scale between subdiffusive and Fickian behavior for all particle sizes and polymer concentrations. Our model generates new physical insight into the effect of length scales on diffusion through dynamic, heterogeneous media.

Thursday 9:30 Constellation D

SM48

### **Size, shape and diffusivity of a single Debye-Hückel polyelectrolyte chain in solution**

W. Chamath Soysa<sup>1</sup>, Burkhard Duenweg<sup>2</sup>, and J. Ravi Prakash<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Monash University, Melbourne, Victoria 3150, Australia;* <sup>2</sup>*Max Planck Institute for Polymer Research, Mainz, Germany*

Brownian dynamics simulations of a coarse-grained bead-spring chain model, with Debye-Hückel electrostatic interactions between the beads, are used to determine the root-mean-square end-to-end vector, the radius of gyration, and various shape functions (defined in terms of eigenvalues of the radius of gyration tensor) of a weakly-charged polyelectrolyte chain in solution, in the limit of low polymer concentration. The long-time diffusivity is calculated from the mean square displacement of the centre of mass of the chain, with hydrodynamic interactions taken into account through the incorporation of the Rotne-Prager-Yamakawa tensor. Simulation results are interpreted in the light of the OSFCK blob scaling theory which predicts that all solution properties are determined by just two scaling variables—the number of electrostatic blobs  $X$ , and the reduced Debye screening length,  $Y$ . We identify three broad regimes, the ideal chain regime at small values of  $Y$ , the blob-pole regime at large values of  $Y$ , and the crossover regime at intermediate values of  $Y$ , within which the mean size, shape, and diffusivity exhibit characteristic behaviours. In particular, when simulation results are recast in terms of blob scaling variables, universal behaviour independent of the choice of bead-spring chain parameters, and the number of blobs  $X$ , is observed in the ideal chain regime and in much of the crossover regime, while the existence of logarithmic corrections to scaling in the blob-pole regime leads to non-universal behaviour. With the inclusion of the characteristic shear rate  $\beta\dot{\gamma}$  as the additional scaling variable in shear flow, the equilibrium blob model provides a framework to obtain parameter free data collapse, even for rheological properties.

Thursday 10:25 Constellation D

SM49

### **A microstructural constitutive model for the rheology of solutions of flexible unentangled polymers**

Ranganathan Prabhakar and Murray J. Shaw

*Mechanical and Aerospace Engineering, Monash University, Clayton, Victoria 3800, Australia*

A new constitutive model is used to predict the concentration dependence of the rheology of unentangled solutions of flexible homopolymers in theta solvents. The model is based on the concept of "blobs". The effect of stretching on average molecular conformation is described through the concept of Pincus-blobs, while correlation-blobs account for the screening of intramolecular interactions due to overlap of anisotropic partially stretched chains. A scaling analysis shows that molecular stretching strongly suppresses the transition from the dilute to semidilute regime. On the other hand, hydrodynamic interactions between stretched molecules are stronger than in the isotropic state. The average friction coefficient thus depends on the conformation and concentration through the number and size of the Pincus or correlation blobs in each chain. Predictions obtained with the model for rheological behaviour in extensional flows are shown to agree well with both experiments and multi-chain Brownian Dynamics simulations.

Thursday 10:50 Constellation D

SM50

### Exploring the effects of compatibilizer on the morphology and interface of polymer blends by means of rheology and dielectric spectroscopy

Avanish Bharati<sup>1</sup>, Ruth Cardinaels<sup>2</sup>, Michael Wübbenhorst<sup>3</sup>, and Paula Moldenaers<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium; <sup>2</sup>Department of Mechanical Engineering, TU Eindhoven, Eindhoven 513, The Netherlands; <sup>3</sup>Department of Physics and Astronomy, KU Leuven, Leuven 3001, Belgium

A bi-phasic PαMSAN/PMMA blend undergoing spinodal decomposition was compatibilized with an interfacially segregated PS-r-PMMA random copolymer. Both the interfacial elasticity as probed by rheology and the interfacial contribution to the dielectric loss were used to study the effect of the copolymer on the interface. The matrix-droplet morphology as a function of coalescence time in a step down experiment in shear rate was characterized by means of small amplitude oscillatory shear. The fact that an interface generates an additional elasticity allows determining the ratio of droplet size ( $R_v$ ) to interfacial tension ( $\alpha$ ) using the Paliere model. From the attenuation of the interfacial contribution to the storage modulus and the reduction in interfacial relaxation time it was inferred that compatibilization led to a reduced interfacial tension resulting in morphology refinement. From dielectric spectroscopy, conductivity free dielectric loss spectra revealed blocking of charge carriers at low frequencies owing to the conductivity contrast of the blend components, resulting in a dielectric interfacial peak. The latter is governed by the intrinsic length scale of the system, i.e. the ratio of domain size ( $D_v$ ) to Debye length ( $L_D$ ). Addition of compatibilizer caused a substantial increase of the peak intensity of the interfacial polarization. To estimate  $L_D$ , the dielectric response of stacked polymer films with interfacially localized copolymer was investigated. The interfacial polarization was significantly suppressed when the thickness of the conducting film approached  $L_D$ , on the basis of which  $L_D$  could be calculated. Upon compatibilization, an increase of the relaxation strength of the interfacial polarization occurred, which corroborated a pronounced decrease of  $L_D$ . In summary, combining the knowledge of rheology and dielectric spectroscopy allows characterization and tuning of bi-phasic morphologies at various length scales.

Thursday 11:15 Constellation D

SM51

### Rheology of polymer nanocomposites using novel evaluation of oscillatory shear flow data

Milan Kracalik

*Institute of Polymer Science, Johannes Kepler University Linz, Linz, Upper Austria 4040, Austria*

Polymer nanocomposites exhibit complex rheological behaviour due to physical and also possibly chemical interactions between individual phases (polymer, nanofiller, compatibilizer), which can be detected by oscillatory shear rheology. Until now, flow behaviour of heterogeneous polymer systems has been usually described by elastic flow part through the viscosity curve (shear thinning phenomenon) or storage modulus curve (formation of secondary plateau) and by plastic flow part through dumping behaviour (e.g. Van Gorp-Palmen-plot, Cole-Cole plot), respectively. On the contrary to typical rheological evaluation, "melt rigidity" approach has been introduced for description of physical network of rigid particles in polymer matrix as relation of  $\omega G' / \omega G''$  over specific frequency range. This approach has been experimentally proved for polymer nanocomposites in order to evaluate both shear as well as elongational flow field. In this contribution, compatibilized LDPE-clay nanocomposites with different dispersion grades have been prepared and changes in physical network have been analysed by novel "melt rigidity" approach using various cumulative rheological parameters. It has been found that information gained from specific cumulative rheological parameters allows detailed comparison even of small differences in physical network of nanocomposites and is in a good correlation with information obtained from conventional evaluation approach like shear-thinning or  $G'$  secondary plateau analysis.

Thursday 11:40 Constellation D

SM52

### Interpenetration, entanglements and bonding interactions in dendronized polymers

Dimitris Vlassopoulos<sup>1</sup>, Salvatore Costanzo<sup>1</sup>, Leon Scherz<sup>2</sup>, Thomas B. Schweizer<sup>2</sup>, Martin Kroger<sup>2</sup>, and Dieter Schlüter<sup>2</sup>

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Dendronized polymers (DPs) represent a new class of hyperbranched polymers with dendrons being grafted to each monomer of their backbone. They exhibit tunable conformations and properties when the backbone degree of polymerization ( $n$ ) and dendron generation ( $g$ ) change, spanning the range from flexible polymers to anisotropic colloidal molecules [1,2]. In addition, given their molecular structure, these polymers exhibit an inherent density heterogeneity [3,4]. In this work we investigate the viscoelastic properties of a series of DPs having different  $n$  and  $g$  and utilize rheology, light scattering and calorimetry to address the following fundamental questions: (i) What are the consequences of density distribution on the rheology and thermal equilibration? (ii) Does an entanglement network form when  $n$  increases, which are the rheological signatures and what is the role of interpenetration at different  $g$ 's? (iii) How do DPs respond to strong shear flows in comparison to classical entangled flexible polymers? To achieve our goal we selectively use additional DPs bearing functional groups able to form associations via hydrogen bonding and  $\pi$ - $\pi$  stacking. Our results are discussed in the context of the classic entanglement picture and recent simulations. They suggest that DPs exhibit extraordinary properties due to their low but tunable plateau modulus and possess similarities with (and differences from) other macromolecules of the same class, most notably bottlebrushes.

[1] A. D. Schlüter et al. ACS Macro Lett. 2014, 3, 991; [2] Y. Guo et al. JACS 2009, 131, 11841; [3] R. Pasquino et al. Macromolecules 2012, 45, 8813; [4] Cordova-Mateo et al. Soft Matter 2014, 10, 1032.

## Symposium SA Self-assembled Systems and Gels

Organizers: Surita Bhatia and Kelly Schultz

Thursday 8:40 Constellation E

SA31

### Flow and gelation of a suspension of microfibers

Antonio Perazzo<sup>1</sup>, Janine K. Nunes<sup>1</sup>, Stefano Guido<sup>2</sup>, and Howard A. Stone<sup>1</sup>

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Microfibers are widely exploited in biomedical applications<sup>1</sup>. A relevant feature of microfibers is that compounds, such as drugs, droplets, and biological materials, e.g., cells, can be readily encapsulated in their structure<sup>2</sup>. Microfluidics provides the possibility to encapsulate compounds and manipulate the physical properties of a single fiber, such as Young modulus, aspect ratio and morphology<sup>3</sup>. The microfibers can be dispersed in a liquid medium thus creating a suspension. In this work we report how a suspension of highly flexible microfibers obtained by microfluidic methods can be converted to a hydrogel by flow-induced gelation without any further chemical cross-linking. We probe its swelling properties once dissolved in water and we demonstrate, by rheological means, how the gelation is elicited by the formation of flow induced irreversible entanglements of the microfibers. A significant consequence of these properties is that the suspension is injectable by a syringe and comes out of the needle directly as a hydrogel with no need of further treatments. This feature makes the microfiber suspension a promising material for scaffold fabrication in situ in biomedical applications.

[1] Jun, Y., Kang, E., Chae, S. & Lee, S.-H. Microfluidic spinning of micro- and nano-scale fibers for tissue engineering. *Lab on a Chip* 14, 2145-2160 (2014). [2] Um, E., Nunes, J. K., Pico, T. & Stone, H. A. Multicompartment microfibers: fabrication and selective dissolution of composite droplet-in-fiber structures. *J. Mater. Chem. B* 2, 7866-7871 (2014). [3] Nunes, J. K., Sadlej, K., Tam, J. I. & Stone, H. A. Control of the length of microfibers. *Lab on a Chip* 12, 2301-2304 (2012).

Thursday 9:05 Constellation E

SA32

### Star telechelic poly(L-lactide) ionomers

Amruta D. Kulkarni<sup>1</sup>, Ashish K. Lele<sup>1</sup>, Sivaram Swaminathan<sup>1</sup>, P R. Rajmohan<sup>2</sup>, Velankar Sachin<sup>3</sup>, and Apratim Chatterji<sup>4</sup>

<sup>1</sup>*Polymer Science & Engineering, National Chemical Laboratory, Pune, India;* <sup>2</sup>*Organic Chemistry Division, National Chemical Laboratory, Pune, India;* <sup>3</sup>*Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA, United States;* <sup>4</sup>*Physics Department, Indian Institute of Science Education and Research, Pune, India*

In this work we investigate the viscoelastic properties of PLA ionomer melts and compare them with PLA base polymers. Specifically, we demonstrate the synthesis of star telechelic PLA anionomers by a three-step procedure involving synthesis of star PLA, converting the hydroxyl end groups into carboxylic acid end groups, and finally converting these into ionic groups. The ionomers are characterized by NMR & IR to determine their exact molecular structure. Melt rheology data showed dramatic increase in the elasticity of the star telechelic anionomer melts relative to the star PLA melts. The viscoelasticity of star telechelic anionomer melts could be modulated by varying the number of ionic groups per molecule. Rheological response suggests formation of a transient network that is created by the association of ionic end groups. Molecular dynamic simulations suggest the presence of ionic clusters. The value of plateau modulus indicates that only a small fraction of clusters link to form sample spanning network. The enhanced elasticity of PLA ionomers could be useful for improving its melt processibility.

Thursday 9:30 Constellation E

SA33

### How do amphiphilic biopolymers gel blood? An investigation using optical microscopy

Srinivasa Raghavan, Ian C. MacIntire, and Matthew B. Dowling

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

Amphiphilic biopolymers such as hydrophobically modified chitosan (hmC) have been shown to convert liquid blood as well as solutions of vesicles/liposomes into elastic gels. This interesting property could make hmC useful as a hemostatic agent in treating severe bleeding. The mechanism for blood gelling by hmC is believed to involve polymer-cell self-assembly, i.e., the insertion of hydrophobic side-chains from the polymer into the lipid bilayers of blood cells, thereby creating a network of cells bridged by hmC. Here, we probe the above mechanism by studying dilute mixtures of blood cells and hmC in situ using optical microscopy. Our results show that the presence of hydrophobic side-chains on hmC induces significant clustering of blood cells. The extent of clustering was quantified from the images in terms of the area occupied by the largest clusters. Clustering increased as the fraction of hydrophobic side-chains increased; conversely, clustering was negligible in the case of the parent chitosan that had no hydrophobes. Moreover, the longer the hydrophobic side-chains, the greater the clustering (i.e., C12 > C10 > C8). Clustering was negligible at low hmC concentrations, but became substantial above a certain threshold. Finally, clustering due to hmC could be reversed by adding the supramolecule alpha-cyclodextrin, which is known to capture hydrophobes in its binding pocket. Overall, the results from this work are broadly consistent with the earlier mechanism, albeit with a few modifications.

Thursday 10:25 Constellation E

SA34

**Improved mechanical behavior with multicomponent nanocomposite hydrogels**Wendy L. Hom and Surita R. Bhatia*Chemistry, Stony Brook University, Stony Brook, NY, United States*

Recently, hydrogels have drawn considerable attention as potential alternatives for biological soft tissues and as vehicles for delivery of pharmaceuticals and biological molecules. The mechanical properties of a new type of nanocomposite gel consisting of varying concentrations of the biopolymer alginate and the synthetic Laponite clay, together with the temperature-sensitive copolymer, Pluronic® F127, (ALP) were prepared using physical association and studied using rheology has the potential to exhibit tough mechanical properties as its individual components have the ability to form strong hydrogels based on their method of synthesis. Nanocomposite gels have been synthesized as one strategy to strengthen conventional hydrogels, which usually consist of a single polymer network. This preliminary work shows that the nanocomposite ALP gels exhibit significantly higher storage and loss modulus ( $G'$ ,  $G''$ ) values than nanocomposite gels composed of only alginate and Laponite, which encourages the synthesis of strong and 'smart' hydrogels. The interaction between the components appears to be synergistic; that is, the resulting multicomponent hydrogels are much more elastic than the individual components. By comparison, the  $G'$  of the nanocomposite gels containing F-127 Pluronic® are two orders of magnitude higher than the control containing just alginate and Laponite.

Thursday 10:50 Constellation E

SA35

**Rheology and microstructure of capillary force induced gels**Sameer S. Huprikar<sup>1</sup>, Ashish V. Orpe<sup>2</sup>, and Ashish K. Lele<sup>1</sup><sup>1</sup>*Polymer Science & Engineering, National Chemical Laboratory, Pune, India;* <sup>2</sup>*Chemical Engineering and Process Division, CSIR-National Chemical Laboratory, Pune, Maharashtra 411008, India*

We report a study on the suspension of non-Brownian hard spheres which undergo gelation on addition of a minute quantity (~ 10%) of a secondary immiscible Newtonian liquid. The suspension to gel transformation takes place due to differences in the wettability of the primary and the secondary liquid with the particle surface [1-3]. The suspension is made out of PMMA particles suspended in a density and a refractive index matched liquid. A secondary liquid, have nearly same density and refractive index as the particles, is added in different amounts to the suspension for a range of particle volume fractions. The flowing characteristics of the suspension/gel are studied using steady shear and oscillatory rheometry in the linear viscoelastic regime. In parallel, the microstructure of the gel is studied using laser imaging by addition of a fluorescent dye to either primary or the secondary liquid.

References: [1] Koos, E. et al. *Science*. 2011, 331, 897-900. [2] Koos, E. et al. *Soft Matter*. 2012, 8, 6620-6628. [3] Domenech, T. et al. *Soft Matter*, 2015, 11, 1500-1516.

## Symposium CR Computational Rheology

Organizers: Jay Schieber and Roland Winkler

Thursday 8:40 Constellation F

CR16

**Program to extract continuous and discrete relaxation spectra from linear rheology**Sachin Shanbhag<sup>1</sup> and Arsia Takeh<sup>2</sup><sup>1</sup>*Scientific Computing, Florida State University, Tallahassee, FL 32306, United States;* <sup>2</sup>*Advanced Cooling Technologies, Inc., Lancaster, PA 17601, United States*

We describe and demonstrate an efficient, open-source, multi-platform computer program called "ReSpect" to infer the continuous and discrete relaxation spectra from linear viscoelastic measurements. The underlying engine to infer the continuous relaxation spectrum is nonlinear Tikhonov regularization in conjunction with the Levenberg-Marquardt method. The discrete spectrum is derived from the continuous spectrum via a new algorithm which optimally positions the discrete modes by balancing demands of accuracy and conditioning.

Thursday 9:05 Constellation F

CR17

**An efficient log-conformation stabilization**Philipp Knechtges, Marek Behr, and Stefanie Elgeti*RWTH Aachen University, Chair for Computational Analysis of Technical Systems, Aachen 52056, Germany*

The robust and stable simulation of viscoelastic flows has been and still is a struggle of computational rheology. One of the most recent attempts to stabilize macroscopic simulations are the log-conformation approaches, as they have been first considered by Fattal and Kupferman in 2004. The important ingredient that make these methods so successful is that they naturally preserve the positive-definiteness of the conformation tensor; a property known to be fulfilled by the analytic undiscretized solution. Irrespective of this advantage, the original log-conformation formulation includes the difficulty that the new set of governing equations requires a spectral decomposition of the log-conformation field; a characteristic highly uncommon for partial differential equations. As such, the latter is especially troublesome for the application of further analytical tools. One of these tools with particular importance for numerical simulations is the Newton-Raphson algorithm as a linearization method with quadratic convergence.

Subject of this talk will be our recent development of the fully-implicit log-conformation formulation [1, 2]; a formulation that synthesizes the stabilization properties of the original log-conformation formulation with a new set of constitutive equations that pave the way for the Newton-Raphson algorithm. Following the theoretical description of the method, the talk will subsequently cover results of an two- and three-dimensional implementation in our in-house flow solver, ranging from benchmark problems to die swell simulations [3].

[1] P. Knechtges, M. Behr, and S. Elgeti. *Journal of Non-Newtonian Fluid Mechanics*, Vol. 214, 78-87, 2014. arXiv:1406.6988. [2] P. Knechtges. *submitted to Journal of Non-Newtonian Fluid Mechanics*, 2015. arXiv:1503.03863. [3] L. Pauli, M. Behr, and S. Elgeti. *Journal of Non-Newtonian Fluid Mechanics*, Vol. 200, 79-87, 2013.

Thursday 9:30 Constellation F

CR18

### **Predicting density variation from polyurethane process modeling**

Rekha R. Rao<sup>1</sup>, Lisa A. Mondy<sup>1</sup>, Kevin N. Long<sup>1</sup>, Christine C. Roberts<sup>1</sup>, Melissa M. Soehnel<sup>1</sup>, Mathew C. Celina<sup>2</sup>, Haoran Deng<sup>2</sup>, Victor E. Brunini<sup>3</sup>, and James J. Tinsley<sup>4</sup>

<sup>1</sup>Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>2</sup>Material Science Center, Sandia National Laboratories, Albuquerque, NM 87185-1411, United States; <sup>3</sup>Systems Engineering Center, Sandia National Laboratories, Livermore, CA 94551-0969, United States; <sup>4</sup>National Security Campus, Kansas City, MO 64147, United States

We are developing numerical methods to predict density variation in polyurethane foams used to fabricate structural parts. The structural response of the part is closely tied to the local density, and it is thought that foam warpage during manufacture and aging is closely tied to these density gradients. The foam of interest is difficult to characterize experimentally, since it is a PMDI polyurethane with a fast catalyst, such that filling and polymerization occur simultaneously. An additional complexity is that the foam is over-packed to twice or more of its free rise density, to reach the density of interest. Thus, developing a relevant model to represent the expansion, filling, curing, and final foam properties is quite challenging. PMDI is chemically blown foam, where carbon dioxide is produced via the reaction of water and isocyanate. The isocyanate also reacts with polyol in a competing reaction, which produces the polymer. A new kinetic approach is taken, which follows a simplified mathematical formalism that decouples these two reactions. The model predicts the degree of polymerization via a Kamal approach, including vitrification and the evolution of the glass transition temperature with cure using the DiBenedetto equation. The model is populated with DSC, IR, and rheology data. The foam expansion kinetics follow the molar concentration evolution of both water and carbon dioxide. The model is fit to volume expansion data and includes a nucleation time. The foam is homogenized into a single-phase material with an evolving gas fraction. Once vitrification occurs, all reactions slow precipitously. We discuss efforts to include this effect into the foaming reaction through bubble-scale modeling. Results from the model are compared to experimental flow visualization data and post-test CT data for the density. Discrepancies between the model and validation experiments are discussed. To improve the fidelity of the model, we plan to include more local effects such as bubble-size and foam drainage.

Thursday 10:25 Constellation F

CR19

### **Concentration coupled flow instability of hard sphere glasses: Modeling and simulation**

Howon Jin<sup>1</sup>, Kyongok Kang<sup>2</sup>, Kyung Hyun Ahn<sup>1</sup>, and Jan Dhont<sup>2</sup>

<sup>1</sup>Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea; <sup>2</sup>ICS-3, Forschungszentrum Juelich, Juelich, Germany

In this study, shear banding instability due to the coupling of shear-rate gradient with concentration has been investigated. The instability, observed in concentrated colloid glasses (Besseling et al., *Phys. Rev. Lett.*, 2010) is phenomenologically similar to gradient banding, but has different molecular origin and physical characteristic such as monotonic slope of the stress curve. To elucidate physical origin of shear-rate gradient concentration coupling mechanism, we modeled the forces exerted on colloid particles, ignoring hydrodynamic interaction. Shear-rate gradient induced mass flux was related to shear-distortion of pair correlation function (or osmotic pressure). Brownian dynamics simulations were performed to calculate pair correlation function under various shear rate and concentration. From the simulation results, explicit expressions for the shear-rate gradient induced mass flux and diffusion coefficient were obtained. Then, the mass flux equation was coupled with the dynamic equation of fluid velocity, which adopts Herschel-Bulkley stress model, describing colloid glasses. In the stress model, non-local contribution of shear rate was added to prevent divergence of spatial gradient under unstable condition. Both mass and momentum equations were combined and solved together in a Couette geometry, with finite difference scheme. In accordance with experiments, shear banding was observed at sufficiently low shear rate and high concentration. One of the shear bands was found to be non-flowing as the local stress cannot overcome the yield stress.

Thursday 10:50 Constellation F

CR20

### **A constitutive model for monodisperse and polydisperse entangled polymers incorporating binary entanglement pair dynamics and a configuration dependent friction coefficient**

David W. Mead<sup>1</sup>, Nilanjana Banerjee<sup>2</sup>, and Joontaek Park<sup>2</sup>

<sup>1</sup>Mead Consulting, Bedford, NH, United States; <sup>2</sup>Chemical & Biochemical Engineering, Missouri University of Science & Technology, Rolla, MO 65409, United States

We present a new model (MBP: Mead-Banerjee-Park) which introduces the concept of a conformation dependent friction coefficient (CDFC) based on the relative orientation of a test Kuhn bond to the surrounding matrix Kuhn bonds and entanglement dynamics (ED) of discrete entanglement pairs into the MLD "toy" model [Mead et al., *J. Rheol.* 59, 335-363 (2015)]. The model for monodisperse system was successfully validated against experimental data in transient and steady extensional and shear flows. It simultaneously predicts the monotonic thinning of the extensional flow curve of monodisperse PS melts [Bach et al., *Macromolecules* 36, 5174-5179 (2003)] and extension hardening of monodisperse

PS solutions [Bhattacharjee et al., *Macromolecules* 35, 10131-10148 (2002)]. The results also show that the rheological properties in nonlinear extensional flows of PS melts are sensitive to CDFC but not to convective constraint release (CCR) while those for shear flows are influenced more by CCR. The model can be extended to polydisperse systems by incorporating the "diluted stretch tube" theory [Mishler and Mead, *J. Non-Newton Fluid.* 197, 61-79 (2013)]. This concept underlines the presence of characteristic time (stretch and orientation relaxation time) spectra for a system with a broad molecular weight distribution (MWD) and leads to a modified entanglement microstructure, i.e. reduction in the number of viable 'stretch entanglements' for a given MWD component. The transient and steady extensional flows of polydisperse PS melts with broad MWD are predicted by the polydisperse MBP model and compared with the corresponding experimental data.

## Poster Session

### Symposium PO Poster Session

Organizers: John Dorgan and Nicolas J. Alvarez

Wednesday 6:05 Atrium/Harborview

PO1

#### **Rheological properties of methylcellulose in the presence of nanocellulose**

Leela Rakesh<sup>1</sup> and Rohit Thota<sup>2</sup>

<sup>1</sup>Math, Applied Mathematics & Polymer Fluid Dynamics, CMU, Mt. Pleasant, MI 48859, United States; <sup>2</sup>School of Engineering, CMU, Mt. Pleasant, MI 48859, United States

Addition of nanocellulose to various polymer matrix provides variety of possibilities of superior properties for various end products process. In order to understand these properties rheological measurements are carried out. In particular, the viscoelastic rheological investigations of nanocellulose in aqueous suspension of MC matrix were investigated using steady and oscillatory experiments by AR 2000 rheometer with cone-plate geometry at room temperature within the linear viscoelastic region. Understanding such properties would certainly help to design and redesign new controls in water-based production of various complex fluid matrix processes. Complex fluids containing nanocellulose are used as pigment flocculants aqueous maintenance for various process applicability such as phase separation, coating, lamination, quality & customer appeal. Samples were covered with thin layer of silicone oil to avoid the water evaporation. Various rheological measurements, such as, steady state flow with increasing & decreasing shear rate and dynamic oscillatory are carried out.

Wednesday 6:05 Atrium/Harborview

PO2

#### **Mussel-inspired self-healing nanocomposite hydrogel with dynamic mechanics by network structure**

Qiaochu Li<sup>1</sup>, Sumeet R. Mishra<sup>2</sup>, Pangkuan Chen<sup>1</sup>, Joseph B. Tracy<sup>2</sup>, and Niels Holten-Andersen<sup>1</sup>

<sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, United States

Network dynamics is a crucial factor that determines the macroscopic self-healing rate and efficiency in polymeric hydrogel materials, yet the rheological study of its controllability is still very limited. Inspired by mussel's adhesion chemistry, we developed a novel approach to assemble inorganic nanoparticles and catechol-decorated PEG polymer into a hydrogel network. When utilized as reversible polymer-particle crosslinks, catechol-metal coordination bonds yield a unique gel network with its relaxation behavior controlled directly by interfacial crosslink structural dynamics. Taking advantage of this polymer-particle interfacial structure-property relationship, we next designed a hierarchically structured gel with two distinct relaxation timescales. By tuning the relative contribution of the two hierarchical relaxation modes, we are able to finely control the gel's rheological behavior from a viscoelastic fluid to a solid yet fast self-healing hydrogel.

Wednesday 6:05 Atrium/Harborview

PO3

#### **Exploring elasticity and energy dissipation in mussel-inspired hydrogel transient networks**

Scott C. Grindy<sup>1</sup>, Robert Learsch<sup>2</sup>, and Niels Holten-Andersen<sup>1</sup>

<sup>1</sup>Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>Massachusetts Institute of Technology, Cambridge, MA, United States

Dynamic, reversible crosslinks have been shown to specifically control the mechanical properties of a wide variety of mechanically tough and resilient biomaterials. We have shown that reversible histidine-metal ion interactions, known to contribute to the strong mechanical properties and self-healing nature of mussel byssal threads, can be used to control and engineer the hierarchical mechanical properties of model polyethylene glycol hydrogels orthogonally from the spatial structure of the material.

Here, we explore the scaling relationships in our model networks to further expand our abilities to control the relative elasticity and energy dissipation on hierarchical timescales. We show that the elasticity is dominated by long-range entanglements, while the dissipation is controlled by the exchange kinetics of the transient crosslinks. Understanding the interplay between elasticity and dissipation allows us to rationally design high-strength hydrogels for specific states of dynamic loading.

Wednesday 6:05 Atrium/Harborview

PO4

#### **Probing the role of cell rheology and friction on tumor cell transport using high throughput microfluidics**

MD Shamin Ahmmed and Siva A. Vanapalli

Chemical Engineering, Texas Tech University, Lubbock, TX 79415, United States

From the primary site, tumor cells are transported through microcirculation to produce secondary colony targets. Two important physical parameters that regulate this transport are cancer cell deformability and friction with microcapillary walls. Although several studies have

investigated flow-induced transport of tumor cells in microfluidic capillaries, the relationship between hydrodynamic forces, cell confinement, cell rheology and friction remains poorly understood. From a cancer perspective, it is also not clear how this relationship influences the metastatic potential of tumor cells. To understand the flow-induced transport of cancer cells in microcapillaries, we engineer a new microfluidic device that contains a dozen constricted microchannels of diameter ranging from 10 - 30  $\mu$ m. The diameters were chosen such that breast cancer cells are confined over a wide range, spanning strong confinement to nearly unconfined flow in the microchannel. In addition, a microfluidic manifold was designed to impose a fixed pressure drop across the dozen channels, allowing us to probe strong and weak confinement regimes simultaneously under identical boundary conditions. We find that the strong confinement regime allows us to quantify the entry time and passage time (or velocity) of tumor cells, which have been reported to be metrics of cell deformability and friction respectively. In the unconfined regime, we identify conditions where tumor cells undergo shear stress induced shape deformation. Thus, for the same cell population we correlate the entry time, passage time and shape deformation, at different imposed pressure drops. To address the effect of cell rheology and friction on these three parameters, we use cytoskeletal drugs and wall-coatings respectively. In summary, the new device and its capabilities will provide fundamental understanding on the role of cell rheology and friction on tumor cell transport.

Wednesday 6:05 Atrium/Harborview

PO5

### **High shear rate rheology of protein solutions**

Steven D. Hudson<sup>1</sup>, Vishnu Dharmaraj<sup>2</sup>, and Yun Liu<sup>3</sup>

<sup>1</sup>*Polymers and Complex Fluids Group, NIST, Gaithersburg, MD 20899, United States;* <sup>2</sup>*Montgomery Blair High School, Potomac, MD, United States;* <sup>3</sup>*NCNR, NIST, Gaithersburg, MD 20899, United States*

Previous measurements, including our own, of the rheology of well-dissolved proteins revealed Newtonian behavior. Reversible self-association caused by short range attraction and long range repulsion markedly affects viscosity, and solution conditions that promote clustering of dissolved monomers may exhibit high viscosity. Here we explore in low-salt lysozyme solutions the extremes of high concentration and low temperature. To test for departures from Newtonian behavior, we modified our previous microcapillary rheometer to access higher shear rates. At shear rates in excess of 1000 /s, we find reversible shear thinning at 40 % mass fraction and temperatures 12 °C and 5 °C, but not at 20 °C and higher. Further studies are underway to understand the rheology and evaluate the dynamics of reversible clusters in these solutions.

Wednesday 6:05 Atrium/Harborview

PO6

### **Modeling the impact of heterogeneous composition on the extrusion driven flow of lignocellulosic biomass using a three fluid model**

Joshua C. Duncan<sup>1</sup>, Michael D. Graham<sup>1</sup>, Daniel J. Klingenberg<sup>1</sup>, and Tim C. Scott<sup>2</sup>

<sup>1</sup>*Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States;* <sup>2</sup>*Forest Products Laboratory, US Forest Service, Madison, WI 53706, United States*

Lignocellulosic biomass is an abundant, renewable, carbon neutral energy source. Processing this material at high concentrations to minimize capital and energy costs leads to challenging rheological behavior. Biomass at high concentrations exhibits a large yield stress and large pressures must be applied to transport the material through pipes. This can be expensive and dangerous in the case of pipe failure. More problematic are large pressure fluctuations associated with heterogeneities in the composition. Understanding how these heterogeneous regions form and impact the flow is critical to maintaining a steady flow of material for downstream chemical processing steps. We have developed a three fluid model for the biomass obtained by volume averaging the equations of motion for each fluid. With this model, the volume fractions of the water, air and biomass (solid) phases are tracked in space and time. The gas is a compressible Newtonian fluid, the water an incompressible Newtonian fluid, and the biomass an incompressible Bingham plastic with a volume fraction-dependent yield stress. Each phase interacts with the other phases through momentum exchange terms in the momentum balances.

In the proper limits (e.g., high momentum coupling between phases) the three fluid model reproduces results reported in the literature for single fluids. For instance, the three fluid model can reproduce the transient behavior reported for a weakly compressible Bingham plastic. The three fluid model can also qualitatively reproduce several biomass extrusion observations. The three fluid model predicts the positive curvature observed in the steady state pressure profile. After the extruder is switched off material continues to flow slowly from the end of the pipe, while the pressure simultaneously decays; both trends are predicted by the model. Ongoing work examining the transient behavior at large solid concentrations suggests that the model may be capable of producing pressure fluctuations as well.

Wednesday 6:05 Atrium/Harborview

PO7

### **Linear and non-linear rheology of model synovial fluids**

Zhenhuan Zhang and Gordon F. Christopher

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

Synovial fluid is the main lubricant in diarthrodial joints. It is primarily composed of hyaluronic acid, albumin, globulin, and lubricin. The rheology of synovial fluid has been widely studied due to its relevance to human joint health. Over the previous 2 years, we have attempted to characterize both the linear and asymptotic non-linear rheology of these solutions in order to understand the role of synovial fluid in hydrodynamic lubrication regimes of human motion. Initial work in characterizing these fluids by both ourselves and other studies has been hampered by the interfacial activity of the dispersed components in synovial fluid. In order to understand their relative impact, we first looked at the interfacial rheology of both individual components and combinations relevant to synovial fluid. We determined in these tests, that interfacial rheology had major impact on the measurement of bulk rheology for these systems, and developed a methodology to abrogate these effects. After characterizing interfacial

rheology of these solutions and removing these effects from bulk measurements, we got a group of very clear rheological data of synovial fluids. In steady shear, shear thinning has been observed due to the hyaluronic acid in synovial fluid. The linear viscoelasticity of synovial fluids is dominated by hyaluronic acid too, resulting in a primarily viscous solution with little to know elasticity. The role of synovial fluid during hydrodynamic lubrication appears to be its asymptotic non-linear response. After analyzing the LAOS responses of synovial fluids by sequence of physical process methods, we found the time dependent storage and loss modulus are timed to the moments of peak strain amplitude/acceleration and shear rate of the knee respectively, which can give great help to human joint lubrication during its hydrodynamic regime. We summarize are findings and present considerations for future work.

Wednesday 6:05 Atrium/Harborview

PO8

### **Effects of granule characteristics on rheological behavior of native potato and corn starch suspensions**

Nasibeh Y. Sinaki and Martin G. Scanlon

*Food Science, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

Starch has extensively been used in various industries, e.g., food, paper, petroleum, ceramics, etc. The flow behavior of suspensions containing starch is therefore of significant interest for these industries. In this study, the effects of granule shape, size and size distribution on the rheological behavior of native (ungelatinized) corn and potato starches were investigated. In addition, the relationship between the viscosity of these suspensions with varying solid volume fractions (F) was studied as a function of suspension temperature. All suspensions were prepared with a continuous phase of 60% sucrose solution to have a density-matched suspension at 20°C. Dilute and intermediate concentration regimes were studied using six different solid volume fractions (1 to 25%). Flow behavior was evaluated using a rotational rheometer and applying steady-state shear flow in a continuous ramp with shear rate increasing from 0.1 to 143.1 s<sup>-1</sup> at 20, 50 and 80°C. The viscosity was higher for corn starch suspensions which contained particles with more angular shape and smaller size compared to those of potato starch suspensions. The reason being is that the drag on corn starch granules was influenced by their sharp edges and resulted in more energy dissipation and higher viscosity of the corn starch suspensions. Also, smaller particle size of corn starch caused higher viscosity due to an increase in attractive interparticle forces. Suspensions exhibited essentially Newtonian behavior at all solid volume fractions, but corn starch suspensions showed evidence of shear thickening at F=25%. The relative viscosity increased with increasing starch content, but decreased with increasing temperature. Maximum solid volume fraction (F<sub>m</sub>) of suspensions increased with increasing temperature due to thermal expansion which leads to lower viscosity according to the Maron-Pierce equation.

Wednesday 6:05 Atrium/Harborview

PO9

### **Investigating molecular interactions between chitosan and insect cuticle protein (CPR27) using active microrheology**

Michael C. Vaclaw<sup>1</sup>, Patricia Sprouse<sup>1</sup>, Neal T. Dittmer<sup>2</sup>, Michael Kanost<sup>3</sup>, Gehrke H. Stevin<sup>4</sup>, and Prajnaparamita Dhar<sup>4</sup>

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Insect cuticle is one of the most abundant materials in nature. The cuticle possesses a wide range of mechanical properties while being composed from a narrow set of components which mostly consist of chitin and protein. These components are organized into a hierarchical structure that bestows the cuticle with its excellent mechanical properties. While the individual components of cuticle have been investigated the molecular interactions occurring between the components are still not well studied. A protein named CPR27 is abundantly found in cuticle and contains a conserved sequence of amino acids known as the Rebers-Riddiford motif that is hypothesized to bind chitin. This study attempts to provide evidence for molecular interactions occurring between CPR27 and the most common chitin derivative: chitosan. Chitosan viscosity calibration curves were obtained using a TA AR 2000 rheometer. Due to limited amounts of CPR27 a homebuilt active microrheology system utilizing magnetic nickel nanorods was used to measure the viscosity of chitosan and chitosan/CPR27 solutions. Viscosities obtained with this system closely matched bulk rheometer data. We found that the chitosan solutions obeyed typical scaling laws for polyelectrolytes in salt solutions where viscosity varies with chitosan concentration in a semi-dilute and an entangled regime. It was observed that the viscosity of chitosan solutions containing CPR27 was significantly lower than the viscosity of solutions containing only chitosan. In addition small visible aggregates were present in solutions containing CPR27 that were not present in solutions without CPR27. Furthermore, lower viscosities and visible aggregates were observed only in the entangled regime. This drop in viscosity together with the presence of visible aggregates at higher chitosan concentrations indicates complexation between CPR27 and chitosan. We believe that these interactions along with other components of insect cuticle may provide a basis for the design of novel biomaterials.

Wednesday 6:05 Atrium/Harborview

PO10

### **Single bacterial adhesive interactions with dental implants**

Shanhong Xu

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The bacterial adhesion and subsequent biofilm formation on oral implant surfaces are essential steps and prerequisites for the pathogenesis of the infection, peri-implantitis, one of the main causes of oral implants failure. In this study, using atomic force microscopy (AFM), subgingival bacterial adhesion to titanium and zirconia implant materials with different microstructure and surface roughness was investigated. Water contact angles were measured on all specimens by the sessile drop technique. We found that the contact angle and the adhesion force increased with the

increasing surface roughness of titanium and zirconia. The bacteria generated stronger adhesive force to the titanium surface than the zirconia. An extended DLVO model was applied to interpret our results. An experimental protocol and some preliminary results will be presented.

Wednesday 6:05 Atrium/Harborview

PO11

### **Spiders tune glue viscosity to maximize adhesion**

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Adhesion in humid conditions is a fundamental challenge to both natural and synthetic adhesives. Yet, glue from most spider species becomes stickier as humidity increases. We find the adhesion of spider glue, from five diverse spider species, maximizes at very different humidities, that matches their foraging habitats. By using high-speed imaging we find that the glue viscosity varies over five orders of magnitude with humidity for each species, yet the viscosity at maximal adhesion for each species is nearly identical,  $10^5$ - $10^6$  cP. Many natural systems take advantage of viscosity to improve functional response, but spider glue's humidity responsiveness is a novel adaptation that makes the glue stickiest in each species' preferred habitat. This tuning is achieved by hygroscopic organic salts that determine water uptake in the glue. We therefore anticipate that manipulation of hygroscopic salts to control viscosity will provide a simple mechanism to design humidity responsive smart adhesives.

Wednesday 6:05 Atrium/Harborview

PO12

### **The rheology of nanoparticles in blood for improved cancer therapy**

Erik Carboni<sup>1</sup>, Brice Bognet<sup>2</sup>, Grant Bouchillon<sup>3</sup>, Andrea Kadilak<sup>1</sup>, Leslie Shor<sup>1</sup>, and Anson Ma<sup>2</sup>

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

References: [1] Davis, ME. Fighting cancer with nanoparticle medicines - The nanoscale matters. *MRS Bulletin*. 2012;37:828-835. [2] Decuzzi P, Lee S, Bushan B, Ferrari M. A theoretical model for the margination of particles within blood vessels. *Annals Biomed. Eng.* 2005;33(2):179-190. [3] Kumar A, Graham MD. Margination and segregation in confined flows of blood and other multicomponent suspensions. *Soft Matter*. 2012;8(41):10536-48. [4] Carboni E, Tschudi K, Nam J, Liu X, Ma A. Particle margination and its implications on intravenous anticancer drug delivery. *AAPS PharmSciTech*. 2014;15(3):762-71.

Wednesday 6:05 Atrium/Harborview

PO13

### **Exploration of rheological and calorimetric properties of egg components as affected by high pressure processing**

Ajaypal Singh and Hosahalli Ramaswamy

*Food Science and Agriculture Chemistry, McGill University, Sainte Anne de Belle, Quebec H9X3V9, Canada*

Effect of high pressure (HP) treatment on rheological and thermal properties of various egg components (whole liquid egg and egg white) was studied as a function of increasing pressure level and treatment time. Differential scanning calorimetry (DSC) and rheometric analysis were utilized to evaluate the extent of protein denaturation and liquid-gel transformation details ( $G'$ ,  $G''$ ). Overall, HP-treated samples exhibited predominantly solid-like ( $G' > G''$ ) behavior in the frequency range employed (0.1-10 Hz). Pressure level (350-550 MPa) and treatment time (5-15 min) contributed significantly towards modification of liquid samples to partial gel formation. Highest level of pressure treatment (Pressure treatment of 550 MPa for 15 min) was sufficient enough to cause complete gelatinization. Egg components exhibited a gradual liquid-solid gel transformation as they coagulated/denatured. Corresponding changes were observed in the flow properties as shown by increasing consistency behavior ( $m$  value) and flow behavior index ( $n$  value)  $< 1$  throughout the pressure treatment.

Wednesday 6:05 Atrium/Harborview

PO14

### **Modification of pasting and rheological properties of native tapioca starch by addition of gum arabic**

Ajaypal Singh and David Geveke

*Food Safety and Intervention Technologies, US department of Agriculture, Wyndmoor, PA 19038, United States*

This study involved studying the addition of gum arabic (GA) to native tapioca starch (TS) to enhance the functionality of TS. GA is well known for its stabilizing, emulsifying, thickening properties. The effects of adding GA (0.1-0.9%) on pasting, rheological and solubility properties of TS

(5%) were analyzed. GA has a higher molecular weight and viscosity than TS and its addition at a very small level (0.1%) to the TS raised the overall viscosity of the TS-GA dispersion. Pasting properties suggested that pasting temperature, setback property and viscosity of the TS-GA dispersion increased with increasing concentration of GA. Dynamic viscoelasticity measurements showed that viscous modulus ( $G''$ ) > elastic modulus ( $G'$ ) at lower concentrations of GA (0.1-0.3%) suggesting a highly viscous behavior, but, at higher concentrations of GA (0.6-0.9%),  $G' > G''$  was observed indicating higher elasticity. These results indicate that  $G'$  and  $G''$  were observed to increase in the presence of GA, suggesting the strong interaction between GA and TS amylose in the composite system. Flow behavior index ( $n$ ) showed that increasing the concentration of GA in the dispersion resulted in decreasing  $n$  value from 0.99 to 0.23 showing pseudoplastic behavior ( $n < 1$ ). However, the consistency coefficient increased from 0.006 to 0.283 Pa/s. A strong correlation between  $G''$  and solubility index was found showing an overall increase in viscosity and solubility of dispersion. These results show that GA can beneficially modify the rheological behavior of the native starch and could broaden the application spectra of native starches in the food industry.

Wednesday 6:05 Atrium/Harborview

PO15

### **Determination of viscoelastic properties of polymers under physiologic conditions**

Eric B. Finkelstein and Patrick T. Mather

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Novel materials are frequently developed for use in biomedical applications that include blood and bodily fluid-contacting devices, cell culture substrates and tissue engineering scaffolds. For a material to be function properly, the material properties must closely resemble those of native biological tissues. Careful tuning of material properties will allow cells to behave physiologically when cultured in contact with the engineered materials. Additionally, material properties can be tuned to avoid potential damage to surrounding tissues when a medical device is utilized. A series of acrylate-based shape memory polymers (SMP) were synthesized for use as cell culture substrates. Since cells are cultured on the materials and expected to behave in a manner sensitive to substrate stiffness, it was important to measure the viscoelastic properties of the materials - with particular attention to tensile storage modulus - under physiologic conditions (hydrated at 37 °C). While this would seem to be a standard application of a dynamical mechanical analyzer (DMA) with immersion fixture, initial experiments revealed challenges rooted in temperature stability. Thus, a reliable method for measuring the storage modulus of wet materials under simulated cell culture conditions (25 °C seeding and 37 °C culture) was developed using a DMA equipped with a tension/film submersion clamp. Under our optimized submersion DMA conditions, temperature stability of 37 °C +/-0.5 °C was achieved, with excellent reproducibility, and applied to the test SMPs for demonstration purposes. The identified protocols established by this work should prove to be a useful method for determining the storage modulus of a wide range of materials being designed for biomedical devices.

Wednesday 6:05 Atrium/Harborview

PO16

### **Light-responsive hyaluronic acid-based hydrogels for controlled drug delivery to pathological cavities**

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Combinations of polymer conjugates affording *in situ* gelation hold promise for treatment of diseases in pathological cavities (*e.g.*, arthritis) and controlled drug release in response to external stimuli. Hyaluronic acid (HA) functionalized with reactive groups is regarded as an excellent biomaterial due to its tunable crosslinking kinetics and mechanical properties. The addition of stimuli-responsive moieties will allow for not only sustained, but controlled drug release from HA gels. To achieve that end, we first employed a biocompatible "click" reaction between cyanobenzothiazole and D-cysteine to produce HA-based conjugates for *in situ* chemical gelation. These gels show interesting rheological properties, such as optimal gelation times and the ability to maintain their mechanical stability for up to two weeks, as well as their viscoelastic behavior after undergoing high shear rates. Further, these gels can act as reservoirs for sustained release of protein therapeutics and had no toxic effect on human keratinocytes. On the basis of this groundwork, we are developing light-controlled physical gels composed of HA functionalized by cyclic peptides containing azobenzene moieties. The addition of azobenzene, a light-responsive molecule, gives us the ability to turn the gel "on" and "off", creating a system for controlled drug release. Using computational analysis, we identified peptide sequences that promote self-assembly between HA chains, allowing for the *in situ* formation of reversible gels. Initial results from the chemical gels allow us to estimate the functionalization density required to produce physical gels with similar rheological properties. The presented results demonstrate the applicability of hyaluronic acid-based systems for *in situ* gelation and their potential for controlled delivery of protein drugs and small molecule therapeutics.

Wednesday 6:05 Atrium/Harborview

PO17

### **Composition-dependent rheological properties of Hagfish defense gel: A network of intermediate filament based threads and mucins**

Gaurav Chaudhary<sup>1</sup>, Douglas S. Fudge<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup>

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Intermediate Filaments (IFs), which are an integral part of most metazoan cells, assemble into networks which render the cell its elastic properties. Here we present the concentration-dependent viscoelastic properties of an IF-based biomaterial which is naturally secreted by hagfish as a defense mechanism against predator attacks [Lim, J. et al., *J Exp Biol* 209(4),702-710 (2006)]. This material is a remarkably dilute network of bundled IF threads and mucins that immobilizes large quantities of water. A single thread (diameter~ 1.5  $\mu$ m) is composed of many 10 nm diameter IFs (with *Eptatretus stoutii* thread keratin  $\alpha$  and  $\gamma$  as major components) axially bundled together attaining length up to about 15 cm [Fudge, D.S. et al., *J Exp Biol* 208(4),4613-4625 (2005)]. The elastic modulus of the assembled network has been cited as one of the lowest obtained for any elastic

biomaterial (0.02 Pa) [Ewoldt, R.H. et al., *Int J Nonlinear Mech* 46(4), 627-636 (2011)]. So far, studies have not focused on the concentration-dependent rheological properties and therefore, network structure and separate roles of mucins and threads are yet to be investigated. We study the viscoelastic moduli dependence on the concentration of both threads and mucins with shear experiments (oscillations and creep, covering a range of timescales and amplitudes). We also look at the possible role of divalent ions as effective cross-linkers, as observed in some IF networks where the side chains of IFs are known to be negatively charged.

Wednesday 6:05 Atrium/Harborview

PO18

### **Dynamics of biopolymers in cartilage extracellular matrix**

Wan-Kyu Oh and Ferenc Horkay

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

Extracellular matrix (ECM) of articular cartilage is mainly composed of aggrecan, hyaluronic acid (HA) and collagen. Chondroitin sulfate (CS) and keratan sulfate, both sulfated glycosaminoglycans (GAGs), are the main components of the bottlebrush-shaped aggrecan molecule. Aggrecan generally forms supramolecular structures in the ECM by binding to HA. The large aggrecan-hyaluronic acid complexes are enmeshed in a collagen network, in which ionic interactions derived from the positively charged collagen molecules and the negatively charged CS provide structural integrity and enhanced stability. The ECM of cartilage exhibits optimized-physiological functions such as load-bearing property, lubrication, and ionic resistance. Understanding the dynamics of these biopolymers and their assemblies is important to design polymer-based biomaterials for tissue engineering applications. We report a systematic study of the dynamic properties of CS, HA, aggrecan, and aggrecan-HA complex in near physiological salt solution. HA reinforces the complexes formed by self-assembly of the aggrecan bottlebrushes. Measurement of the viscoelastic properties reveals that the aggrecan-HA assemblies exhibit microgel-like behavior.

Wednesday 6:05 Atrium/Harborview

PO19

### **Altered sputum microstructure as a marker of airway obstruction in cystic fibrosis patients**

Gregg A. Duncan<sup>1</sup>, James Jung<sup>1</sup>, Michael P. Boyle<sup>2</sup>, Natalie E. West<sup>2</sup>, Jung Soo Suk<sup>1</sup>, and Justin Hanes<sup>1</sup>

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**Introduction:** Highly viscoelastic mucus secretions of CF patients that remain stagnant in the lung leads to obstructed airways prone to recurrent infections. To date, conventional rheological measurements are primarily used to assess the pathological features of mucus in the airway. However, this approach is limited in detecting microscopic properties of mucus on the length scale of viruses, bacteria, and neutrophils. We have shown in prior work based on the transport of muco-inert nanoparticle (MIP) probes in CF sputum that patients can carry significantly different microstructural properties. In this study, we aim to determine the factors leading to the patient-to-patient variations in CF sputum microstructure and their clinical implications.

**Results:** 100 nm MIP transport was sensitive to patient-to-patient difference in CF sputum microstructure. Elevated mucus and DNA content most significantly altered CF sputum microstructure. Reduction in sputum mesh pore size is characteristic of CF patients with highly obstructed airways as indicated by measured FEV1. Treatment of CF sputum with dornase alfa leads to significant increases in the pore size of the sputum mesh structure.

**Conclusion:** We developed a novel method to sensitively detect patient-to-patient differences in CF sputum microstructure using muco-inert nanoparticles as probes. This microstructural read-out may potentially serve as a novel biomarker for airway obstruction in CF and as an additional parameter for assessing mucolytic activity.

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Wednesday 6:05 Atrium/Harborview

PO20

### **Microstructure and rheological function of food co-texturizers**

Christopher M. Gregson<sup>1</sup>, Matthew Sillick<sup>1</sup>, Xin Yang<sup>1</sup>, Paulo Santos<sup>1</sup>, and Jegede Layo<sup>2</sup>

<sup>1</sup>*Systems Design & Measurement, Ingredient Incorporated, Bridgewater, NJ 08807, United States;* <sup>2</sup>*Sensory, Ingredient Incorporated, Bridgewater, NJ 08807, United States*

Measurement of microstructure and rheological function are key tools for designing foods with desired textural attributes as they reveal the mechanistic links between formulation/process and sensory performance. However, food microstructures are often complex multiphase materials. Identifying specific ingredients and determining their roles in modulating rheology and sensory performance can be challenging.

Specialty co-texturizers are often used at low concentrations to significantly modulate the texture of granular starch thickened foods. We used co-texturizers tagged with a dichlorotriazine-based reactive dye to visualize their location within a model pudding system using Confocal Laser Scanning Microscopy. Particle tracking, and both small and large deformation shear experiments were performed to determine local and bulk rheological properties, respectively. A descriptive panel performed sensory measurements on samples made using untagged co-texturizers and hedonic scores resulted in understanding consumer drivers of texture preference.

We found that the co-texturizer resides in the interstitial phase between starch granules, and influences both local rheology and the ability of the starch granule to accommodate bulk flow. Waxy corn based N-DULGE® SA1 co-texturizer (Ingredient, USA) induces weak gelation resulting in higher elastic modulus and yield stress, whereas tapioca starch based N-DULGE® C1 co-texturizer (Ingredient, USA) enhances flow characteristics

as exhibited by higher phase angle, lower G' and higher power law coefficient. These properties in turn yield differences in sensory characteristics including spoon indent, firmness, melt-away, slipperiness, mouth coating and creaminess.

The results show how food texture can be modulated using specialty co-texturizers and how bulk rheology and microstructure can be used to enable consumer preferred textures with rational formulation design.

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Wednesday 6:05 Atrium/Harborview

PO21

### **Using capillary break-up technique to study the extensional behavior of chocolate melts**

Francesca De Vito<sup>1</sup>, Fabian Meyer<sup>2</sup>, and Fritz Soergel<sup>2</sup>

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Rheology has long played important roles in food industry, from food acceptability, processing to handling. Rheological measurements are therefore routinely performed in the food industry to gain insights to the rheology-property, rheology-process, and rheology-structure relationships for better food development and manufacturing. The challenges, however, often arise from the complexity of food materials, both structurally and rheologically. For example, 3D printing of chocolate has gained considerable interest in recent years, mainly due to its ability to produce nearly unlimited choice of shapes that are not available with traditional processing techniques. Chocolate products, however, often consist of mixtures of both solids and fluid structural components, which exhibit vastly different rheological behavior. The complexity is further compounded by the mix of shear and extensional flow as chocolate is being "printed". It's generally accepted that no single test can provide a complete rheological profile of a material. Careful selection of complementary techniques/instruments is always beneficial. While there is an abundance of literature on the shear behavior of chocolate melts, investigation on their response to extensional deformation is still scarce. In this presentation, we demonstrate the feasibility of employing capillary break-up (CaBER) technique to study the extensional behavior of some chocolate products. The relationship between break-up time and product composition will be discussed. The practice and underlying principle of these measurements should be applicable to other foodstuff as well.

Wednesday 6:05 Atrium/Harborview

PO22

### **Applications of rheology in pharmaceutical formulation development via hot melt extrusion (HME)**

Fengyuan Yang

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As more synthetic biodegradable and/or biocompatible polymeric excipients have been applied to drug products, polymer engineering and processing have gained more attention in the pharmaceutical industry. For instance, hot melt extrusion (HME) is an established manufacturing technique to improve bioavailability of active pharmaceutical ingredients (API), via enhanced dissolution rates and solubility. Since the HME operation involves nonisothermal flow of polymer/API melts in geometrically complex conduits it is appropriate to examine the rheological behavior of polymer and polymer/API melts to guide formulation development and manufacture. The aim of this study is to utilize viscoelastic properties of polymer and polymer/API physical mixtures to assess and optimize processing conditions for the preparation of amorphous solid dispersions via HME. Several poorly water-soluble APIs are physically mixed and extrusion compounded with copovidone as the polymeric excipient. Linear viscoelastic measurements were performed using a parallel plate rheometer, as a function of API concentration, frequency, temperature and time. In general, the incorporated API molecules impart a plasticizing effect on the flow of the polymer matrix, manifested by significantly decreased viscosity as the API loading is increased. At a given API concentration, the API phase affects the rheological response of the polymer/API system as crystalline/aggregated forms of the API exhibit a more elastic response than its corresponding amorphous/dispersed form. In addition, temperature and time sweeps of polymer/API mixtures demonstrate the potential for predicting the thermodynamic and kinetic evolution of amorphous solid dispersions from crystalline API and polymer. In summary, systematical rheological studies of polymer/API mixtures significantly facilitate the development and process definition of novel formulations and products via HME.

Wednesday 6:05 Atrium/Harborview

PO23

### **Examination of the viscosity of a monoclonal antibody solution as a predictor of viral filtration performance**

Kevin D. Stewart<sup>1</sup>, Jai Pathak<sup>2</sup>, Kelcy J. Newell<sup>1</sup>, and Matthew Dickson<sup>1</sup>

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During optimization of a viral filtration step for a therapeutic monoclonal antibody (mAb), the mAb solution exhibited poor virus filter throughput. Virus filtration is a standard purification step used in virtually all mammalian cell culture-derived clinical manufacturing processes. To minimize costs associated with viral clearance evaluations and to minimize commercial manufacturing costs and processing time, there is a drive to find predictors of viral filtration performance to maximize virus filter throughput. An examination of mAb solution viscosity under various solution conditions, including the addition of a chaotropic agent, was performed to determine if a correlation could be established between solution viscosity and viral filtration throughput performance. Preliminary results suggest a correlation between the mAb solution viscosity and virus filtration throughput at a given pH.

Wednesday 6:05 Atrium/Harborview

PO24

**High throughput rheological characterization of small volume biopharmaceutical formulations**David Nieto Simavilla, Ivan Akhremitchev, and Seong-gi Baek*RheoSense Inc., San Ramon, CA 94583, United States*

During the process of discovering novel drugs, biopharmaceutical industries produce large number of formulations with small recipe variations. One important aspect in the characterization of new drugs is their viscosity fingerprint (i.e. viscosity dependence in shear rate and temperature). Viscosity is a good indicator of small concentration and molecular structure changes that play a key role in the efficacy of the final product. However, in the early stages of development, available sample volume for testing and characterization is very limited. Conventional rheometry often requires large sample volume (in the order of 1 mL or higher). Microfluidic based rheometers can offer extensive rheological characterization at a fraction of the volume. A single point viscosity measurement can be performed with just a few  $\mu\text{L}$ . Another advantage of microfluidic-based rheometers is that, due to their small size, they can achieve much higher shear rates than conventional rheometers without inducing flow instabilities. This opens the door for the study of high shear applications such as injectability of non-Newtonian therapeutics. In this study, we introduce a hybrid of microfluidic and MEMS Viscometer/Rheometer On a Chip, together with its key applications. This technology is amenable to automation, allowing high throughput and robust measurements of viscosity that require little to none user assistance during testing. We present automated viscosity measurements of Bovine Serum Albumin (BSA) and Immunoglobulin G (IgG) as a function of shear rate, temperature, concentration and pH. These are used to determine protein stability and melting temperature. Additionally, this technology presents superior repeatability that allows for intrinsic viscosity measurements. Intrinsic viscosity can be used to establish molecular size in the formulation environment.

Wednesday 6:05 Atrium/Harborview

PO25

**Shear flow behavior of opuntia ficus indica (Nopal) mucilage aqueous solutions with different maturation ages**Francisco Rodríguez-González<sup>1</sup>, César N. Muñoz-López<sup>1</sup>, and José Pérez-González<sup>2</sup><sup>1</sup>*Departamento de Biotecnología, CEPROBI, Insitituto Politécnico Nacional, Yautepec, Morelos 62731, Mexico;* <sup>2</sup>*Departamento de Física, ESFM, Insitituto Politécnico Nacional, México D. F., México D. F. 07738, Mexico*

*Opuntia ficus indica* (Nopal) is cultivated in different countries for alimentary and industrial purposes. The mucilage obtained from Nopal is a polysaccharide which may be used as a rheological modifier. Besides, it is popular knowledge its capacity to form films, a fact that may be used to incorporate Nopal mucilage in inexpensive decorative paints or making protective films for foods. Despite the large amount of practical applications of Nopal, there is a dearth of systematic studies focused on the understanding of the rheological behavior of its mucilage solutions. The purpose of this investigation was to gain a deeper inside into the knowledge of the rheological behavior of Nopal mucilage solutions. In this work, a study of the effect of different maturation times of Nopal on the shear flow behavior of its mucilage solutions was carried out. Steady and dynamic shear flow experiments were performed by using a stress-controlled rheometer at a temperature of 25 °C with the cone and plate and Couette geometries. Aqueous mucilage solutions were prepared at concentrations of 2, 4 and 6 wt%, respectively from fruits having ages of 20, 40 and ~600 days, respectively. It was found that the shear viscosity of the solutions increased with mucilage concentration as well as with the fruit age for a given concentration. Moreover, mucilage solutions at 4 and 6 wt% from the old fruits behaved as weak gels. Solutions prepared from young fruits mucilage did not exhibit elasticity, meanwhile those from the old fruits showed highly elastic behavior for concentrations = 4 wt%; the first normal stress difference was an increasing function of the shear stress, but decreased with concentration for a given shear stress. Finally, mucilage solutions at 4 and 6 wt% from the old fruits followed the Cox-Merz relationship at low angular frequencies/shear rates, but deviate from it once normal stresses became significant. The results in this work are explained on the basis of an increase of the mucilage molecular weight with the age.

Wednesday 6:05 Atrium/Harborview

PO26

**Cooperative motion of active Brownian spheres in three-dimensional dense suspensions**Roland G. Winkler, Adam Wysocki, and Gerhard Gompper*Institute of Complex Systems, Forschungszentrum Jülich, Jülich, NRW 52425, Germany*

Assemblies of intrinsically active objects represent an exceptional class of non-equilibrium systems. Examples range from the macroscopic scale of human crowds to the microscopic scale of cells and motile microorganisms such as bacteria. A generic phenomenon of dense living fluids is the emergence of self-organized large-scale dynamical patterns like vortices, swarms, networks, or self-sustained turbulence. This intriguing dynamical behavior is a consequence of the complex interplay of self-propulsion, internal or external noise, and many-body interactions. Experiments and simulations indicate that alignment induced by particle interactions, e.g., inelastic collisions between elongated objects or hydrodynamic interactions, lead to clustering and collective motion. Surprisingly, spherical self-propelled particles in 3D, which lack an alignment mechanism, also exhibit an activity-induced phase separation and long-lived cooperative motion [1].

Here, we present results of Brownian dynamics simulations of self-propelled hard-sphere colloids over a wide range of densities and self-propulsion strengths [1]. We discuss the separation of the motile particles into a dilute, gas-like phase, and a dense, liquid-like phase at sufficiently large activity and density. Below a critical density, isolated liquid droplets appear, whereas above that density a bicontinuous structure is formed. The interior dynamics of the liquid domains displays a strong heterogeneity in space and time. Thereby, the dynamical behavior is highly collective, despite the absence of an alignment mechanism. We show that spatial displacement correlation functions are nearly scale-free for systems with densities close to and even above the glass transition density of passive systems. This collective dynamics can only arise from a spatial sorting of particles with similar orientation. The reorientation of particles at an interface provides such a sorting mechanism.

[1] A. Wysocki, R. G. Winkler, G. Gompper, EPL 105, 48004 (2014)

Wednesday 6:05 Atrium/Harborview

PO27

### **Dissipative particle dynamics simulation of water insoluble drugs via smart micelles**

Leela Rakesh

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Dissipative particle dynamics (DPD) simulation technique is used to simulate the distribution of water insoluble drugs such as Naproxen molecules in the water soluble drug carrier and smart micelle forming molecules. Such carrier materials, Naproxen molecules are adsorbed on the surface of the carrier molecules and a shell spherical to cylindrical structure formation is seen depending upon the pH or acidic to alkalinity. Various distribution of naproxen forms are observed depending upon the carrier alkalinity & acidity molecules. The release performance of the carrier fluid is predicted based on the simulated microstructure. A release performance of naproxen is also discussed based on the simulation characteristics.

Wednesday 6:05 Atrium/Harborview

PO28

### **Numerical study of thin viscoelastic films on substrates**

Shahriar Afkhami

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We numerically study the interfacial dynamics and instability of a thin viscoelastic film on a substrate. Governing equations are the incompressible Navier-Stokes equations and a linear viscoelastic constitutive model of Jeffreys type. We use the long wave approximation to describe the non-linear evolution of the interface. We consider different regimes of slippage, and in each regime, we investigate the role of the liquid viscoelasticity and the contact angle on the thin film break-up. The numerical solution of full non-linear equations are compared with the results of linear stability analysis.

Wednesday 6:05 Atrium/Harborview

PO29

### **Modeling the rheological response of common food products using fractional constitutive equations**

Tarun Kamath, Caroline E. Wagner, and Gareth H. McKinley

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It is common practice to derive constitutive equations for viscoelastic fluids by modeling them as combinations of Hookean springs and Newtonian dashpots. Examples include the Maxwell and Kelvin-Voigt models, in which one spring and one dashpot are placed in series and in parallel, respectively, resulting in different behavior upon imposition of stresses or strains. Many real materials do not obey either of these models, and the practice of adding elements to obtain better fits to experimental data often makes the model parameters empirical in meaning. Since a simple sum of viscous and elastic elements cannot capture the behavior of complex fluids, the concept of the springpot was introduced: a fractional mechanical element for viscoelasticity which interpolates between the response of a spring and a dashpot. A springpot is described by two parameters: a fractional exponent ranging from 0 (for purely elastic materials) to 1 (for purely viscous materials) and a quasi-property, characterizing the magnitude of the material response. Here we introduce a simple graphical computer script (developed in MATLAB) which returns the model parameters for both the Fractional Maxwell and Fractional Kelvin-Voigt models by fitting experimental rheological data obtained in small amplitude oscillatory shear (SAOS), creep deformation, or stress relaxation experiments. We present the resulting model parameters for experimental data obtained for a wide array of viscoelastic liquid foodstuffs, including nectar, honey, and pudding-like fluids created from concentrations of a commercially available Nestlé food additive, Thicken Up Clear. We show that fractional viscoelastic constitutive models fit the rheological data for all three foods very well, and thus demonstrate how commonly used qualitative adjectives that are used to describe food properties can be quantified numerically.

Wednesday 6:05 Atrium/Harborview

PO30

### **A viscosity model for concentrated suspensions of rigid, randomly oriented spheroids**

Salah Aldin Faroughi and Christian Huber

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To quantify the deformation and transport of complex fluids, e.g. suspensions, over a wide range of particle volume fraction and shear conditions a rheological model with predictive capability is required. The main focus of this study is on the effect of particle shape and shear conditions on the rheological behavior of non-Brownian suspensions of rigid, randomly oriented spheroids. We propose a framework that forms the basis for a predictive closed-form model to parameterize the evolution of suspensions' microstructures and its effect on the effective viscosity. We specifically study common factors that influence the microstructure of a suspension under deformation that lead to shear thinning, e.g., the effect of particle shape, ordering and modality alteration. We find that two state variables, the intrinsic viscosity and the self-crowding factor (accounts for the dead fluid fraction in the void between particles) control the state of dispersion of particles in dense suspensions. A combination of these two variables is shown to be invariant with the imposed shear stress, and depend only on the particle aspect ratio. This result, tested against available experimental and new numerical data on suspensions of randomly oriented spheroids, allows us to derive a predictive model (and hence a constitutive rheological model) for the effective viscosity of concentrated suspensions of spheroids subjected to low (near zero) strain rates. At higher imposed shear rates, one only needs to constrain one of the state variables, independently, to parameterize the state of dispersion of the suspension and its effective viscosity. This simplification is possible because of the existence of a factor that combines the state variables that is invariant with respect to shear

conditions. Alternatively, the proposed model provides the means to estimate the value of the state variables from the viscosity measurements made in the laboratory and get some constraints about the microstructural organization of the suspension.

Wednesday 6:05 Atrium/Harborview

PO31

### **Modelling polymer structure in 3D printing**

Claire McLlroy and Peter D. Olmsted

*Department of Physics, Georgetown University, Washington, DC 20057, United States*

3D-printing has the potential to transform manufacturing processes as we know them, yet improving the strength of printed parts, to equal that of traditionally-manufactured parts, remains an underlying issue. 3D printing via fused deposition modelling involves melting a thermoplastic, followed by layer-by-layer extrusion of the molten viscoelastic material to fabricate a three-dimensional object. The key to the ensuring strength at the weld between these layers is successful inter-diffusion. However, prior to welding, both the extrusion process and the cooling temperature profile can significantly affect the polymer micro-structure and, consequently, how well the polymers are able to "re-entangle" across the weld. In particular, polymer alignment in the flow can cause de-bonding of the layers, creating defects in the final printed object. We have developed a simple one-dimensional model of the non-isothermal extrusion process to explore the effects that typical printing conditions and rheology have on the structure of the polymer melt. We incorporate both the stretch and orientation of the polymer using the Rolie-Poly constitutive equation and introduce flow-induced crystallisation to examine solidification.

Wednesday 6:05 Atrium/Harborview

PO32

### **Neutron irradiation damage simulation**

Yan Peng

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Damage in nuclear core cartridge is formed by neutron irradiation. The phenomena and principles of this neutron irradiation obey on thermal transfer process, which includes rheology process of fuel material. The corresponded numerical simulation of this damage can simulate the helium effects in irradiated metals and the damage by charged-particle irradiation.

Wednesday 6:05 Atrium/Harborview

PO33

### **Structure and rheology of binary mixtures of PEO-PPO-PEO block copolymer mixtures in the protic ionic liquid ethylammonium nitrate**

Ru Chen<sup>1</sup>, Carlos R. López-Barrón<sup>2</sup>, and Norman J. Wagner<sup>1</sup>

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

The structural and rheological properties of a model series of binary Pluronic block copolymer mixtures dissolved in a protic ionic liquid are studied as a strategy to modulate and control the soft solid behavior of amphiphilic block copolymers in ionic liquids. The properties of the soft solids are controlled via tuning the mixture composition of Pluronic block copolymers P123 and F127 self-assembled in deuterated ethylammonium nitrate (dEAN). Equilibrium microstructures are studied by linear viscoelasticity and small angle neutron scattering (SANS), while the shear induced microstructures are probed by in situ rheo-SANS in the radial direction (1-3 plane of flow) under steady and oscillatory shear flow using recently developed time resolved methods [1, 2, 3]. Solutions with total Pluronic composition of 27.5 wt% and 50/50 mass ratio of P123/F127 in dEAN form closed packed micellar phases similar to those formed in parent homopolymers. [4] The application of shear flow in a Couette geometry leads to layering of the closed packed phases. It was also observed that relatively low amplitude oscillations induces slightly different ordering than steady shear. This study points out a strategy for modification of the structural, and hence rheological, properties of Pluronic block copolymers in ionic liquid solvent, providing insights useful for comparing the properties of self-assembled amphiphilic block copolymers in molecular versus ionic liquid solvents under rest as well as steady and dynamic oscillatory shear flows.

References: [1] C. R. López-Barrón et al. *Journal of Rheology*, 2015, 59(3), 793-820. [2] C. R. López-Barrón et al. *Physical Review Letters*, 2012, 108, 258301. [3] A. P. R. Eberle and L. Porcar, *Current Opinion in Colloid & Interface Science*, 2012, 17, 33-43. [4] G. E. Newby et al. *Journal of Colloid and Interface Science*, 2009, 329, 54-61.

Wednesday 6:05 Atrium/Harborview

PO34

### **Impact of thermal history and applied flow fields on water-swollen block copolymer micelle crystals**

Melissa M. Dao and Lynn M. Walker

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Understanding the effect of processing conditions on the local structure is imperative for properly developing applications involving block copolymer soft solids. Block copolymer soft solids are formed as a disordered triblock copolymer solution transitions to a lyotropic liquid crystal of micelles. Depending on the polymer architecture, the soft solids go through an order-order transition (OOT) from cubically packed spherical micelles to hexagonally close packed cylindrical micelles. Here, we present our work on the effect of thermal history and applied flow fields on the cubic micellar phase. Thermal history is varied by forming the cubic phase from a disordered liquid and from an aligned cylindrical phase through the OOT. Following the formation of the cubic phase, applied flow fields (high amplitude and high frequency oscillations) are used to macroscopically align the micellar crystals. The crystal structure is characterized using small angle neutron scattering (SANS) while the

mechanical behavior is probed using rheology. Changes in the polycrystallinity of the system is observed with varying thermal history while applied flow fields change the relative orientation and local stacking of the close pack micellar planes. The findings of this work show the local order of soft solids can be controlled by processing conditions.

Wednesday 6:05 Atrium/Harborview

PO35

### **Rheological characterization of triblock polymer solutions for roll to roll membrane production**

Eduard A. Caicedo-Casso<sup>1</sup>, Jessica Sargent<sup>2</sup>, Jacob L. Weidman<sup>3</sup>, Bryan W. Boudouris<sup>2</sup>, William A. Phillip<sup>3</sup>, and Kendra A. Erk<sup>1</sup>

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Ultrafiltration membranes are created by self-assembly of block polymer and non-induced phase separation techniques ("SNIPS") to provide a platform with a hierarchical, well-defined porous network. This platform has a selective layer containing a high density of uniform nanopores, and a gutter layer which features an open and interconnected microporous network. The layer combination results in a membrane with high permeability and selectivity along with good mechanical strength. Previous research has demonstrated the membrane's capabilities in water purification, drug delivery, and virus filtration applications [1]. However, a major challenge towards creation of a commercial product is to manufacture these membranes by continuous casting techniques. In this study, we use rheometry as a powerful tool to characterize block polymer solutions that are then used to create ultrafiltration membranes via roll-to-roll casting techniques. The rheological properties of a poly(isoprene-*b*-styrene-*b*-*t*-butylmethacrylate) block polymer (37.6-44.8 kg/mol) in solution at concentrations of 13.5-15 wt.% with tetrahydrofuran and dioxane are correlated directly with the structure and properties of the cast membrane. Shear thinning behavior followed by Newtonian behavior is observed, displaying a transition at shear rates ranging from 1 s<sup>-1</sup> to 10 s<sup>-1</sup>. Thinning behavior is consistent with the response of a weakly self-assembled polymeric structure in solution. Newtonian behavior most likely indicates the disruption of the polymeric structure at increasing shear rates. Viscosity curves show that polymers with polydispersity index (PDI) above 1.4 do not display strong shear thinning. In addition, effects from solvent evaporation were also evaluated. Concentric cylinder and cone-plate rheometer geometries were used to demonstrate that a closed coating system is needed when using roll-to-roll techniques for casting, such as a slot die fixture.

[1] Y. Zhang, J. et. al. *J. Appl. Polym. Sci*2015, DOI: 10.1002/app.41683.

Wednesday 6:05 Atrium/Harborview

PO36

### **Deformation effects on fracture-healing behavior of model thermoreversible triblock copolymer gels via shear rheometry**

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Fracture-healing characteristics of model thermoreversible physically associating triblock copolymer gels were investigated by shear rheometry. The triblock is an ABA type copolymer of poly(methyl methacrylate) endblocks connected by poly(*n*-butyl acrylate) midblock that self-assemble into endblock aggregates in 2-ethyl hexanol. Gels were formed at various temperatures ranging from 20-28°C and polymer concentrations of 5-6 vol %. Fracture experiments at constant shear rates probed the shear stress response of the gels at differing levels of strain. Previous work in our group(1) investigated fracture experiments during testing of 40 seconds. In this present work, fracture events happened at the same instance, but the experimental time was varied to observe the changes of deformation on the system. Fractured gels were allowed to rest and then tested again at specific times to measure the network recovery. Timescales of healing and Arrhenius-type kinetics of gels at different gel concentrations and deformation time were determined and compared with one another. Timescales for fully healed gel networks ranged from several minutes for elevated temperatures to multiple hours for cooler gel temperatures. Activation energies for healing the gels were determined using temperature and 100% healing times to investigate the energy barrier for network healing. As polymer concentration is increased, the activation energies are decreased from ~500 kJ/mol to 300 kJ/mol as there are more aggregates for the chains to re-associated into. Changing the experimental strain also decreased the activation energy of the gels. Fracture of the gels at higher deformation caused a more uniform fracture plane and propagation of any instabilities in the gel's structure. Lower deformation strains caused fractures in the gel and a decrease in the stress response, but likely do not propagate throughout the gel causing a faster healing response of the network.

(1) Thornell, T.; Erk, K.; et.al, *ACS Macro Lett.* 2014, 3 (10), 1069-1073.

Wednesday 6:05 Atrium/Harborview

PO37

### **Rheology of self-assembled amphiphilic block copolymer mesophases**

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Amphiphilic molecules self-assemble at water/oil interface and form mesomorphic structures, known as mesophases. The self-assembled mesophases can take various forms that provide a broad range of applications in drug delivery, templating synthesis, and nanostructure production. Mesophases are usually characterized by small-angle X-ray scattering (SAXS), but their rheological behavior is not well understood. Thus, there is a research gap since information about the flow behavior of mesophases is essential if they are utilized for reactive processing. In this work, mixtures of water, butanol or xylene, and poly(ethylene oxide) -*b*-poly(propylene oxide) -*b*-poly(ethylene oxide) copolymers, known as Pluronics surfactants, are prepared in hexagonal and lamellar structures. The rheological fingerprints of such mesophases are studied through flow curve, strain sweep, and frequency sweep measurements.

Wednesday 6:05 Atrium/Harborview

PO38

**Self-healing sulfur based copolymer IR lenses**Ngoc A. Nguyen<sup>1</sup>, Jared J. Griebel<sup>2</sup>, Jeffrey Pyun<sup>2</sup>, and Michael E. Mackay<sup>1</sup><sup>1</sup>*Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States;* <sup>2</sup>*Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United States*

Self-healing and stimuli-responsive materials are being studied intensively for various applications by utilizing metal-ligand, hydrogen bonding, and pi-pi stacking interactions. Concurrently, sulfur is a by-product of the petroleum industry and there are limited uses of it. In our research, element sulfur (S<sub>8</sub>) was utilized to synthesize a useful random copolymer (S-r-DIB) via inverse vulcanization of sulfur with 1,3-diisopropenylbenzene (DIB). Fascinatingly, these copolymers can be mechanically strong, thermally tunable and melt processed for use as the active layer for lithium- sulfur batteries. Herein, we first report self-healing IR optic components by using the very dynamic covalent bond (-S-S-). The dynamic bonds can be thermally activated and tuned by changing the sulfur/ DIB ratios. The scratched IR lenses with high sulfur content, over 50wt%, can be healed and recover their optical properties after thermal annealing. The effect of S-S dynamic bonds on rheological, mechanical and thermal properties of these copolymers (S-r-DIB) under different processing conditions was investigated and discussed within the poster.

Wednesday 6:05 Atrium/Harborview

PO39

**Rheology and structural investigation of fumed silica based shear thickening fluids**Justin Warren<sup>1</sup>, Santanu Kundu<sup>2</sup>, Katie Weigandt<sup>3</sup>, Thomas Lacy<sup>1</sup>, Hossein Toghiani<sup>2</sup>, and Charles U. Pittman<sup>4</sup><sup>1</sup>*Aerospace Engineering, Mississippi State University, MS State, MS, United States;* <sup>2</sup>*Dave C. Swalm School of Chemical Engineering, Mississippi State University, MS State, MS, United States;* <sup>3</sup>*NIST Center for Neutron Research, Gaithersburg, MD 20899, United States;* <sup>4</sup>*Chemistry Department, Mississippi State University, MS State, MS, United States*

Shear thickening fluids (STFs) are increasingly being investigated in various applications ranging from improving the ballistic impact resistance of body armor to shielding spacecraft structures from micrometeoroid/ orbital debris (MMOD) impact. Spacecraft MMOD shields can be subjected to wide temperature variation, often more than  $\pm 100$  °C. Therefore, an understanding of shear-thickening responses as a function of temperature is critical. Here we report the results of rheological characterizations as well as small angle and ultra small angle neutron scattering (SANS and USANS) experiments performed on fumed silica based STFs where both the temperature and shear rate were varied. In addition to varying the mass fractions of the dispersed phase, the interactions between the dispersed and continuous phases were controlled by altering the surface chemistry of the suspended fumed silica particles and the molecular architecture and molecular weight of the suspending media. STFs were prepared by suspending fumed silica nanoparticles with different surface functionalities in polyethylene glycol (molecular weight of 200 g/mol and 400 g/mol) and polypropylene glycol (molecular weight 700 g/mol). Rheological characterizations were performed in a shear-rheometer over a temperature range of -60 °C (melting point of the continuous phase) to +50 °C, and SANS and USANS rheological experiments were carried out over a temperature range of -40 °C to +40 °C. The STFs' viscosity was greatly dependent on temperature and shear rate, and the scattering results indicated changes in the microstructure of the STFs with increasing shear rate likely related to transient structure formation.

Wednesday 6:05 Atrium/Harborview

PO40

**A study of the viscosity of suspensions of solid particles: Applications to red blood cells**Francis E. Mensah*Natural and Physical Sciences, Virginia Union University, Richmond, VA 23227, United States*

A considerable amount of research has been done in predicting the viscosity of dilute suspensions. In this study, we review works done by pioneers such as Einstein who considered spherical particles, Barnes, Krieger and others. The application of models from these pioneers to the red blood cells (RBC) reveals a promising new model in the prediction of the viscosity of the RBC in suspension.

Wednesday 6:05 Atrium/Harborview

PO41

**Dynamics of nanoparticles in wormlike micelle solutions**Jonghun Lee<sup>1</sup>, Aline G. Iankovski<sup>1</sup>, Suresh Narayanan<sup>1</sup>, Alec R. Sandy<sup>1</sup>, and Robert L. Leheny<sup>2</sup><sup>1</sup>*Argonne National Laboratory, Lemont, IL 60439, United States;* <sup>2</sup>*Johns Hopkins University, Baltimore, MD, United States*

Wormlike micelles form when amphiphilic molecules self assemble into elongated, tube-like structures in aqueous solution. The viscoelastic properties of these complex fluids are governed by the nanometer scale internal structure. However, due to this heterogeneous microstructure, understanding the correspondence between macroscopic mechanical behavior and microscopic dynamics is challenging. Studying dynamics of nanoparticles in these complex fluids can be helpful to link the microscopic and macroscopic behaviors. We have investigated the dynamics of silica nanospheres and gold nanorods of various sizes dispersed in wormlike micelle solutions with an entanglement mesh size that was tuned by varying the concentration of amphiphiles to be comparable to the size of the particles. We will describe results for the nanoparticles' dynamics obtained with x-ray photon correlation spectroscopy (XPCS) and compare these dynamics to the solution rheology.

Wednesday 6:05 Atrium/Harborview

PO42

**Structural measurements of yielding colloidal gels**Jialun Wang<sup>1</sup>, Benjamin J. Landrum<sup>2</sup>, and Roseanna N. Zia<sup>2</sup><sup>1</sup>*Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, United States;* <sup>2</sup>*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States*

We study the evolving structure of a reversible colloidal gel as it yields under a fixed, externally imposed shear stress via large-scale dynamic simulation. In our recent work, we characterized the macroscopic characteristics of the so-called delayed yield of such gels, finding a qualitative dependence of the yield behavior, and subsequent flow characteristics, on the strength of the applied stress. To understand the microstructural origins of these phenomena, we tracked the positions of all particles throughout simulation, and developed measurements to elucidate structural evolution during initial creep, the yield event, and post-yield flow (and sometimes subsequent re-solidification). In this poster I will highlight new techniques we have developed, utilizing real-space and reciprocal space measurements, connecting bond-level and large-scale structural rearrangements, during this highly transient process. A comparison to results from neutron scattering experiments is made.

Wednesday 6:05 Atrium/Harborview

PO43

**A microstructural description of shear thickening suspensions**Abhinendra Singh<sup>1</sup>, Romain Mari<sup>1</sup>, Ryohei Seto<sup>2</sup>, Jeffrey F. Morris<sup>3</sup>, and Morton M. Denn<sup>3</sup><sup>1</sup>*Levich Institute, City College of New York, New York, NY, United States;* <sup>2</sup>*Mathematical Soft Matter Unit, Okinawa Institute of Science and Technology, Onna, Okinawa Prefecture 904-0495, Japan;* <sup>3</sup>*Levich Institute and Department of Chemical Engineering, City College of New York, New York, NY 10031, United States*

The mechanism of shear thickening in dense suspensions has been recently linked to a transition from a lubricated "frictionless" to an unlubricated "frictional" rheology. Recent particle simulations have been successful to quantitatively reproduce both the continuous and discontinuous shear thickening as observed experimentally. However, a microstructural description of these suspensions is still lacking, which would aid in understanding and predicting the flow behavior of shear thickening suspensions. To tackle this challenging issue, we explore various microscopic quantities, like the inter-particle force distribution, the particle motion correlations, and the anisotropy (in both contact and force network).

Wednesday 6:05 Atrium/Harborview

PO44

**Colloids in semi-flexible networks: Templated assembly and stimuli-responsive elasticity**N Ashwin K. Bharadwaj<sup>1</sup>, Marta Hatzell<sup>2</sup>, Jin Gu Kang<sup>2</sup>, Kenneth S. Schweizer<sup>2</sup>, Paul 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>*Materials Science and Engineering, University of Illinois at Urbana Champaign, Urbana, IL 61801, United States*

We explore large mesh semi-flexible networks as a key component of polymer/colloid composites. A fibrillar biopolymer gel network of bovine fibrin is used in these studies. First, for templated assembly of carboxylate-modified latex (CML) colloids along the semi-flexible network components which have an elongated structure due to a large persistence length. Second, the large persistence length creates a network which is nonlinear elastic and stiffening, so that adding stimuli-responsive soft colloids, which swell in response to temperature, creates a field-controllable elastic stiffening of the network. We characterize the fibrin network and the resulting composites using shear and extensional rheology. A nonlinear strain-stiffening response is common under both deformation modes. Using insights from rubber elasticity theory, we model the fibrin gel matrix as an elastic network of nonlinear springs. The micro-mechanical model predicts the experimental stress-strain response, and permits inference of microstructural features in the framework of a worm-like chain model. We then study the extent to which hard colloids (CML) can be introduced into the fibrin gel matrix. We study gel network formation in the presence of varying concentrations of hard sphere colloids. Additionally, we electrophoretically drive conductive colloidal particles into the gel network and study the composite architecture and its mechanical properties. Bi-fluorescent confocal imaging and scanning electron microscopy reveals regimes in which colloidal assembly occurs along network components. Finally, we use field-responsive swellable microgel particles to demonstrate stimuli-induced rheological changes in the fibrin network. We describe how such composites with field responsive nonlinear elastic mechanical properties may have energy harvesting applications.

Wednesday 6:05 Atrium/Harborview

PO45

**Improving rheology and dispersion of graphene in polyethylene by various methods**Muhammad Z. Iqbal<sup>1</sup>, Frederick C. Prehn Jr.<sup>2</sup>, Stephen G. Boyes<sup>2</sup>, Ahmed A. Abdala<sup>3</sup>, Vikas Mittal<sup>4</sup>, and Matthew W. Liberatore<sup>1</sup><sup>1</sup>*Chemical and Biological Engineering, Colorado School of Mines, USA, Golden, CO 80401, United States;* <sup>2</sup>*Department of Chemistry, Colorado School of Mines, USA, Golden, CO 80401, United States;* <sup>3</sup>*Qatar Environmental and Energy Research Institute, Doha, Qatar;* <sup>4</sup>*Department of Chemical Engineering, The Petroleum Institute, Abu Dhabi, Abu Dhabi 2533, United Arab Emirates*

Research in processing polyolefins and their nanocomposites has always been of great interest. Newly discovered nanomaterials such as graphene poorly disperse in polyolefins due to aggregation and van der Waals stacking of graphene sheets. In this poster presentation, we show different methods of improving graphene dispersion in polyethylene (PE) by 1) blending PE with oxidized polyethylene (OPE), 2) chemically functionalizing the surface of graphene, and 3) using graphene-carbon black synergy. The effects of these modulations on polymer-polymer and polymer-particle interactions are presented by means of melt rheology, small angle x-ray scattering (SAXS), morphology, and mechanical properties. In the first part, OPE solvent blended in PE shows complete miscibility. The decrease in zero shear viscosity of PE with increasing

OPE reveals that OPE acts as a plasticizer. In addition, inclusion of OPE decreases the lamellar region thickness in PE, which eventually increases the elastic moduli (i.e., increased brittleness). PE/OPE blends-graphene nanocomposites show very interesting non-Einstein behavior. Incorporating graphene in neat PE and 80/20 PE/OPE blends increases the viscosity and other rheological properties. However, in 60/40 blends, adding graphene reduces the viscosity up to 1 wt% graphene. In order to reduce the cost of PE nanocomposites, we also used graphene/CB synergy in PE. Different ratios of CB/graphene (1/1, 5/1, 10/1) are used to determine stable dispersions that gives better rheological and electrical properties. Moreover, various methods of improving the dispersion of graphene-CB hybrid filler in PE are explored such as the use of surfactants, compatibilizers, and covalently functionalizing graphene. The electrical conductivity and morphology in these blends and composites are also reported.

Wednesday 6:05 Atrium/Harborview

PO46

### **Dynamic transition of a colloidal gel using multiple particle tracking microrheology**

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

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Crystallized hydrogenated castor oil (HCO) is a naturally sourced material with industrial application as a base for commercial goods. A phase change (gel $\rightarrow$ sol) occurs due to an osmotic gradient when HCO gels are submerged in water, and previous work with these gels has focused on the equilibrium (gel or sol) material properties using bulk rheology. Multiple particle tracking (MPT) microrheology is used to quantify dynamic material properties during both the critical transition and at equilibrium of an HCO colloidal gel. MPT uses fluorescent video microscopy to capture the displacement of probe particles embedded in the gel. The mean-squared displacement is quantified from the particle trajectories and is related to rheological properties using the Generalized Stokes-Einstein Relation. The gel-sol transition is induced by submerging HCO gel in water, while the sol-gel transition is completed by diluting the HCO gel with water to 3.1wt% gel and then contacting with surfactant. Probe movement is tracked during expansion and contraction of the gel until a steady state is reached. Material properties and heterogeneities in the probe microenvironments are measured during the dynamic material transition. A reduced time,  $t_r = |t_{gel} - t|/t_{eq}$ , is reported, and time cure superposition shows the gel undergoes a phase change at approximately  $t_r = 0.75$  for both transitions, indicating that the material properties of the gel are reversible. Heterogeneity of the gel during the phase change is quantified by comparing particle trajectories using an F-test with a 95% confidence interval to determine if movement of individual particles is statistically different. The phase change exhibits rheological heterogeneous microenvironments that are homogeneously distributed throughout the field of view. The quantification of the gel-sol transition and equilibrium material properties using MPT quantifies how HCO gels will behave in consumer goods, and allows for more bio-based products to be developed.

Wednesday 6:05 Atrium/Harborview

PO47

### **Aging and jamming behavior in model soft colloidal system**

Qi Li, Xiaoguang Peng, and Gregory B. McKenna

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Aging behaviors and structural recovery for the PS-PNIPAM/AA colloidal system are investigated in our experiments by using diffusing wave spectroscopy (DWS). The experimental sample for this research is a core-shell PS-PNIPAM/AA thermosensitive dispersion, with a degree of polydispersity of 25%, determined by dynamic light scattering (Nanotrack 250), to prevent the sample from crystallization. The sample is from the same batch as previous works from our group [1-3]. The sample concentrations range from 13.2 wt% to 16 wt%. A complete temperature dependence and a concentration dependence of the  $\alpha$ -relaxation dynamics for our colloidal system is obtained. Jamming behaviors were discovered at lower temperatures for different mass concentration samples. The classic Vogel-Fulcher-Tammann (VFT) model of glass forming system is applied. The results deviate drastically from the classic model and the super-Arrhenius signature disappears below the glass transition temperature. A further comparison of the microscopic rheology and macroscopic rheology was made in our research.

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Wednesday 6:05 Atrium/Harborview

PO48

### **Drop formation of carbon nanotube suspensions for inkjet printing**

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Inkjet printing is capable of depositing a wide range of materials, such as metallic and carbon particles, polymers, and ceramics, to fabricate flexible electronics and 3-D objects. Inkjet printing is typically characterized by high shear rate ( $> 10^4 \text{ s}^{-1}$ ), short residence time (5 - 250  $\mu\text{s}$ ), and high actuation frequencies ( $\sim 20 \text{ kHz}$ ) that are orders of magnitude larger than what is accessible using conventional rheometers ( $\sim 15 \text{ Hz}$ ). In this poster, we will present the development of a stroboscopic imaging platform coupled with a custom-built print chamber, where acoustic waves of arbitrary waveforms can be applied to drive an ink fluid out of a nozzle. We have combined the imaging platform with digital imaging to investigate the drop formation of fluids containing carbon nanotubes (CNTs) - rolled graphene cylinders with a diameter of ca. 150 nm and an aspect ratio exceeding 40. Of particular interest is how the inclusion of CNTs with different states of aggregation affects the classical Plateau-Rayleigh instability, which further influences the jet breakup and CNT drop size distribution. The findings may have broader impact on understanding the reliability and resolution of inkjet printing high-aspect ratio particles like CNTs.

Wednesday 6:05 Atrium/Harborview

PO49

**Polymer coating over solid particles with in-situ curing: Experiments and computational insights**Shimiao Zhang<sup>1</sup>, Lai Chi Lily So<sup>2</sup>, Santiago Faucher<sup>2</sup>, and Li Xi<sup>1</sup><sup>1</sup>Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada; <sup>2</sup>Hatch Ltd, Mississauga, Ontario L5K 2R7, Canada

In hydraulic fracturing or "fracking" operations, solid particles are often injected with the fracking fluid. These particles, or proppants, will prop up the induced cracks in the rock formations to ensure the continuous flow of oil or gas from the reservoir. Proppants tend to degrade over time in the high-pressure and high-acidity environment under the well. In this study, resin (polymer) coatings are developed to improve the proppant stability. In the coating process, the resin is melted and mixed with the proppant particles while a crosslinking agent is added to induce its curing in situ. For optimal coating outcome, operating parameters must be carefully chosen to achieve the desired balance between the fluid mechanics of polymer melts and crosslinking kinetics. Experiments are carried out to systematically study the effects of different coating conditions and characterize the coating quality. Molecular dynamics simulation is used to provide further insights into the formation kinetics of polymer networks and their structure-property relationship. Improvements made in this study can benefit the process development of polymer coating on granular materials in general.

Wednesday 6:05 Atrium/Harborview

PO50

**Rheology and microstructure of thermoreversible gels composed of adhesive hard silica rods**

Ryan P. Murphy and Norman J. Wagner

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Colloidal suspensions containing anisotropic particles such as proteins, clays, carbon nanotubes, graphene, cellulose nanocrystals, and other inorganic mineral crystals are widely used in various particle-based technologies including pharmaceuticals, consumer products, composite materials, coatings, and paints. Particle shape is known to significantly influence the thermodynamic and rheological properties of colloidal suspensions, for example, by affecting the maximum packing fraction, liquid crystal phases, orientation under external fields, shear thinning and thickening, and elasticity at low volume fractions. Despite the growing interest in anisotropic particle suspensions, a comprehensive understanding of how particle shape affects dynamic arrest transitions is lacking. Thus, a new model system was developed with control of both particle shape and interaction strength to quantify these effects on gelation and glass formation. The model system of adhesive hard rods (AHR) consists of octadecyl-coated silica rods having short-range, thermoreversible interactions. This tunable model system will enable mapping of a fundamental state diagram for anisotropic particle suspensions as a function of particle shape, volume fraction, and relative interaction strength. Rheological measurements of AHR gels showed a thermoreversible transition from a fluid to gelled state. Furthermore, the gel-transition temperature was found to increase and broaden with increasing aspect ratio. Neutron and x-ray scattering were used to probe the gel microstructure as a function of temperature, finding distinct differences above and below the rheologically-determined transition temperature. Ongoing work to further quantify the effect of particle shape and interaction strength on gel and glass formation will provide both fundamental and practical insight into particle technologies and manufacturing processes that employ anisotropic particles suspensions.

Wednesday 6:05 Atrium/Harborview

PO51

**Rheology of meniscus-bound particulate suspensions**

Junyi Yang and Sachin S. Velankar

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Previous studies show that addition of small amounts of wetting fluid can drastically change the rheology of a particulate suspension. We conduct a fundamental morphological and rheological study of this phenomenon using particle-filled polymer blends. The advantage of such blends over small-molecule systems is that since polymers blends can be quenched by cooling, particle-scale morphological studies can be conducted by scanning electron microscopy.

Experiments are restricted to a composition regime where the polymer that preferentially-wets the particles is more dilute than the particles themselves. Morphological studies show that wetting fluid binds the particles into large aggregates. Rheological studies under molten conditions show that the blends containing the wetting fluid possess a yield stress (whereas the original suspension without wetting fluid did not) The yield stress depends on composition of the particles as well as the wetting fluid. At stresses far exceeding the yield stress, the blends flow with a viscosity that depends on particle volume fraction, but is insensitive to the wetting fluid fraction. The yield strain, measured by by oscillatory rheometry and creep-recovery, are in the range of 0.1 to 1%.

Wednesday 6:05 Atrium/Harborview

PO52

**Effects of confinement on the mechanical properties of hydrophobically-modified hydrogels**

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Hydrogels formed by hydrophobic physical crosslinks have high mechanical strength (>100kPa).<sup>1</sup> Surfactants, such as sodium dodecyl sulfate (SDS), can be used to control the mechanical strength and modulus of these hydrogels. Here we describe the change in the viscoelastic behavior of physically crosslinked copolymer hydrogels synthesized from N,N-dimethylacrylamide (DMA) and 2-(N-ethylperfluoro-octane sulfonamido) ethyl methacrylate (FOSM) by the addition of a SDS solution. Without confinement, SDS dissociates the FOSM micelle-like microstructure and facilitates swelling, which decreases the crosslink density of the hydrogel and reduces the modulus and strength of the hydrogel. With 1-

dimensional macroscopic confinement, similar behavior was observed, but only for soaking times in the salt solution  $< \sim 15$  h. For longer times ( $> 15$  h), SDS improved the mechanical strength and modulus of the hydrogel presumably by reducing the imperfections in the hydrogel network and forming complexes with FOSM.

1. Hao, J.; Weiss, R. A. Mechanical Behavior of Hybrid Hydrogels Composed of a Physical and a Chemical Network. *Polymer* **2013**, *54*, 2174-2182.

Wednesday 6:05 Atrium/Harborview

PO53

### **Transient chaos and molecule formation in chains of paramagnetic particles under rotating fields**

Hamed Abdi, Rasam Soheilian, Randall Erb, and Craig E. Maloney

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We study a numerical model of small clusters of micron-sized super-paramagnetic particles subjected to a 2D rotating magnetic field and compare this with recent experimental results. As expected, low rotation rates allow short stable chains to track the orientation of the field, while intermediate rotation rates cause the chains to break up as the hydrodynamic forces become too strong to allow the chain to track the field. At the highest rates, the magneto-static forces become essentially isotropic, and the short chains collapse into planar, close-packed clusters. These three regimes are found in both our numeric and experimental studies. Here we present new evidence for a regime of transient chaos at intermediate rates. In the chaotic regime, we measure the largest Lyapunov exponent and the transition rate for escape into a periodic orbit. Specifically, for chains of four particles, we find that the transition time is long - on the order of several hours for field precession rates on the order of 1Hz. The structures formed in the stable periodic orbits consist of either compact, planar, close-packed clusters or molecules consisting of a central particle with three particles orbiting. Once entered, the periodic orbits - either close-packed clusters or colloidal molecules - are stable indefinitely, and we have checked this for millions of field precessions. We also discuss the impact of the form of the inter-particle potential and the hydrodynamic interactions on the transient chaos regime, the transition times, and the stability of the periodic orbits.

Wednesday 6:05 Atrium/Harborview

PO54

### **Velocimetry using magnetic particles**

Carlton F. Brooks<sup>1</sup>, Martin B. Nemer<sup>1</sup>, Emily K. Stirrup<sup>1</sup>, Oksana Guba<sup>2</sup>, Bart G. van Bloemen Waanders<sup>2</sup>, Harriet Li<sup>2</sup>, Joseph Buttacci<sup>1</sup>, and Christine C. Roberts<sup>1</sup>

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Tracking the motion of fluids inside opaque containers with complex geometry is challenging, with most methods requiring expensive non-invasive methods (e.g. X-rays or MRI) which may not be able to resolve phenomena on the timescale of the flow being investigated. Here we present some foundational experimental and numerical results demonstrating our capability to track the motion of magnetic particles by sensing the time varying magnetic field emitted outside the container. Commercially-fabricated 3-axis magnetic sensor components were assembled on custom circuit boards and used as elements of a reconfigurable sensor array. We subjected a magnetic sphere to simplified motions, such as translation, rotation, and rigid-body rotations and verified our inversion-scheme's ability to locate the particle. We also examined the effects of various container materials on screening the magnetic field and how this screening affects the accuracy in locating the particle. As a test case of a particle moving in a fluid, we dropped a magnetic sphere in a viscous fluid inside a cylinder. Using the response from the magnetic field we determined the position and orientation of the particle and were able to measure the viscosity of the fluid.

Wednesday 6:05 Atrium/Harborview

PO55

### **Development of liquid metal suspensions with tunable viscosity and magnetic susceptibility for magnetohydrodynamics**

Florian Carle<sup>1</sup>, Kunlun Bai<sup>1</sup>, Joshua Casara<sup>2</sup>, Kyle Vanderlick<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>University of California-Merced, Merced, CA, United States

A new magnetic liquid metal has been developed with both high conductivity and magnetic susceptibility for magnetohydrodynamics applications. Iron and Zinc particles (from 30nm to 600  $\mu\text{m}$ ) were suspended in liquid gallium and two of its alloys. Hydrochloric acid solution is used to control the oxidation by cleaning the oxidation layer off the eGaIn and the metallic particles ensuring wetting and a stable suspension. A key feature of these suspensions is the ability to tune their properties. By suspending different packing fractions of iron (magnetic) and zinc (non-magnetic) particles, the viscosity can be increased by two orders of magnitude and independently the magnetic susceptibility can be increased by  $10^5$  compared to pure Gallium. The enhanced properties of the fluid make it practical to study magnetohydrodynamics on a laboratory scale.

Wednesday 6:05 Atrium/Harborview

PO56

### **A parsimonious hydrodynamic model for colloidal gelation**

Zsigmond Varga and James W. Swan

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

Colloidal gels are formed during arrested phase separation. Models for microstructural evolution during colloidal gelation have often struggled to match experimental results with long standing questions regarding the role hydrodynamic interactions. We hypothesize that long-ranged

hydrodynamic interactions between the suspended particles are key for colloidal gelation. A simplified hydrodynamic model will be discussed that tests this hypothesis by including only long-ranged interactions via the Rotne-Prager-Yamakawa tensor (RPY). We show simulations of gelation with and without hydrodynamic interactions between the suspended particles executed in HOOMD-blue. The disparities between these simulations are striking and mirror the experimental-theoretical mismatch in the literature. The hydrodynamic simulations agree with experimental observations, both for diffusion-limited and reaction-limited cluster aggregation. These results confirm that long-ranged hydrodynamic interactions are sufficient for establishing the gel boundary, structure and coarsening kinetics observed in experiments and more sophisticated simulation methods. A simple macroscopic model of coagulation and compaction of particulate aggregates is used to explain these disparities - why Brownian Dynamics simulations fail to produce gels consistent with experimental evidence while Stokesian Dynamics, and RPY simulations reflect experimentally observed structure and kinetics with much greater fidelity. Near the gel boundary, there exists a competition between compaction of individual aggregates which suppresses gelation and coagulation of aggregates which enhances it. The time scale for compaction is mildly slowed by hydrodynamic interactions, while the time scale for coagulation is greatly accelerated. This enhancement to coagulation leads to a shift in the gel boundary to lower strengths of attraction and lower particle concentrations when compared to models that neglect hydrodynamic interactions.

Wednesday 6:05 Atrium/Harborview

PO57

### **A study of the rheological characteristics of magnetorheological (MR) fluids and the influence of periodic magnetic fields**

Alina K. Latshaw

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Magnetorheological (MR) fluids are intelligent materials capable of reversibly transitioning from a liquid to a solid-like material in the presence of an external magnetic field. Conventional MR fluids are comprised of micron-sized, highly magnetizable particles dispersed in a carrier fluid. In the absence of magnetic fields, MR fluids exhibit thixotropic behavior akin to colloidal suspensions. When subjected to an external magnetic field, the particles magnetize and attract one another, forming flocculated aggregates or networks along the field flow within milliseconds. The formation of this anisotropic structure provides a means to tailor fluid characteristics such as yield stress and viscosity by controlling the strength of the magnetic field, resulting in a material capable of reacting and adapting to various external stimuli. Applications for these materials include shock absorbers, dampers, control valves, and artificial joints. A significant amount of research has focused on shear properties of these fluids as a function of magnetic strength under a constant magnetic field. However, the application of periodic field profiles permits fundamental and applied investigations of hysteresis between the magnetic field and rheological properties. In this poster, we will introduce TA Instrument's new magneto rheology accessory and showcase its unique capabilities by applying custom magnetic fields under simultaneous rheological measurements. We will also analyze the influence of periodic magnetic fields on the viscoelastic properties of commercially available MR fluids, focusing specifically on the time-dependent behavior due to colloidal interactions and magnetization of the particles.

Wednesday 6:05 Atrium/Harborview

PO58

### **Gel point determination thanks to microrheology**

Jonathan Denis

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This work presents a new technique of passive microrheology for the study of the microstructure viscoelastic properties and the gel point transition for polymers and hydrogels. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from the thermal energy, that is to say the Brownian motion. Our technique is based on Diffusing Wave Spectroscopy. It consists of Dynamic Light Scattering (DLS) extended to an opaque media. In a DWS experiment (more precisely Multi Speckle-DWS in our case), a coherent laser beam is applied to the sample containing scatterers (particles, droplets, fibers...). The light is multi-scattered by these scatterers, which leads to interfering backscattering waves. An interference image is detected by a multi-pixel detector. In dynamic mode, the scatterers motion (resulting from thermal energy) induces spot movements of the speckle image. A patented algorithm enables the treatment of this speckle image in order to determine the scatterers mobility in terms of speed and displacement which are directly related to the samples viscoelastic properties. The determination of the Mean Square Displacement (MSD) curve enables to characterize completely the viscoelastic properties of a sample. The technique allows to measure particles displacement in a spatial range between 0,1 and 100 nm and a time scale between 10<sup>-3</sup> and 10<sup>5</sup> seconds. This work presents a rescaling data processing known in rheology as time cure superposition [1], [2] to determine the gel point transition and gel strength parameters. Results will show the automatic determination of the gel point versus time for gelling systems, gel point versus concentration for xanthan polymer, cross-linker concentration effect on the gel point.

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

Wednesday 6:05 Atrium/Harborview

PO59

### **The glass transition, cyclic fatigue fracture, and the mechanics of polygonal development in cooling basalt**

Michael P. Ryan

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Inter-crystalline glass is a ubiquitous component in basalt, the common volcanic rock type of Earth's ocean basins and oceanic islands. In Hawaii, eruption temperatures are in the 1190 - 1150 °C range and the solidus is reached at about 1000 - 980 °C. Inter-crystalline super cooled melt reaches the glass transition, T<sub>g</sub>, at 750 °C, and subsequent cooling occurs in a high temperature mix of crystals and glass: a rheological, 'sand-and-molasses'

mixture. Strong temperature gradients and 'zero-displacement' lateral boundary conditions conspire to set up thermal stresses in the cooling mass. The result is stress relief via elastic-plastic crack growth that is incremental and cyclic in time and space. This cyclic fatigue fracture is defined by abrupt elastic crack growth in the crystal + glass domain, and plastic crack tip blunting in the crystal + super cooled melt domain. The crack growth increment is preserved on the crack face as a fatigue striation. As the crack lengthens and advances orthogonal to the basalt isotherms, it (and neighboring cracks) define polygonal columns in three dimensions. Under conditions of maximum local equilibrium, such polygons are hexagonal in plan form with faces meeting at 120 degree triple junctions. In forming the polygons, Nature strikes an optimal balance between the maximum reduction in the thermally-induced elastic strain energy per unit volume and the creation of the minimum fracture surface area (atomic bond breaking and work of fracture term) per unit volume. This balance occurs via cyclic fatigue fracture at the elastic-plastic interface.

Wednesday 6:05 Atrium/Harborview

PO60

### **Time-dependent development of viscoelastic heterogeneity during gelation of gelatin gel**

Weixiang Sun, Wei Hong, and Zhen Tong

*Research Institute of Materials Science, South China University of Technology, Guangzhou, China*

The time-dependent gelation process of gelatin gels at constant temperature was monitored by particle tracking microrheology. Probe particles were added to the samples and their thermal motions were tracked by a video camera. Besides the ensemble-averaged mean square displacement (MSD), the van Hove function, the non-Gaussian parameters and the 4-point susceptibility were also calculated from the raw trajectory of the probe particles. Both the size of the most typical regions of viscoelasticity and the corresponding relaxation time grew with time during gelation. The growth curves were compared with those of the static structural parameters such as the density of crosslinking as well as macroscopic rheological results such as the plateau moduli. Unlike the cases of colloidal gels and glasses whose smallest structural unit of the dynamics was a single particle ( $\sim O(1)$  micron), the gelatin gels has the smallest structural unit of a single chain segment ( $\sim O(1)$  nm). In other words, the observed dynamical heterogeneity in gelatin gel was much larger in length scale than those observed in colloidal gels and glasses.

Wednesday 6:05 Atrium/Harborview

PO61

### **Determination of wax crystallization/gelation temperature by rheometry, DSC and CPM**

Felipe Paiva and Verônica Calado

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During an oilfield operation, startup of a gelled pipeline may be necessary. Gelation occurs because, during cooling of a waxy crude oil, wax starts to crystallize. While the flow properties are relatively simple above the oil's gelation temperature, in the sense that it behaves as a Newtonian fluid, they change to a very complex non-Newtonian behavior upon cooling below this temperature. There is a lack of precision in the measurement of this property with respect to the technique that is used. For example, while Rheometry detects the temperature at which the oil gels, Cross Polar Microscopy (CPM) yields higher temperature values and is able to detect the appearance of the first wax crystals, or the Wax Appearance Temperature (WAT) [1]. Therefore, it is believed that there needs to be a sufficient amount of crystallized wax in a sample for rheometric effects to be distinguished [1-3]. There is also evidence that small gap sizes and commonly used geometries, such as the cone and plate, induce paraffins to crystallize earlier [3]. In this work, the thermal-cycle test used by Marchesini et al (2012) [3] is used for evaluating the effect of rheometer gap size and cooling rate on the gelation temperature of two Brazilian crude oil samples. Furthermore, the results from Rheometry are compared to those obtained by Differential Scanning Calorimetry (DSC) and CPM in order to shed light onto the sensitivity of WAT measurement techniques.

References: [1] Roenningsen, H.P.; Bjoerndal, B.; et al. Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. *Energy & Fuels*, v. 5, n. 6, p. 895-908, 1991. [2] Venkatesan, R.; Singh, P.; et al. Delineating the Pour Point and Gelation Temperature of Waxy Crude Oils. *SPE Journal*, v. 7, n. 4, p. 349-352, 2002. [3] Marchesini, F.H.; Aliche, A.A.; et al. Rheological characterization of waxy crude oils: Sample preparation. *Energy and Fuels*, v. 26, n. 5, p. 2566-2577, 2012.

Wednesday 6:05 Atrium/Harborview

PO62

### **Strong shear thinning with a fast response in a visco-plastic suspension of long and single-walled carbon nanotubes**

Shunsuke Sakurai<sup>1</sup>, Kamada Fuminori<sup>2</sup>, Don N. Futaba<sup>1</sup>, and Kenji Hata<sup>1</sup>

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Owing to their remarkable properties such as high electrical conductivity, mechanical flexibility, and surface area, single-walled carbon nanotube (SWCNT) films with micrometer thicknesses has shown great potential for use in a variety of applications, such as electrodes of Li-ion battery or supercapacitor, actuators, and filters. Therefore, the development of the coating process for SWCNT film with micrometer thickness using concentrated SWCNT suspension is desirable. However, due to the several problems in concentrated suspension such as sedimentation and flow-induced aggregation, the coating process of SWCNT has been usually applied only to the very thin film.

In this work, we have developed the high concentration (1 wt%) and high viscous suspension of SWCNT (SWCNT paste), by sonication of SWCNT with a high aspect ratio (diameter: 3 nm, length: c.a. 0.1-1 mm) under extremely vigorous stirring. In SWNT paste, SWNTs are suspended to form agglomerates consisting of three-dimensional networks. Several unique fluidic behaviors are found in SWCNT paste, such as plastic deformation, strong shear-thinning (viscosity under shear four orders of magnitude less than at rest), and fast (< 0.1 sec) recovery of viscosity after the release of shear. Consequently, fabrication of thick (> 10  $\mu$ m), uniform (Ra/t < 10%), and large-area (>A4 size) SWNT film has been easily achieved by conventional coating technique using SWCNT paste.

This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Wednesday 6:05 Atrium/Harborview

PO63

### **Particle-particle interaction and shear rheology relationships in strongly flocculated particulate suspensions**

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The shear rheology of strongly flocculated suspensions is important for industrial applications. Above a critical solid concentration, known as the gel point, the suspensions can withstand an applied force before yield, but show a solid-like behaviour at concentrations below the gel point. Understanding suspension rheology requires assimilation of the bulk rheology to the inter-particle interactions. Many attempts have been made to correlate the two aspects, but the current understanding of micro-macro relationship still have not been able to explain several flow phenomena, such as non-linear elasticity, time- and rate-dependent yield.

Rheological experiments were conducted using a controlled-stress rheometer with a vane technique. The results showed rate-dependent yield and non-linear viscoelasticity followed by time-dependent yield. The behaviour have not been fully understood and is crucial for the existing constitutive models development since neither visco-plastic models like Bingham or Herschel-Bulkley, nor linear viscoelastic models, such as Standard Linear Solid, can represent the behaviour. The importance of sub-yield elasticity model prediction for industrial processes, such as start-up, pipeline flow and slumping, motivates the micro-macro relationship study.

The microscopic scale study focuses on the friction force between two spherical micrometer-sized particles using Atomic Force Microscope (AFM). A probe particle on the cantilever is pushed against a scanned particle on a surface to obtain the topography and measure the cantilever deflection. With a given calibration constant, the lateral cantilever deflection is converted to a friction force to obtain the friction coefficient.

The AFM results are correlated to the shear rheology. The main goal is to investigate the effects of friction force on the bulk rheology of concentrated suspensions. This work extends our fundamental understanding of the inter-particle forces and shear rheology relationship of particulate suspensions.

Wednesday 6:05 Atrium/Harborview

PO64

### **Study the rheological behavior and microstructure of bimodal highly filled PE/CaCO<sub>3</sub> composites**

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Compounds of Low Linear Polyethylene (LLDPE) contacting various loadings of natural CaCO<sub>3</sub> particles, of several particle size distributions (nano and micro), were studied using dynamic mechanical parallel plate rheometer and scanning electron microscopy (SEM). In addition to highly filled suspensions indicate unique properties, different behaviors will be visible when the two different particle size have used in a competition. In this study, various parameters have evaluated such as particle size, particle composition, mixing ratio in bimodal suspension and other process parameters like the use of lubricant in the highly filled component by using different rheological behaviors such as complex modulus, creep, wall slip and the effect of these were studied on aggregate defeat in the composition and better particle distribution. All these steps were performed to find an optimum of a percent particles in concentration bimodal suspensions that its viscosity is minimum and the best dispersion of particles.

Wednesday 6:05 Atrium/Harborview

PO65

### **Explaining interfacial behavior of a particle laden interface using microstructure analysis**

Sourav Barman and Gordon F. Christopher

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Pickering emulsion, a particle stabilized emulsion, can be found in the wide range of product and applications in industry. The bulk rheological behavior of Pickering emulsion depends significantly upon the interfacial viscoelasticity of the particle laden interface. To characterize the rheology of these systems a double wall ring interfacial geometry on a rotational rheometer has been utilized. Furthermore, this tool has been to allow simultaneous visualization of interfacial microstructure. Using this setup, we have been able to correlate rheology to microstructure and interparticle forces, in order to determine the fundamental mechanisms that drive particle laden interface rheology. In particular, we have examined the role of surface coverage, bulk salt concentration, and ionic and non-ionic surfactants on the linear viscoelastic behavior of these systems. In response to steady shear deformation, a transition from shear thinning due to aggregated cluster breakup to yielding at a slip plane within the interface have been identified. Furthermore, the role of capillarity on interfacial viscoelastic moduli magnitude and trends has been examined by modifying the relative strength of electrostatic and capillary forces through salt and surfactants. Viscoelastic moduli magnitude appear to be dictated by local caging and capillary force strength, whereas rheological trends are dictated by longer range microstructure deformation. We present conclusions from work conducted over the last 4 years on the properties of particle laden interfaces and hypothesize on future work.

Wednesday 6:05 Atrium/Harborview

PO66

**Particle-modified structured emulsion droplets**Tamás A. Prileszky and Eric M. Furst*Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States*

Emulsions are ubiquitous in consumer products, industry, and science, found wherever two immiscible fluids must be mixed. While exceedingly common, emulsions are almost universally limited by the spherical shape of the underlying droplets, which minimizes contact area between phases. Considering that the efficacy of most emulsions is contingent on fast mass transfer between phases, shape-limited surface area significantly degrades total mass flux between phases.

Enhancing the efficacy of emulsions, then, is an exercise in surface-area augmentation, which can be accomplished through either droplet size reduction or shape change. Achieving the latter case requires that elasticity be introduced to emulsion droplets. Endoskeletal droplets—a class of structured emulsion—are emulsions incorporating a soft crystalline network into the dispersed-phase droplets, allowing anisotropic shape retention while maintaining a free fluid interface. In addition, the low melting temperature of the internal network allows modest temperature increases to eliminate the yield stress, which makes endoskeletal droplets capable of losing their shape as a result of external stimuli.

The existence of a free fluid interface in endoskeletal droplets permits particles to be incorporated into either the interface or internal network. Both endoskeletal droplets and particle-modified emulsions have rich behavior sets that extend the applications of standard emulsions. By combining the benefits of particles and endoskeletal droplets, their impacts are intensified: response to external stimuli becomes easier to control, interactions between droplets can be tuned, and particles can be assembled at the interface based on local curvature.

Wednesday 6:05 Atrium/Harborview

PO67

**Rheology of multi-component systems of oil-in-water emulsions with associative polymers**Barbara V. Farias and Saad A. Khan*Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

Creams and lotions based on oil-in-water emulsions are commonly used to prevent or treat dry skin disorders. However, the accumulation of traditional surfactants in the skin can promote the washout of skin lipids in cleansing. An alternative for traditional surfactants is the use of hydrogenated phosphatidylcholine (HPC), a class of phospholipids that is an essential building block of all natural cells. This phospholipid is capable of forming a lipid lamellar structure similar to the permeability barrier of the skin, and since it is hygroscopic it drags water with it when permeating the epidermis. This increases hydration and enhances the performance of skincare products. Flow properties are among the most valuable physical attributes of cosmetic products. Since rheology has the ability of measuring, adjusting and predicting these properties, it is a useful tool in the study of emulsion-based skin care systems. In this study we will investigate the effect of composition of these complex systems containing oil-in-water emulsion with phospholipid and a polymer thickener. In particular, we will examine how adding different amounts of a polymer, HPC and emollients (oil phase) affects the rheological behavior. The role of associative versus non-associative polymers as well as different types of emollients will be examined. Results obtained on apparent viscosity, moduli and sol-gel transition as a function of composition, and structural breakdown/recovery as a function of shear will be used to obtain a rheological understanding of these complex systems in terms of their microstructures.

Wednesday 6:05 Atrium/Harborview

PO68

**Effect of polymer confinement on the film drainage behaviour between a deformable droplet and mica – an RICM study**Suraj Borkar and Arun Ramachandran*Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada*

We consider the dynamic effects of confinement of macromolecular liquids, such as polymers, on the film drainage process between a drop and a flat surface. Under confinement of the order of a few molecular length scales, layering and adsorption of long chains of polymers can cause entropic repulsion due to a reduced configurational freedom. This repulsive force can prevent film rupture and instead may result in the formation of an equilibrium film. In the current work, experiments were conducted with deformable droplets settling under gravity in a suspending liquid for Bond numbers of  $O(10^{-4})$ . The film drainage was studied using a microinterferometric technique namely, Reflection Interference Contrast Microscopy (RICM), for two different systems : a) silicone oil drops in paraffin oil, b) glycerol drops in silicone oil. The RICM analysis for obtaining the film drainage profiles, was carried out using a combination of simple cosine theory and ray tracing algorithm. For the silicone oil-paraffin oil system, the film drainage behavior observed was as expected from simulations based on thin film drainage equations. On the other hand, glycerol drops of radii smaller than  $130\ \mu\text{m}$ , resulted in the formation of an equilibrium film of silicone oil with an approximate thickness of  $10\ \text{nm}$ . The origin of this repulsive force is attributed to the presence of an immobilized layer of adsorbed polymer chains. Film drainage observed in glycerol drops of radii larger than  $130\ \mu\text{m}$ , was found to destabilize in a non-axisymmetric mode. The rapid growth of this asymmetric instability can lead to much higher stresses ( $O(100\ \text{Pa})$ ), overcoming the yield stress of the adsorbed polymer layer. The equilibrium film thickness for smaller drops, was found to increase with increasing molecular weights of silicone oil, suggesting that the repulsive force is also a function of the radius of gyration of the suspending medium.

Wednesday 6:05 Atrium/Harborview

PO69

**Dry-brushes entropic attraction affecting the coalescence rate of viscous polymeric drops stabilized by block-copolymer surfactants**Carolina Vannozzi*Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA, United States*

The effect of the interfacial diffusivity of block-copolymers (BCs) on the binary flow-induced coalescence of polymeric drops was investigated via boundary integral simulations in our previous study [1], by assuming Stokes flow and that the BCs act as insoluble surfactants. However, we needed to introduce an additional attractive force to match the simulations with the experimental drainage times, measured in a computer controlled four-roll mill by Leal and co-workers [2]. This led us to speculate that the entropic attraction between the facing drop interfaces, having the BCs in a dry-brush regime, was the main cause of this enhanced attractive force [1].

To test this hypothesis, here, we present simulation results of the effect on coalescence of this entropic attractive force. The force was previously calculated via self-consistent mean field theory as a function of the distance between the drop interfaces and incorporated as a disjoining pressure in the boundary integral code.

[1] Vannozzi C "Coalescence of surfactant covered drops in extensional flows-Effects of the interfacial diffusivity" Phys. Fluids, 2012. [2] Yoon Y, Hsu A, Leal L. G. "Experimental investigation of the effects of copolymer surfactants on flow-induced coalescence of drops" Phys. Fluids 2007.

Wednesday 6:05 Atrium/Harborview

PO70

**Rheology, diffusion, and velocity correlations in the bubble model**Arka P. Roy<sup>1</sup>, Kamran Karimi<sup>2</sup>, and Craig E. Maloney<sup>3</sup>*<sup>1</sup>Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States; <sup>2</sup>University Joseph Fourier, Grenoble, France; <sup>3</sup>Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States*

We present results on spatio-temporal correlations in the so-called mean drag version of the Durian bubble model in the limit of small, but finite, shearing rates,  $\dot{\gamma}$ . We study the rheology, diffusion, and spatial correlations of the instantaneous velocity field. The quasi-static (QS) effective diffusion coefficient,  $D_e$ , shows an anomalous system size dependence indicative of organization of plastic slip into lines along the directions of maximum shearing. At higher rates,  $D_e$  decays like  $\dot{\gamma}^{-1/3}$ . The instantaneous velocity fields have a spatial structure which is consistent with a set of spatially uncorrelated Eshelby transformations. The correlations are cut off beyond a length,  $\lambda_c \sim \dot{\gamma}^{-1/3}$  which explains the  $D_e \sim \dot{\gamma}^{-1/3}$  behavior. The shear stress,  $s$ , follows a similar rate dependence with  $ds = s - s_y \sim \dot{\gamma}^{-1/3}$  where  $s_y$  is the yield stress observed in the QS regime. These results indicate that the form for the viscous dissipation can have a profound impact on the rheology, diffusion and spatial correlations in sheared soft glassy systems.

Wednesday 6:05 Atrium/Harborview

PO71

**Rheological characterization of pickering emulsions with a non-Newtonian dispersed phase**Purba Chatterjee, Greg Sowiak, Tyler Gruttadauria, and Patrick T. Underhill*Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

Particle-stabilized emulsions or Pickering-Ramsden Emulsions are commonly encountered in nature and many industries including the crude-oil industry where clay particles stabilize crude-oil waxes, in the food industry where biopolymers stabilize lipids and oils and in pharmaceuticals as topical and oral drug formulations. While the most common type of Pickering Emulsion studied has a Newtonian dispersed phase, our interest is in emulsions with a dispersed phase that can be non-Newtonian and in understanding how this can alter the bulk properties of the emulsion. In this poster, we will discuss our experimental observations with silica-stabilized paraffin wax-in-water emulsions. The wax can be subjected to a phase change, allowing us to use temperature to control the properties of the dispersed phase and hence the emulsion. At lower temperatures, the deformability of the droplets and mobility of particles at the interface are significantly restricted. Our preliminary results show that these features, modulated by temperature, affect the bulk emulsion viscosity, state of flocculation of emulsion droplets, shear stability and viscoelasticity. 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.

Wednesday 6:05 Atrium/Harborview

PO72

**Linking the physical properties of foams generated from consumer products to in-use experience**Jerome J. Nash<sup>1</sup> and Jeffrey D. Martin<sup>2</sup>*<sup>1</sup>Materials Engineering, Purdue University, West Lafayette, IN 47906, United States; <sup>2</sup>Johnson & Johnson Consumer, Inc., Skillman, NJ 08855, United States*

The physical properties of foams generated during use of consumer cleansing products play a significant role in the way consumers experience such foams. Characterization of the structural and mechanical properties of foams via dynamic foam analysis and rheometry provides a broader understanding of the physical behavior of foams during use. If correlations exist between these physical properties and consumer impressions, these correlations could be used to develop a predictive consumer-technical model for cleansing foams.

Characterization methods were validated using two commercial products as model systems: NEUTROGENA® Rainbath® Body Wash and GILLETTE® Shaving Foam. The validated methods were then used to characterize several proprietary Johnson & Johnson body wash chassis formulations containing various conditioning and structuring polymers. An "interested scientist" study was then conducted to determine if any correlations exist between the physical properties of the foams and the consumer experience during use.

Possible correlations were seen between several physical characteristics of the prototype product foams and their in-use feel and behavior. These correlations can be used to develop a consumer-technical model linking the consumer experience of cleansing foams to their physical properties.

Wednesday 6:05 Atrium/Harborview

PO73

### **Capsule motion in a microfluidic cross-junction**

Pompon M. Udipabu and Panagiotis Dimitrakopoulos

*Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111, United States*

In this work we investigate the motion of an elastic capsule flowing along a microfluidic cross-junction device. We consider an initially spherical capsule with an elastic membrane obeying the strain-hardening Skalak law and investigate the effects of viscosity ratio, capsule size and lateral flows on the motion of capsule in the microfluidic cross-junction. Our work shows that the intersecting vertical flows at the cross-junction behave like a constriction region and thus result in a rich deformation behavior and dynamics for the capsule. In the talk we will discuss the effects of the capsule size, viscosity ratio, and flow rates on the capsule elastic properties.

Wednesday 6:05 Atrium/Harborview

PO74

### **Dynamics of an elastic capsule in a microfluidic T-junction**

Abdollah Koolivand, Ikechukwu Okoro, and Panagiotis Dimitrakopoulos

*Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111, United States*

In this work we study computationally the transient and steady-state dynamics of an elastic capsule placed at the center of a T-junction microchannel. We consider hard-straining elastic capsules with size comparable to the cross-section of the microfluidic channels, and investigate the effects of flow rates, viscosity ratio and capsule size on the physical and geometric properties of the capsule. Our study shows that the asymmetric flow around the capsule in the microfluidic T-junction results in a non-trivial capsule dynamics both during transient times and at steady state.

Wednesday 6:05 Atrium/Harborview

PO75

### **Polypropylene foam pressure drop fundamentals**

Kurt A. Koppi

*Core R&D, The Dow Chemical Company, Midland, MI 48667, United States*

A technique for quantifying the viscosity of polypropylene-based foam formulations has been developed. The technique consists of measuring die pressure as a function of flow rate using a small-scale foam extrusion line equipped with a multi-hole die. The influence of various process and material parameters was investigated including flow rate, temperature, die geometry, foaming agent level, foaming agent type, and polymer blend composition.

Wednesday 6:05 Atrium/Harborview

PO76

### **Investigation of rheological properties of PA6/TPU nanocomposites by Palierne emulsion model**

Alireza Mojarrad<sup>1</sup> and Leila Mahdavi<sup>2</sup>

<sup>1</sup>Azad University of Shiraz, Tehran, Iran; <sup>2</sup>Sahand Petroplastic Company, Tehran, Iran

This paper deals with the dynamic rheological behavior of polyamide6/thermoplastic polyurethane (PA6/TPU) blends uncompatibilized blends and those compatibilized with a ethylene acrylate terpolymer. The rheological properties of the blends predicted by the Palierne emulsion model were compared with those obtained from experimental data. The Palierne model succeeded well in describing PA6/TPU compatibilized blends with relatively low dispersed phase contents. The model predicts the general viscoelastic behavior observed for emulsions including molten polymer blends: shoulder in  $G'$  at low frequency. The model predictions were found to be in good agreement with experimental linear viscoelastic data obtained on a PA6/TPU blends.

Wednesday 6:05 Atrium/Harborview

PO77

### **Role of the interfacial resin-asphaltene complex films in the stability of water-in-bitumen emulsions**

Rohini Gupta, Adam K. Schmitt, Matthew D. Reichert, Daniel S. Miller, Timothy J. Young, Tom H. Kalantar, and Tzu-Chi Kuo

*Dow Chemical Company, Midland, MI 48674, United States*

In this work, we investigate the effect of additives on the intervening film between adjacent droplets of a water-in-bitumen emulsion, where bitumen itself is a mixture of species, roughly classified as saturates, aromatics, resins, and asphaltenes. Such emulsions manifest as a result of high-shear mixing during hot water extraction in tar sand mining process. The oil/water interface is known to be stabilized by an interfacial resins-asphaltenes complex film. The goal is to obtain water-free bitumen by destabilizing the intervening liquid film. The modes of emulsion destabilization are: (a) coalescence of neighboring droplets due to drainage and instability of the intervening film and (b) chemical potential driven

coarsening (Ostwald ripening). We study the influence of chemical additives on the interfacial film and its rheological properties with the intent of observing these modes, and breaking the emulsion to extract water-free bitumen.

Wednesday 6:05 Atrium/Harborview

PO78

### **Kinetics of cyclopentane hydrate formation analysis through interfacial rheology**

Bruna C. Leopercio<sup>1</sup>, Paulo R. de Souza Mendes<sup>1</sup>, and Gerald G. Fuller<sup>2</sup>

<sup>1</sup>*Mechanical Engineering, Pontifícia Universidade Católica-RJ, Rio de Janeiro, RJ 22453-900, Brazil;* <sup>2</sup>*Department of Chemical Engineering, Stanford University, Stanford, CA, United States*

Hydrates are crystalline, ice-like structures that arise when water is brought into contact with lower molecular weight hydrocarbons on ideal conditions of pressure and temperature. These clathrate-class crystals are detrimental to the production and transportation of oils and gas since they solidify to form sludge networks that can clog piping systems. Thus, hydrates represent a major engineering problem in flow assurance. Motivated by the knowledge that the formation of hydrates is an interfacial phenomenon, this paper innovates by describing the use of interfacial shear rheology as a means of following the kinetics of hydrate formation. A new brass reservoir was developed so it could be accomplished. It is used together with a du Nouy ring as a means of dynamically probing the interface at small strains. Cyclopentane and water are used to form hydrates. The protocol consists on: first tracking the freezing of the surface of the air/water interface in the absence of a hydrocarbon. Once that occurs, cyclopentane is introduced on top of the water and the temperature is then raised above the freezing point of water. Different heat rates are evaluated. The interfacial shear moduli are then tracked as a function of time to reveal the growth of hydrates at the water/cyclopentane interface.

Wednesday 6:05 Atrium/Harborview

PO79

### **Rheo-optical study on reverse thread-like micelles of lecithin in organic solvents**

Tadashi Inoue and Momoko Furuta

*Osaka University, Toyonaka, Japan*

In reverse micellar systems, in which aggregates of hydrophilic groups of surfactants are formed in oils, formation of "thread-like" or "worm-like" micelles is very limited and in most cases additional key agents are required to stabilize the aggregates. Their viscoelastic properties are influenced by the stabilizer. In this study, we performed dynamic viscoelastic measurements on lecithin/citric acid reverse micelles. Our result shows that the complex modulus,  $G^*$ , looks like entangled polymer systems or single relaxation type, which is often observed for the ordinary thread-like micelles in aqueous solutions like CTAB/NaSal. However, dynamic birefringence measurements shows the breakdown of the stress-optical rule, which is valid for the ordinary thread-like micelles in aqueous solutions. Similar breakdown of the stress-optical rule is sometime observed for thread-like aggregates of supramolecules. We speculate that the lecithin system has anomalous relaxation modes at high frequencies, which is insensitive to birefringence. Such relaxation modes might be related with contraction of micelles originated by some structural change of aggregates due to softness of core.

Wednesday 6:05 Atrium/Harborview

PO80

### **Microrheological study of viscoelastic materials by magnetic tweezers**

Mingyang Tan and Travis W. Walker

*Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States*

The behavior of heterogeneous soft solids is complex, as they exhibit both viscous and elastic properties that depend on the length-scales of their microstructures. Bulk rheological measurements can provide advanced metrics, such as modulus; however, the measurements of these physical properties are averaged over length-scales on the order of millimeters or greater. For homogeneous materials, bulk rheology is usually sufficient; however, heterogeneous soft solids with microstructures on the micron length-scale can have significantly different rheological responses, depending on the length-scale of the probe. Microrheology applies an external driving force to move micro-particles to probe the physical properties of a material on a length-scale down to a micron and below. In this study, magnetic tweezers, which create a magnetic field to drive magnetic micro-particles, are used to investigate the rheological properties of viscoelastic materials by oscillating and pulling the micro-particles. We investigate the rheological properties of viscoelastic mucus by using micro-particles with different sizes and surface chemistries. We also investigate the alignment of magnetic microdisks in viscoelastic materials using rotating magnetic fields and compare the dynamics of the alignment to our previous work with Newtonian fluids.

Wednesday 6:05 Atrium/Harborview

PO81

### **Enhanced microfluidic mixing via a tricritical spiral vortex instability**

Simon J. Haward<sup>1</sup>, Kazumi Toda-Peters<sup>1</sup>, Robert J. Poole<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>*School of Engineering, University of Liverpool, Liverpool L69 3GH, United Kingdom*

We present the results of fluorescence confocal microscopy measurements made on Newtonian fluids and dilute polymer solutions flowing through cross-slot devices with small characteristic dimensions  $w \sim O(100 - 1000 \mu\text{m})$  and a range of aspect ratios,  $0.5 < a = d/w < 4$ , where  $w$  is the channel width and  $d$  is the channel depth. At small Reynolds numbers,  $Re$ , the flow is two-dimensional and a sharp symmetric boundary exists between fluid streams entering the cross-slot from opposite directions. Above an a dependent critical value  $Rec(a) \sim 20-100$ , the flow bifurcates to an asymmetric state (though remains steady and laminar), and a single three-dimensional spiral vortex structure develops around the central

axis of the outflow channel. Image analysis allows an assessment of the mixing quality between the two incoming fluid streams (one stream fluorescently-dyed with rhodamine b), which undergoes a significant increase following the onset of the instability. For  $Re > Rec$ , the mixing parameter grows according to a sixth-order Landau potential. Fitting parameters indicate the transition is second order at  $a = 0.5$ , and passes through a tricritical point, becoming first order for  $a > 1$ . A simple scaling of the fitting parameters with  $a$  allows full collapse of the experimental data. This instability can be used to drive enhanced mixing at the moderate  $Re$  that can be achieved in microfluidic devices and we show that further mixing enhancement can be achieved by patterning the surfaces of the channel walls. The effect of adding a small concentration ( $\sim 0.01$  wt%) of high molecular weight polymer is to reduce the value of  $Rec$  in comparison to the Newtonian solvent.

Wednesday 6:05 Atrium/Harborview

PO82

### Viscoelastic flow development in planar microchannels

Li Zhuo<sup>1</sup> and Simon J. Haward<sup>2</sup>

<sup>1</sup>Tongji University, Shanghai 200092, China; <sup>2</sup>Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan

We have experimentally investigated the hydrodynamic entrance behaviors of a Newtonian fluid (deionized water) and a well-characterized viscoelastic fluid (semi-dilute PEO solution) through a micro-fabricated capillary entrance geometry. Micro-particle image velocimetry ( $\mu$ -PIV) was used to capture the flow patterns upstream and quantitatively characterize the velocity profiles downstream of the contraction plane. The results show that the presence of polymers significantly modifies the developing flow field in the capillary region compared with the Newtonian fluid, resulting in a significantly increased entrance length ( $L_e$ ). The developing flow for PEO solution strongly depends on the upstream flow conditions prior to the capillary entrance, and the flow profile within the capillary region evolves from parabolic to flattened and finally concave with increasing Weissenberg number in the range  $10.8 < Wi < 256.2$  (though for modest Reynolds numbers  $Re=11.5$ ). Measurements of the excess pressure drop across the contraction as a function of  $Wi$  strongly suggest that an increase in the extensional viscosity in the central region of the channel is responsible for the generation of the complex flow kinematics. The detailed flow evolution from the upstream to downstream gives insights into the relaxation process of the extended polymers through the contraction. Furthermore, these quantitative results are expected to be useful in optimizing industrial processes, the design of "lab-on-a-chip" devices involving viscoelastic fluids and also have important implications for the applicability of microchannels in complex fluid rheometry.

Wednesday 6:05 Atrium/Harborview

PO83

### Flow-induced helical coiling of semiflexible polymers in structured microchannels

Roland G. Winkler<sup>1</sup>, Raghunath Chelakkot<sup>2</sup>, and Gerhard Gompper<sup>1</sup>

<sup>1</sup>Institute of Complex Systems, Forschungszentrum Jülich, Jülich, NRW 52425, Germany; <sup>2</sup>Department of Physics, IIT Bombay, Bombay, India

Buckling is a common phenomena of slender bodies, like long filaments and thin sheets, under an external load. Specifically, slender rods or semiflexible (bio)polymers exhibit a buckling instability under compression, when the load exceeds a critical value. In the simplest situation of Euler buckling of a rod, the symmetry is broken by buckling perpendicular to its axis in an arbitrary direction. Typically, buckling transitions are considered under equilibrium conditions. However, very little attention has been paid to conformational instabilities far from equilibrium, which exhibit qualitatively new features compared to equilibrium ones. Here, the transport of semiflexible polymers in microchannels and capillaries presents a new opportunity to study the non-equilibrium behavior of such filaments [1]. Vice versa, a detailed understanding of the dynamical process involved in such a transport is of paramount importance in many applications. This applies, in particular, to many biologically-relevant polymers, such as DNA, actin filaments, and microtubules, which are semiflexible; an example is DNA sorting in micro channels.

We investigate flow fields of spatially varying flow strength [2]. Such a situation is easily realized in flows through spatially-structured microchannels, e.g., in a region where the channel width changes from narrow to wide. By mesoscale hydrodynamic simulations of a semiflexible polymer in such a microchannel, we observe a buckling of the polymer as it enters the wider channel section. Buckling is often the first step in the formation of more complex structures. Indeed, we observe that buckling is followed by a flow-induced helical coiling of the polymer. Results are presented for the helix properties and its dependence on the diameter ratio of the channel, the polymer bending rigidity, and the flow strength.

[1] R. Chelakkot, R. G. Winkler, G. Gompper, EPL 91, 14001 (2010). [2] R. Chelakkot, R. G. Winkler, G. Gompper, Phys. Rev. Lett. 109, 178101 (2012).

Wednesday 6:05 Atrium/Harborview

PO84

### Effect of polymer adsorption on vortex dynamics in micro contraction channel flow of particulate suspensions

Youngeok Kim and Kyung Hyun Ahn

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

In this study, the effect of interactions between polymers and particles on the vortex developments in micro contraction channel flow was investigated. It is important to comprehend the behaviors of viscoelastic fluids in contraction flow because it appears in many processes. Many materials used in industry are not simply polymeric solutions or melts but also suspensions consisting of particles as well as polymers. However, the researches on the interaction between polymer-particle and their flow behaviors inside the contraction geometry are rare.

The micro contraction channels fabricated by PDMS and wide-field fluorescence microscopy were employed. Silica particles were synthesized by Stober method. To control polymer adsorption onto the silica surface, poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) were used. While a large amount of PEO can adsorb onto the silica surface, PAA rarely adsorbs onto the surface because of the electrostatic repulsive force.

For PEO/silica suspension, both the viscosity and the storage modulus significantly decreased when a small amount of silica particle (1.0wt%) was added into PEO 1.0wt% solution. The steric hindrance by PEO which is adsorbed onto the silica surface caused the storage modulus to decrease, resulting in reduced vortex size. The main factor that determines the vortex size was not the viscosity but the storage modulus. Both storage modulus and vortex size were increased as the amount of silica was increased. Unlike PEO/silica system, PAA cannot adsorb onto the surface of silica particle and the storage modulus did not change when 1.0wt% of silica was added into 1.0wt% of PAA solution. Also, the vortex size of PAA/silica suspension did not change much compared to that of PAA solution, unlike the PEO/silica suspension.

In conclusion, whether or not a polymer can interact with particle can have a strong influence not only on the rheological properties but also on the vortex dynamics.

Wednesday 6:05 Atrium/Harborview

PO85

### **Investigating the non-linear behaviour of semi-dilute PAAM aqueous solutions with a microfluidic, three-dimensional "cross-slot" flow geometry**

Alfredo Lanzaro<sup>1</sup> and Xue-Feng Yuan<sup>2</sup>

<sup>1</sup>*School of Chemical Engineering and Analytical Science, the University of Manchester, Manchester, Greater Manchester M1 7DN, United Kingdom;* <sup>2</sup>*The National Supercomputer Centre, Interdisciplinary Institute of High-Performance Computing, Guangzhou, China*

We investigate the flow of polyacrylamide (PAAm) aqueous solutions in a microfluidic, highly three-dimensional "cross-slot" flow geometry using our Rheo-chip platform [1,2,3,4]. The effects of varying the Weissenberg ( $1 < Wi < 100$ ) as well as the Elasticity ( $1.8 < El < 58.4$ ) numbers on the non-linear behavior of the model polymer solutions are quantitatively studied by means of micro-PIV and pressure drop measurements. The non-linear extensional viscosities are characterized up to deformation rates as high as  $10^5 \text{ s}^{-1}$ . Moreover, the velocity measurements are quantitatively analyzed using our numerical method [2,3] to define a "local Deborah number" field, which creates an instant snapshot of the local stretch underwent by polymer chains in complex flow conditions. We demonstrate that our technique provides a fast and reliable measurement of the extensional properties of the model fluids over a range of deformation rates unachievable by most commercial rheometers, and using far less fluid compared to other systems previously discussed in the literature. It is envisaged that our Rheo-chip technology will bring a step change to quantitative rheological characterization of complex fluids of industrial interest (e.g. biopharmaceuticals, inks, shampoos, toothpastes) allowing for fast and high-throughput formulation screening.

[1] A. Lanzaro and X.-F. Yuan, *J Non-Newtonian Fluid Mech*, 2011; 166:1064;1075. [2] A. Lanzaro and X.-F. Yuan, *J Non-Newtonian Fluid Mech*. 2013. [3] A. Lanzaro, Z. Li and X.-F. Yuan, *Microfluidics and Nanofluidics*, 2015; 18:819-828. [4] X.-F. Yuan, US Patent App. 13/813,933, 2011.

Wednesday 6:05 Atrium/Harborview

PO86

### **Stress overshoot in the start-up of shear deformation of polymer modified asphalt**

Fardin Khabaz and Rajesh Khare

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States*

Stress overshoot phenomenon in start-up shear of entangled polymer melts and solutions is well known in literature. Both chain orientation and chain stretching phenomena have been considered to be the reason behind the observed stress overshoot. In this work, we have used molecular simulations to study the stress overshoot phenomenon in polymer modified asphalt, a system of practical interest.

Specifically, we have used molecular dynamics (MD) simulations to investigate the rheology of atomistically detailed model structures of styrene-butadiene rubber (SBR) modified asphalt. The model structures were subjected to shear deformation using nonequilibrium molecular dynamics (NEMD) simulation technique. The shear stress was observed to exhibit an overshoot in the start-up phase of the shear deformation of the polymer modified asphalt system, such a stress overshoot was not exhibited by the neat asphalt system. The stress-strain behavior of the polymer modified asphalt system was studied at different shear rates and temperatures. An analysis of energy components and chain topology is used to elucidate the mechanism of stress overshoot in the system.

Wednesday 6:05 Atrium/Harborview

PO87

### **Consequences of stress-concentration coupling in polymer solutions under transient shear flow**

Michael Cromer<sup>1</sup>, Joseph Peterson<sup>2</sup>, Glenn H. Fredrickson<sup>2</sup>, and Gary Leal<sup>2</sup>

<sup>1</sup>*Rochester Institute of Technology, North Chili, NY 14514, United States;* <sup>2</sup>*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

We have shown that steady-state shear banding is possible in the flow of polymer solutions via the Helfand-Fredrickson coupling mechanism using a two-fluid Rolie-Poly model. In this talk we delve further into the characteristics of this phenomenon, in particular transient phenomena. We use an updated version of the model and consider the case of a circular Taylor-Couette cell. For the homogeneous, monotonic Rolie-Poly model it is well known that 'transient shear banding' and elastic recoil are possible even if the eventual steady state is (almost) linear. We know how the concentration coupling affects the steady state; the question we seek to answer here is how this coupling affects the transients. We will focus on 4 time scales: i. Onset of transient banding, ii. Onset of local concentration gradients, iii. Onset of 'large' concentration differences, iv. Long-time diffusive process to steady state. Ultimately, we show that the inhomogeneous, as opposed to homogeneous, Rolie-Poly model captures several transient phenomena on experimental time scales with realistic parameters.

Wednesday 6:05 Atrium/Harborview

PO88

**Modeling of rheological behavior of PA6/ABS nanocomposites by power-law like model**Alireza Mojjarrad<sup>1</sup>, Maryam Zarghami Dehaghani<sup>2</sup>, Yousef Jahani<sup>3</sup>, and Mehdi Barikani<sup>3</sup><sup>1</sup>*Azad University of Shiraz, Tehran, Iran;* <sup>2</sup>*Sahand Petroplastic, Tehran, Iran;* <sup>3</sup>*Iran Polymer and Petrochemical Institute, Tehran, Iran*

In this work, we studied power-law model for investigation of immiscible polyamide6/acrylonitrile butadiene styrene (PA6/ABS) blends filled with nanoclay and compare its predictions with the experimental measurements. Consequences of the power-law model are compared with results of experimental observations of the rheological properties special at low frequency region. The power-law model can be applied in order to evaluation the rheological properties of these blends. A good fit of the data is obtained for all of the blends in all the frequencies region. This means that the rheological behavior of these types of blends at all frequencies region is justified with the power-law model. The  $\eta^*$ - $\omega$  curves indicate a linear power-law like behavior with two unlike slopes at the low and the high frequency regions. Therefore the power-law model was applied to the  $\eta^*$ - $\omega$  curves of the samples at the low frequency region.

Wednesday 6:05 Atrium/Harborview

PO89

**The role of nanoclay in promoting co-continuous morphology in PA6/ABS blends**Alireza Mojjarrad<sup>1</sup> and Maryam Zarghami Dehaghani<sup>2</sup><sup>1</sup>*Azad University of Shiraz, Tehran, Iran;* <sup>2</sup>*Sahand Petroplastic, Tehran, Iran*

This paper reports the effect of nanoclay on the morphology of co-continuous immiscible polyamide6/acrylonitrile butadiene styrene (PA6/ABS) blends. For this purpose, blends based on the PA6/ABS/Nanoclay with different compositions from PA6, ABS, and nanoclay were prepared. Then Phase morphology behavior of PA6/ABS/Nanoclay blends was studied using scanning electron microscopy (SEM). The results showed that the compatibilization effect of the nanoclay would decrease the size of the dispersed phase droplets. Also, addition of the nanoclay and ABS led to a significant morphology alteration into a co-continuous structure. It can be seen that the polydispersity tend to decreases when nanoclay loading in PA6/ABS blends increases. This is due to a greater break-up for all of the blends, which could lead to an increase of homogeneity of size distribution of dispersed phase.

Wednesday 6:05 Atrium/Harborview

PO90

**Relaxation mechanism and molecular structure study of polymer blends by rheological and SANS experiments**Ludovica Hengeller<sup>1</sup>, Qian Huang<sup>1</sup>, Andriy Dorokhin<sup>2</sup>, Nicolas J. Alvarez<sup>3</sup>, Kristoffer Almdal<sup>2</sup>, Jacob Kirkensgaard<sup>4</sup>, Kell Mortensen<sup>4</sup>, and Ole Hassager<sup>1</sup><sup>1</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark;* <sup>2</sup>*Department of Micro- and Nanotechnology, Technical University of Denmark, Kgs. Lyngby Copenhagen, Denmark;* <sup>3</sup>*Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA, United States;* <sup>4</sup>*Xray and Neutron Science, Niels Bohr Institute, Copenhagen, Denmark*

Industrial polymers are largely polydisperse systems. One step towards understanding polydisperse polymers is the characterization of bi-disperse blends. Even though linear viscoelastic properties of bi-disperse polystyrene blends have been investigated thoroughly both theoretically and experimentally in recent years [1], both nonlinear shear and extensional flow properties are lacking. The purpose of the present study is to investigate the nature of interactions, namely polymer-polymer, in strong elongational flow using a bi-disperse polystyrene blend of 95 K and 545 K Mw with 50% weight ratio. We present both uniaxial extension and stress relaxation experiments to determine if orientation and extension of long PS chains induce orientation and extension in shorter chains. The extensional viscosity of systems investigated, provides only indirect evidence about the extent to which the molecules have been unraveled and stretched by the flow field. More directed information is obtained by neutron scattering on quenched liquid bridges of polystyrene. Preliminary results of such experiments will be presented.

References: [1] Nielsen J. K.; Rasmussen, H. K.; Hassager O., and McKinley G. H., "Elongational viscosity of monodisperse and bidisperse polystyrene melts", *J. Rheol.* 2006, 50, 453-476. [2] Huang, Q.; Alvarez, N. J.; Matsumiya Y.; Rasmussen, H. K.; Watanabe H. and Hassager O. "Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions", *ACS Macro Lett.* 2013, 2, 741-744.

Wednesday 6:05 Atrium/Harborview

PO91

**Effect of nanoclay on the co-continuous morphology of PA6/ABS nanocomposite blends**Alireza Mojjarrad<sup>1</sup>, Maryam Zarghami Dehaghani<sup>2</sup>, Yousef Jahani<sup>3</sup>, and Mehdi Barikani<sup>3</sup><sup>1</sup>*Azad University of Shiraz, Tehran, Iran;* <sup>2</sup>*Sahand Petroplastic, Tehran, Iran;* <sup>3</sup>*Iran Polymer and Petrochemical Institute, Tehran, Iran*

This paper reports the influence of nanoclay on the morphology of co-continuous immiscible polyamide6/acrylonitrile butadiene styrene (PA6/ABS) blends. The unfilled blends display phase inversion and a co-continuous structure at a ratio of 60/35/8 PA6/ABS/Com by weight. Upon addition of nanoclay in the presence of compatibilizer a finer structure is obtained. This transformation is associated to the presence of finely dispersed nanoclay particles that are localized selective within the PA6 matrix. The results showed that the compatibilization effect of the nanoclay would decrease the size of the dispersed phase droplets. Also, addition of the nanoclay led to a significant morphology alteration into a co-continuous structure. It can be seen that the polydispersity tend to decreases when nanoclay loading in PA6/ABS blends increases. This is due to a greater break-up for all of the blends, which could lead to an increase of homogeneity of size distribution of dispersed phase.

Wednesday 6:05 Atrium/Harborview

PO92

**Development of high performance electrospun materials and their composites**

Jay H. Park and Gregory C. Rutledge

*Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Ultra-high molecular weight polyethylene (UHMWPE) gel-spun fibers are often regarded as "high performance" fibers owing to their superior mechanical properties. The high modulus and strength of these fibers are believed to originate from the combined contributions of molecular orientation and crystallinity. However, conventional gel-spun fibers are typically 10's of micrometers in diameter, so that their specific surface area (for bonding to matrix) is small, and inter-fibrillar distances within a composite are large. In an effort to achieve a similarly high degree of molecular orientation and crystallinity with fibers having high specific surface area, we seek to develop a novel "gel-electrospinning" technology in which electrical forces are used to induce a high extensional strain rate ( $\sim 1000 \text{ s}^{-1}$ ) in a polymer gel at elevated temperature. Building on our previous effort to study the correlation between the tensile modulus and strength of a single electrospun fiber and its improved molecular orientation, we have designed and built an apparatus to electrospin ultrahigh molecular weight polyethylene (UHMWPE) fibers from solutions of, e.g., xylene, cyclohexanone and tert-butyl ammonium bromide at elevated temperature. Here, we report the highest reported tensile modulus and toughness of these fibers, along with their crystallinity and molecular orientation, to demonstrate the correlation among these parameters. We also demonstrate that the key to the production of these fibers is careful control of the temperature in several process zones, including the solution reservoir, the spinneret, the space around the jet itself, and the collector. Ultimately, our goal is to produce electrospun polymeric fibers that are comparable to conventional high performance materials such as Spectra®.

Wednesday 6:05 Atrium/Harborview

PO93

**Flow induced crystallization of isotactic polypropylene**Fawzi G. Hamad<sup>1</sup>, Ralph H. Colby<sup>2</sup>, and Scott T. Milner<sup>1</sup>*<sup>1</sup>Chemical Engineering, Penn State University, University Park, PA 16802, United States; <sup>2</sup>Chemical Engineering and Materials Science and Engineering, Penn State University, University Park, PA 16802, United States*

Semi-crystalline polymers exhibit flow induced crystallization (FIC), in which brief intervals of strong flow followed by a temperature quench increases the nuclei number density and transforms the morphology. One main requirement for FIC is applying sufficient specific work ( $W = \text{stress} \times \text{strain}$ ) to form flow-induced nuclei. The objective of this study is to explore the relation between amount of specific work and crystallization kinetics, crystal morphology, and nuclei persistence time during FIC. The crystallization kinetics of isotactic polypropylene is studied in a rotational rheometer. Samples are sheared above  $T_m$  and then quenched below  $T_m$  while the phase angle ( $\tan\delta$ ) is monitored at a fixed frequency and strain, as a sensitive probe of the onset of solid-like behavior after different shear conditions. The crystallization rate generally increases with increasing applied work, up to a value beyond which the rate remains constant. Samples with lower isotacticity show the fastest crystallization rates after shear (whereas quiescent crystallization rates show the expected opposite trend with tacticity). Using polarized optical microscopy and AFM, we image the changes in morphology of the previously sheared polypropylene sample. Micrographs show that flow promotes the formation of rice grain crystals that are roughly  $4 \mu\text{m}$  long, and  $1 \mu\text{m}$  in diameter. Flow-induced nuclei that promote this morphology have a long persistence time and require prolonged annealing at elevated temperature to erase. This persistence time was determined by monitoring the crystallization temperature of a sheared sample in the DSC after annealing at elevated temperatures until it returns to the quiescent crystallization temperature.

Wednesday 6:05 Atrium/Harborview

PO94

**Regio regularity effects on chain mobility and entanglement for poly(3-hexylthiophene)**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>Chemical Engineering and Materials Science and Engineering, Penn State University, University Park, PA 16802, United States*

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a conjugated polymer that can serve as the active layer in a variety of electronic devices, such as solar cells and thin-film transistors. However, fundamental properties of P3HT, including the glass transition temperature ( $T_g$ ) and the entanglement molecular weight ( $M_e$ ), are still in dispute. These parameters play a central role in the microstructures of P3HT, such as intercrystalline connectivity and tie chains, which are believed to ultimately influence bulk electrical charge transport. In addition, P3HT can serve as an example to verify recently proposed scaling relationships for semiflexible polymers. A wide range of molecular weights of both regiorandom (RRa) and regioregular (RRe) P3HT have been studied using oscillatory and steady shear rheology. Coupled with the molecular weight distribution from GPC,  $M_e$  was extracted by fitting the linear viscoelastic data of multiple molecular weight samples using BoB software. Furthermore, by using low-temperature oscillatory shear, two  $T_g$ s for both RRe and RRa P3HT were identified, which correspond to the segmental backbone motion and the side chain glass transition at lower temperature. RRe P3HT has a significantly larger  $M_e$  than RRa P3HT, which might originate from the difference in side chain packing evidenced by their different lower  $T_g$  values. Thus, further investigation on their packing lengths through dilute solution light scattering will be crucial to understand entanglement in these semiflexible polymers.

Wednesday 6:05 Atrium/Harborview

PO95

**Theory of flow induced molecular weight migration in polymer melts**John R. Dorgan*Chemical Engineering, Colorado School of Mines, Golden, CO 80401, United States*

Flow induced migration, whereby polymers are spatially fractionated across a flow field according to molecular weight, represents a significant complication in the processing of polymer melts. Despite the long history of this subject, molecular weight based migration remains poorly understood and is not incorporated into common constitutive models. A simple analytical theory is presented which predicts migration phenomena based on the minimal entropy generation principle from non-equilibrium thermodynamics. A new dimensionless grouping,  $Do$ , is found as the ratio of the gradient of the polymer volume fraction to the gradient of the logarithm of shear rate. The concentration of a low molecular weight species at the wall increases rapidly with its bulk concentration. This result explains the utility of low molecular weight processing aides and the enhanced processibility of bimodal molecular weight polyolefins.

Wednesday 6:05 Atrium/Harborview

PO96

**Determining the effect of humidity on static friction of polymers**Kartik S. Pondicherry<sup>1</sup> and Prajakta A. Kamerkar<sup>2</sup><sup>1</sup>*Rheology Product Development, Anton Paar GmbH, Graz 8054, Austria;* <sup>2</sup>*Anton Paar USA, Ashland, VA 23005, United States*

Tribological behavior of materials is influenced by their surface characteristics which include roughness, chemical potential, visco-elastic properties, and presence of adsorbed layers. For water-absorbing materials, such as polymers, humidity strongly alters the tribological properties. Defined temperature and humidity conditions are needed to characterize tribological systems containing these types of materials. This study presents a unique combination of accurate humidity control and high precision tribological testing methodology and subsequent investigation of the influence of humidity on the static friction between steel-polymer contacts at model scale.

Wednesday 6:05 Atrium/Harborview

PO97

**Damping and mechanical properties of semi-crystalline polymers using oscillatory rheology and molecular modeling**Zeena Cherian, Brian Koo, and Sriraj Srinivasan*Analytical & Systems, Arkema, King of Prussia, PA 19406, United States*

Dynamic mechanical analysis (DMA) is an essential analytical technique used to understand the end use performance of viscoelastic polymeric materials. DMA measures the modulus (stiffness) and damping (energy dissipation) of material as it undergoes periodic deformation. The damping properties and changes in mechanical properties with temperature and time help in the design of new products and prediction of properties. In this study, the frequency-dependent dynamic mechanical behavior of a series of polymers has been investigated in the solid state as a function of temperature. In addition to glass transition, the sub-ambient  $\gamma$  (?),  $\beta$  ( $\beta$ ) relaxation of commercially available polymers has been identified. To understand the origin of these sub-ambient molecular relaxations that would dictate the product performance, low-shear and oscillatory-shear molecular dynamics simulations have been used. The initial findings from combinatorial experimental and molecular modeling techniques will be presented.

Wednesday 6:05 Atrium/Harborview

PO98

**Coil-stretch hysteresis in planar mixed flows of polymer solutions at finite concentrations**Chandi Sasmal and J. Ravi Prakash*Chemical Engineering, Monash University, Melbourne, Victoria 3150, Australia*

In 1974, de Gennes conjectured that in extension-dominated flows, depending on the deformation history, it is possible for a dilute polymer solution to manifest multiple values of stress at a single strain rate, and consequently exhibit hysteretic behaviour. The importance of de Gennes contention has paradigm changing implications for the modelling of polymer solution rheology. Experimental proof for de Gennes hypothesis was established 30 years later by showing individual DNA molecules in ultra-dilute solutions subjected to planar elongational flow can be either coiled or highly stretched depending on the history of deformation. While de Gennes arguments and the experimental validation were restricted to dilute solutions, recent scaling arguments and experiments carried out at Monash University suggest that the concentration of polymers has a significant non-monotonic influence on the extent of coil-stretch hysteresis. Additionally, it has been known since de Gennes early theory, that increasing the fraction of shear in a mixed flow of planar shear and extension dramatically decreases the magnitude of coil-stretch hysteresis. We discuss the development of a mesoscopic Brownian dynamics simulation algorithm that is capable of accurately describing polymer solutions undergoing planar mixed flows at finite polymer concentrations. The simulations permit the examination of the competing roles of polymer concentration and flow mixedness on the extent of coil-stretch hysteresis, and provide a fascinating insight into the influence of non-linear phenomena on the molecular scale on macroscopic solution properties.

Wednesday 6:05 Atrium/Harborview

PO99

**Eutectic gallium indium rheology**Uranbileg Daalkhaijav<sup>1</sup>, Yigit Menguc<sup>2</sup>, and Travis W. Walker<sup>1</sup><sup>1</sup>*Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States;*<sup>2</sup>*Mechanical Engineering, Oregon State University, Corvallis, OR 97331, United States*

Eutectic gallium indium (EGaIn) alloy is a liquid metal at room temperature that can fill microchannels to act as electrical sensors and conducting wires for small electronic systems. EGaIn has a yield stress that, when surpassed, allows the liquid to freely flow to fill the channels and to form a stable structure that is not toxic like mercury would be. This yield stress of the alloy is caused by a gallium oxide skin that forms on the metal extremely quickly when exposed to air. The oxide skin is assumed to be the dominant structure, dictating the rheological behavior of this alloy. Our parallel plate experimental results, which are adjusted for just the oxide skin component of the alloy at the edge of the upper geometry, are consistent with previous findings doing the same measurements. In addition, interfacial rheological measurements using a double-wall ring apparatus show consistent results to the adjusted parallel plate tests, confirming the strength of the oxide layer. From our results, a frequency sweep shows typical gel behavior that is elastically dominated. The oxide layer yields at a stress of approximately 0.3 N/m, then the material flows freely with no further increase in stress and is shown to shear thin.

Wednesday 6:05 Atrium/Harborview

PO100

**Nonlinear rheology of oligomeric ionomers: Shear-thickening and shear-thinning behavior of sulfonated polystyrene melts**Chongwen Huang<sup>1</sup>, Quan Chen<sup>2</sup>, and Robert A. Weiss<sup>1</sup><sup>1</sup>*Department of Polymer Engineering, The University of Akron, Akron, OH, United States;* <sup>2</sup>*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, CAS, Changchun, Jilin 130022, China*

Shear thickening behavior, which is often observed for associating polymer solutions, was recently reported for ionomer melts<sup>1</sup>. In order to better understand the mechanism of shear thickening in these melts, the nonlinear rheological behavior of oligomeric sulfonated polystyrene ionomers (SPS) with different degrees of sulfonation and different alkali metal cations were measured at a variety of temperatures using steady shear. When the Weissenberg number,  $Wi$ , defined as the product of applied shear rate and the characteristic relaxation time of the ionic associations, approaches unity, shear thickening was observed, but only for samples with a sulfonation degree close to the gel point<sup>2</sup>, which is defined when each chain has on average one ionic group. Below the gel point, only shear thinning behavior was observed, and above the gel point, melt fracture occurred. The magnitude of shear thickening increases with the decrease of temperature, molecular weight of the PS precursor and the increase of ionic strength of the metal cation,  $q/a$ , where  $q$  and  $a$  are the charge and radius of the cation, respectively.

[1] Weiss, R. A.; Zhao, H. J. *Rheol.* 2009, 53, (1), 191. [2] Chen, Q.; Huang, C.; Weiss, R. A.; Colby, R. H. *Macromolecules* 2015, 48, (4), 1221-1230.

Wednesday 6:05 Atrium/Harborview

PO101

**Shear rheometry of hydrolyzed polyacrylamide solutions for enhanced oil recovery**Anna V. Walter and Kendra A. Erk*School of Materials Engineering, Purdue University, West Lafayette, IN 47907-2045, United States*

Enhanced oil recovery (EOR) is used to access the oil remaining in oil basins after traditional recovery methods are deployed. In typical recovery, water is injected into the basin to reestablish the pressure differential, driving the oil to the surface. When polymer is added to this water, recovery is greatly increased due to the higher viscosity of the solution. The most commonly used polymer in EOR is partially hydrolyzed polyacrylamide (HPAM), an acrylamide polymer with 15-35% of repeat units replaced by acrylic acid. Due to their extremely high molecular weights, up to 10 million g/mol, even low concentrations of these polymers cause a great increase in solution viscosity. Shear rheometry was used to investigate the rheological behavior of polymer solutions in water to model the behavior of such solutions during EOR. Solutions with low concentrations (~0.15 wt%) of commercial HPAM polymers were made to model the solutions used industrially; viscosity curves were determined via shear rheometry. In absence of ions, polymer solutions were shear thinning; viscosity at low shear rates decreased as polymer concentration decreased. Monovalent salts ( $\text{Na}^+$ ) or divalent salts ( $\text{Ca}^{2+}$ ) were added to polymer solutions with concentrations varied from ~0.001-0.3 M, covering a range of basin salinities. Monovalent salts in solution decreased viscosity at all shear rates and, at high concentrations of salt, behavior changed from shear thinning to Newtonian at shear rates of ~1 (1/s). In solutions with divalent salts, viscosity was lower than that with the same monovalent salt concentration. At all tested concentrations of divalent salts, solutions also exhibited a transition from shear thinning to Newtonian behavior. Mixtures of monovalent and divalent salts were also used with similar results; the total concentration of salt has the greatest apparent effect on behavior. Further investigation with model polymers will allow polymer solutions tailored more specifically to the water chemistry in oil basins.

Wednesday 6:05 Atrium/Harborview

PO102

**Optimal polyelectrolyte assembly in solution using macro and microscale flows**Nikolas Wilkinson<sup>1</sup>, Eric Ruud<sup>2</sup>, and Cari Dutcher<sup>2</sup><sup>1</sup>*Chemical Engineering, University of Minnesota, Minneapolis, MN 55455, United States;* <sup>2</sup>*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 due to the polymers unique ability to form mesoscale structures in solution. There are a number of known potential mechanisms for the mesoscale solute assembly, including charge neutralization, polymer depletion, polymer bridging, polymer adsorption, and patch flocculation, but the impact of time-dependent chemical and hydrodynamic conditions on assembly kinetics and final microstructure still remains largely uncertain. We seek to improve understanding of the dynamics of particle-particle, polymer-polymer, and polymer-particle interactions in complex aqueous solutions, and in complex hydrodynamic flows. Here, we explore assembly dynamics using cationic polyacrylamide, a polymer commonly used in water treatment. Particles used in this study include monodispersed PS beads as well as more complex bentonite clays, ranging in size from 0.015  $\mu\text{m}$  to 2  $\mu\text{m}$ . For the inorganic clay systems, we present surprising evidence that the zeta potential of the bentonite clay has no direct effect on flocculation performance. Instead, we find that the solution pH controls flocculation performance indirectly through influencing bentonite particle size and structure prior to polymer injection. Likewise, we show that ionic strength effects optimal polymer dosing concentrations and turbidity reduction, via kinetic trapping of the initial clay morphology and size. Solutions were studied with a pH varying from 3 to 11, with a three-fold change in zeta potential, and over 4 orders of magnitude in ionic strength. This work sheds more light on the complexities of polymer flocculation, towards improving dosing and treatment optimization for more efficient water treatment. For the beads, we use microscopy to explore fundamental particle-particle and particle-polymer assembled structures with negatively charged polystyrene microbeads.

Wednesday 6:05 Atrium/Harborview

PO103

**The effect of ionic strength on the shear rheology and microstructure of branched wormlike micelles (WLMs)**Michelle A. Calabrese, Norman J. Wagner, and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States*

Branching affects the material properties of wormlike micelles (WLMs) (Rogers et al., COCIS, 2014). The mechanism underlying the effect of branching on flow properties is studied by combined rheology and flow- and rheo-SANS measurements of the microstructure of two sets of WLM solutions. In the first, the degree of branching in mixed cationic/anionic surfactant (CTAT/SDBS) WLMs is controlled via the addition of sodium tosylate (Schubert et al. Langmuir 2003) and is verified by cryo-TEM. In these solutions, the ionic strength is altered when branching is induced. The ionic strength of the second set of WLM solutions is held constant by adding NaTos and NaCl, which is known to have a lesser effect on micellar branching (Schubert et al. Langmuir 2003). The structure and segmental alignment of WLMs were examined under steady shear in the flow-gradient and flow-vorticity planes using new SANS sample environments (Gurnon et al., JoVE, 2014). The structural projections in both planes provide insight into the micellar topology and alignment under steady shear flows. Segmental orientation and alignment in the flow-gradient plane are non-monotonic functions of branching, ionic strength and radial position. The results of this study help to decouple the effect of ionic strength and micellar topology on the measured nonlinear shear rheology of WLM solutions, providing a thorough data set for the development and rigorous testing of microstructure-based constitutive equations as well as guidance for formulating WLMs for specific rheological properties.

Wednesday 6:05 Atrium/Harborview

PO104

**Wormlike micellar solutions containing cationic surfactant and anionic hydrotropic salt**Ya Zhao<sup>1</sup>, Simon J. Haward<sup>2</sup>, and Amy Q. Shen<sup>2</sup><sup>1</sup>*University of Washington, Seattle, WA, United States;* <sup>2</sup>*Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan*

Aqueous micellar solutions of cationic surfactant cetyltrimethylammonium bromide (CTAB) and organic hydrotropic salt 3-hydroxy naphthalene-2-carboxylate (SHNC) in the semi-dilute regime have been characterized by linear and nonlinear rheology, and dynamic light scattering (DLS). The strong hydrophobicity and naphthalene structure present in the SHNC induces significant growth of CTAB wormlike micelles and promotes stable micellar network formation. Focusing primarily on 75mM CTAB/SHNC solution, we correlate the rich rheological behavior with structural transition of the micelle network under different deformation histories with temperatures in the range  $20\text{C} < T < 40\text{C}$ . Viscous dissipation dominates at low temperature, while short range interactions among micellar head groups, reformation and re-organization of micellar networks play important roles at higher temperatures, leading to complex stress responses under large deformations. The influence of double benzene rings on the response of transient and large amplitude oscillatory shear flows in the system was further elucidated by comparing the rheological behavior of CTAB/SHNC and CTAB/NaSal at the same salt and surfactant concentrations. Our studies distinguished SHNC as a stable hydrotrope in a semi-dilute cationic surfactant system under thermal variations, with potential applications such as drag reduction and fracturing fluids in oil recovery.

Wednesday 6:05 Atrium/Harborview

PO105

**Influence of relative humidity on the curing behavior of silicone sealants**Gunther Arnold<sup>1</sup>, Raha Roohnia<sup>1</sup>, and Gina Paroline<sup>2</sup><sup>1</sup>Anton Paar Germany, Ostfildern, Scharnhausen 73760, Germany; <sup>2</sup>Anton Paar USA, Ashland, VA 23005, United States

Room temperature vulcanizing silicone sealants possess an array of advantageous properties making them practical to use and easy to handle. Once cured, the sealants exhibit a wide range of use temperatures and good resistance to UV, chemicals, and water. These properties result in silicone sealants enjoying a broad field of applications which thusly also occur in a broad range of environmental conditions. Key influencers to the curing time are environmental relative humidity and temperature. This research presents a special rheological measuring system designed to optimize exposure of the sample surface to the test environmental conditions coupled with a unique humidity and temperature controlled chamber for a rotational rheometer. The resulting data confirms the benefit of such a test configuration to discover the impact of temperature and humidity on the curing profile of silicone sealants.

Wednesday 6:05 Atrium/Harborview

PO106

**How supramolecular assemblies control dynamics of associative polymers**Hadi Goldansaz<sup>1</sup>, Evelyne van Ruymbeke<sup>1</sup>, and Michael Wübbenhorst<sup>2</sup><sup>1</sup>Bio and Soft Matter, Université catholique de Louvain, Louvain-La-Neuve, Belgium; <sup>2</sup>Department of Physics and Astronomy, KU Leuven, Leuven 3001, Belgium

Dynamics of supramolecular networks made up of partially hydrolyzed poly(n-butyl acrylate) [PBA] is investigated. These linear entangled random copolymers [PBA-r-AA] self-assemble via hydrogen bonding interactions between carboxylic acid groups. Two types of supramolecular assemblies are revealed, i.e. binary assembly of carboxylic acid dimers and collective assembly of dimers into distinct Poly(acrylic acid) [PAA] domains. The latter is proved by emergence of new relaxation processes in broad band dielectric spectroscopy while the former is evident by increase of glass transition temperature as well as retardation of segmental mobility observed by rheology. Therefore a sea-island morphology containing geometrically confined PAA nanodomains embedded in a PnBA-rich matrix is suggested for the supramolecular network. Thermodynamic theories are employed to prove existence of an interlayer with restricted mobility between the two phases. A fraction of PBA-r-AA segments which are trapped between more than one PAA domain is considered to describe the low frequency plateau in storage modulus that is seen beyond the plateau modulus of PnBA as well as strain hardening in both shear and elongation fields. Finally based on the observation in this work and wealth of literature on supramolecular systems, a general microstructure is proposed for the associating polymers in which supramolecular moieties are situated along the contour length. This microstructure appropriately describes different dynamic observations made by rheology, calorimetry and dielectrics.

Wednesday 6:05 Atrium/Harborview

PO107

**Rigorous analysis of polarized Raman scattering experiments in uniaxial deformations**David W. Mead*Mead Consulting, Bedford, NH, United States*

In this paper we perform a rigorous analysis of the polarized Raman scattering experiment. The experimental observable in a Raman scattering experiment is the intensity of the scattered light which is proportional to the Raman tensor, a fourth order tensor possessing transverse isotropy with respect to the Kuhn bond within which it is contained. Symmetry considerations dictate that 5 independent projections of the scattered light are required to completely specify the Raman tensor and the second and fourth moment of the orientation distribution function of chain segments. A segmental additivity theorem is proven which is necessary to properly interpret experimental data. A rigorous analysis of the experiment is performed by executing a fourth moment Kuhn-Grün analysis. Additionally, a spherical harmonic analysis performed by Bower generates a system of 5 algebraic equations in 5 unknowns. We solve this system of nonlinear equations analytically and demonstrate that, although there are multiple solutions, there is only one solution that is physically meaningful. Results of the Kuhn-Grün analysis reveal that only when large, finite deformations are performed is it possible to experimentally resolve the fourth moment of the segmental orientation distribution function. Experimental data published by Archer, Fuller et al is examined in the context of our rigorous analysis of the Raman scattering problem.

Wednesday 6:05 Atrium/Harborview

PO108

**Updates in rotational rheometry and viscometry**David J. Moonay*Brookfield Engineering Labs., Inc., Middleboro, MA 02346, United States*

Customers require various instruments for viscometric and rheological analyses. This paper describes advances in Brookfield rheometers and viscometers, and corresponding software, meeting those needs. PGFlash(tm) software's improvements allow creation of multi-step programs that may be saved onto Flash Drives ("USB sticks") and downloaded into various DV2T Viscometers and DV3T Rheometers. Rheocalc T(tm) software improvements in graphing multiple data files, enhancements to "21 CFR" capabilities, and its "Wizard" for creating simple tests, are discussed. RST Rheometer system improvements allow more types of tests to be graphically displayed in standalone mode, as well, for example. Data are also presented for representative materials, obtained through various tests with different instruments.

Wednesday 6:05 Atrium/Harborview PO109

**Oscillatory tests with a QC level, ball bearing, rheometer**

Fabian Meyer, Jan P. Plog, and Jint Nijman  
*Thermo Fisher Scientific, Karlsruhe, Germany*

Oscillatory tests are becoming more and more important in today's quality control for various industries including the cosmetics and food industry. This because many product-relevant parameters like the gel-point and gel stability cannot be probed using steady shear tests. However, standard medium range air-bearing rheometers are often too big of an investment for many companies and can also be too sophisticated for non-trained lab personnel. At the other hand simple low-cost viscometers are not capable of performing oscillatory tests. In this poster we want to present how well simple oscillatory tests can be conducted with a new ball bearing, quality control level, rheometer. Strain sweep as well as frequency sweep data will be presented in Controlled Stress (CS) as well as in Controlled Deformation (CD) mode. Data obtained from measurement on standard materials as well as on technical samples will be shown and compared to data obtained from a research grade rheometer to discuss comparability.

Wednesday 6:05 Atrium/Harborview PO110

**New applications for science and industry using a universal extensional fixture on a rotational rheometer**

Roman Führer<sup>1</sup> and James Eickhoff<sup>2</sup>

<sup>1</sup>*Rheology Product Development, Anton Paar GmbH, Graz 8054, Austria;* <sup>2</sup>*Anton Paar USA, Ashland, VA 23005, United States*

Extensional rheology fixtures for rotational rheometers have found primary use in characterizing tensile properties of thermoplastic melts and elastomers. The precise control of EC motor based rheometers and their ability to make both native controlled strain and native controlled stress measurements lead to success in more widespread applications for extensional tests. This study focuses on uses of extensional rheology for solving industrial problems such as paint film strength and accelerated aging of polyolefin films to detect batches which will suffer from shrinkage problems under normal use.

Wednesday 6:05 Atrium/Harborview PO111

**Study of flow induced crystallization and shear induced orientation using polarized microscopy and imaging**

Loredana M. Völker-Pop<sup>1</sup> and Tharanga D. Perera<sup>2</sup>

<sup>1</sup>*Anton Paar Germany, Ostfildern 73760, Germany;* <sup>2</sup>*Anton Paar USA, Ashland, VA 23005, United States*

Knowledge about crystallization processes and crystal orientation is essential for material, process and product development as they heavily influence the properties of the final product. Combining rheological measurements with polarized light imaging and microscopy allows observation of effects such as flow induced crystallization in polymers and shear induced orientation in liquid crystals. This study describes an experimental setup for polarized light microscopy and polarized light imaging in combination with a rotational rheometer. Data is presented showing the uses of these two techniques to explore the connection between macroscopic properties under shear and the corresponding microstructure, i.e. to observe orientation behavior in liquid crystals and shear induced structural transitions in polymers.

Wednesday 6:05 Atrium/Harborview PO112

**New oscillatory method for determining the low temperature behavior of asphalt binders by using a dynamic shear rheometer**

Oliver Sack<sup>1</sup> and Philipp Rückert<sup>2</sup>

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Understanding the low temperature behavior of asphalt binders is of great importance for the pavement industry. Viscoelastic properties of asphalt binder can change due to local environment conditions. The knowledge of these changes provides an indication of the long term stability of pavements. Existing techniques for determining low temperature properties of asphalt binders cover only a limited temperature range. This study covers a promising new method wherein solid bars of asphalt are characterized over a wider temperature range to better elucidate low temperature performance.

Wednesday 6:05 Atrium/Harborview PO113

**Rheo-microscopy: Direct observation of microstructural changes in samples during rheological tests**

Bharath Rajaram

*TA Instruments, New Castle, DE 19720, United States*

Understanding the relationship between a sample's structure and its rheological properties is relevant to a wide range of materials and applications, and is critical to improving product performance during processing, storage and handling, and end-use applications. Under quiescent conditions, a number of standalone techniques can be used to observe and correlate the sample structure with material properties - these include brightfield and confocal microscopy, and scattering techniques such as light, X-ray, or neutron scattering. However, the observation of the sample structure during steady or oscillatory shear deformation has required the construction of elaborate, customized shear cells designed around specific test requirements. In this study, we report on the recent development of a microscopy accessory that can be used with commercially available rheometers for simultaneous visualization of sample structure during rheological tests. The accessory provides a platform for high quality and high resolution imaging of the sample at high frame rates. Designed to be flexible and modular, the accessory is capable of brightfield,

fluorescence, and cross-polarization microscopy under ambient and controlled temperature conditions. Moreover, the device can be coupled with a counter-rotating stage to extend the range of applicable flow conditions and create a zero-velocity stagnation plane for imaging. A number of examples are presented to highlight the application of these microscopy modes for observing and quantifying structure-property relationships across a wide range of materials.

Wednesday 6:05 Atrium/Harborview

PO114

### **Characterization of anisotropic microstructure formation using 2D-SAOS**

Sarah K. Cotts and Bharath Rajaram

*TA Instruments, New Castle, DE 19720, United States*

2-Dimensional Small Amplitude Oscillatory Shear, or 2D-SAOS, is a novel technique that has been successfully employed to characterize microstructural orientations in anisotropic materials. The technique involves applying small amplitude oscillatory shear simultaneously in two directions using a specially designed cup and bob geometry and exploits the unique orthogonal deformation capabilities available on the ARES-G2 rheometer. In this study, we demonstrate the sensitivity of 2D-SAOS measurements for quantifying the shear-induced structural anisotropy during the sol-gel transition of a sample with non-spherical fillers. Previous efforts in published literature have used shear rheology to study the changes in mechanical properties and molecular structure associated with the sol-gel phase transition. While this approach is sufficient for isotropic materials, it does not provide complete characterization of highly oriented materials, such as those with high amounts of anisotropic filler (rod-like or plate-like particles), or ordered systems like self-assembled block copolymer micelles. The application of 2D-SAOS to study such materials allows for a complete understanding of oriented systems, revealing the mechanical signatures of microscopic orientation in a single experiment.

Wednesday 6:05 Atrium/Harborview

PO115

### **Investigating both torsional and bending orientation-dependent mechanical properties using a single rotational rheometer**

Nathan D. Hesse

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Dynamic mechanical analyses in both rotational and linear directions are well known for the viscoelastic characterization of solid and soft-solid materials. Typically for solid materials, two separate analytical instruments would be used to perform the oscillatory shear or linear testing. By using the unique force rebalanced transducer of both the ARES G2 or the Discovery Hybrid Rheometer (DHR) a single instrument has the ability to make both measurements. In this study, orientation-dependent mechanical properties from both torsional and linear dynamic measurements will be demonstrated from a single instrument.

Wednesday 6:05 Atrium/Harborview

PO116

### **Applicability of passive microrheology for rheological measurements of stimulation fluids**

Yan Gao, Phil Sullivan, and Alhad Phatak

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Simulation fluids used in the oil field to improve hydrocarbon recovery rates contain additives for transporting and suspending solids, reducing friction pressure, and preventing loss. The ability of the fluids to perform depends on the fluid rheology, and, typically, flow properties are optimized for a specific function. Mechanical rheometers are used extensively in the industry to measure fluid rheology, but, for a number of reasons, these rheometers often fail to obtain accurate measurements. We propose that the problems involved with using mechanical rheometers can possibly be addressed by passive microrheology. More importantly, passive microrheology is intrinsically noninvasive, making it ideal for fragile samples. It enables quiescent rheology measurement for samples in which gelation kinetics can be affected by shear. Microrheology has also been proposed as a high-throughput tool for sample screening. Despite the great promise of microrheology, this method has not been systematically studied to explore possible applications for oilfield fluids. In this study, we applied diffusing wave spectroscopy (DWS) for microrheological tests on three typical stimulation fluids: gelation kinetics of crosslinked guar derivatives, gel-breaking kinetics of linear guar with a breaker, and gelation kinetics of interpolymer complexes. For crosslinked guar, the result shows crossover between  $G'$  and  $G''$  during the aging of the sample, indicating transition from sol to gel. For gel breaking, a steady decrease of modulus is observed, and the breaking kinetics are controlled by the concentration of the breaker. For interpolymer complexes, the dependence of gelation kinetics on pH is well captured by passive microrheology: the crossover of  $G'$  and  $G''$  shifts to shorter times as fluid pH increases. The experiments validate microrheology as a means of tracking gelation kinetics and the gel-breaking process. Moreover, the DWS method can be used as a facile approach for rheological measurements.

Wednesday 6:05 Atrium/Harborview

PO117

### **Application of the Electro-Magnetically Spinning (EMS) viscometer**

Masanori Yasuda<sup>1</sup>, Peter Wyss<sup>1</sup>, Taichi Hirano<sup>2</sup>, and Keiji Sakai<sup>2</sup>

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Viscosity is one of the important mechanical properties of liquid materials, especially when they are used for the industrial applications. Up to now, various kinds of viscometers have been proposed, among which rotational type viscometers are most widely used. In rotational viscometers, a shear deformation is introduced by a rotor, and the relation between the rotational speed of the rotor and the applied torque gives the viscosity.

However, some problems to be settled remain; one of the most troublesome problems in conventional viscometers is that the probe rotor is in direct contact with the sample. Operators must thus clean the rotor before/after every measurement. To solve these problems, we have developed a new viscometer which employs the Electro-Magnetically Spinning (EMS) technique. In this technique, torque is applied in a non-contact manner to a metal sphere probe. The probe is immersed in a liquid sample in a sample cell sealed by a cap. A rotating magnetic field is applied to the probe, which generates an eddy current in the probe and the Lorentz interaction between the current and the magnetic field applies torque to the probe. Then the probe spins following the rotation of the magnetic field. By measuring the rotational speed of the probe sphere with laser light scattering technique, we can determine the sample viscosity. The sample can be confined in an isolated sample cell and, therefore, the system is completely free from contamination. The EMS viscometer has unique features distinct from conventional viscometers. It is suitable for a wide range of viscosity in the order of  $10^{-4}$  up to  $10^3$  Pa·s or higher. The required sample volume is only 0.3 ml. We introduce some applications of rheology measurements using the EMS viscometer, including the observation of the hardening process of adhesives, the accurate determination of the critical anomaly around the phase transition of liquid crystals, and the melting process of inorganic glasses.

Wednesday 6:05 Atrium/Harborview

PO118

### **The Wilhelmy balance rheometer**

Joseph R. Samaniuk and Jan Vermant

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We present an analysis of a modern Wilhelmy balance that can be used to correct raw oscillatory data to report dynamic, dilatational rheological material functions of complex fluid-fluid interfaces. Making accurate dilatational rheological measurements of fluid-fluid interfaces is necessary for a full understanding of interfacial rheology, but these measurements have proven more challenging than those for interfacial shear rheology. A number of devices and techniques have been developed to make dilatational measurements at interfaces, including the pendant drop technique, and the capillary-stress tensiometer, but there are still concerns about the effects of surface curvature in these techniques and contributions from bulk flow. A Wilhelmy balance can be used in a Langmuir trough where surface curvature is not a concern, and the current widespread use of the Wilhelmy balance for making thermodynamic measurements of interfacial tension means that dilatation measurements are accessible to interface-science laboratories with no additional equipment.

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

Wednesday 6:05 Atrium/Harborview

PO119

### **Development of electro-magnetic rheology spectrometer**

Keiji Sakai, Miki Hirano, Yusuke Matsuura, and Taichi Hirano

*Institute of Industrial Science, University of Tokyo, Tokyo, Japan*

We developed a new type of viscometer, which enables completely remote measurement of the viscosity under an isolated environment. The principle of the measurement is based on the electro-magnetically driving technique of the probe rotor in the sample, which was originally developed by us and has already been applied to the commercially available EMS viscometer. A temporally modulated magnetic field is generated by the rotation of the magnets placed underneath the sample cell. A probe rotor is an aluminum disk supported by the center rod, which is immersed in the sample. An electrical current is induced in the metal probe disk by the modulation of the magnetic field and the Lorentz interaction between the magnetic field and the induced currents drives the disk to rotate following the motion of the magnetic flux. The rotation of the probe disk is recorded by a video camera and its angular velocity is obtained by the computer image analysis. The shear rate dependence of the viscosity is obtained by measuring the rotational speed of the probe disk changing the driving torque. The viscosity probe is a flat disk and the configuration is the same as that of the parallel plate viscometer, however, we employed a new method of analyzing the flow curve, in which we convert the apparent relation between the applied torque and the rotational speed of the disk to the true flow curve through the numerical operation. The experimental flow curves obtained for the standard sample of the shear thinning showed very good agreement with those given by the conventional viscometer equipped with a cone plate viscosity probe. The accuracy of the measurement is better than 1 % for the viscosity of pure water and the range of the viscosity is from 0.1 mPa·s to 100 Pa·s. A remarkable feature of the system is that the probe and the sample container are disposable, therefore, the system would be a powerful tool for the use in the medical and biological fields, in which the contamination to/from the sample would be a serious problem.

Wednesday 6:05 Atrium/Harborview

PO120

### **Fluidized bed rheology**

Denis Schütz<sup>1</sup>, Elke Riedl<sup>1</sup>, and Gina Paroline<sup>2</sup>

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Granular media, bulk solids, and, in particular, fluidized beds are complicated. However, suspension rheology and the rheology of fluidized beds share certain similarities such as classification as two-phase systems and the complex interplay between particle-particle interaction, bulk viscosity of the non-solid phase, and the frictional and collisional parts of the solid phase. Despite the difficulty, characterization of powder flow is necessary for proper process design, quality control of the powders themselves, and especially for proper reactor design and other fluidized bed applications. The presented work introduces a novel experimental design based around a high precision air bearing rheometer for characterization of basic powder properties, such as cohesion strength, as well as True Powder Rheology in a fluidized state which enables rotational and oscillatory tests augmented through the use of a classical pressure drop device. Data presented includes powder flow characterization in fluidized as well as consolidated states.

Wednesday 6:05 Atrium/Harborview

PO121

**A new dielectric-rheoSANS Instrument for simultaneous characterization of flow-dependent conductivity and microstructure of semi-solid flow battery electrodes**Jeffrey J. Richards<sup>1</sup>, Paul Butler<sup>1</sup>, and Norman J. Wagner<sup>2</sup><sup>1</sup>NCNR, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States; <sup>2</sup>University of Delaware, Newark, DE 19716, United States

Semi-Solid Flow Batteries (SSFBS) have the potential to serve as a high energy density, scalable grid-scale storage technology. Current implementations of this technology utilize carbon black in the liquid electrodes alongside the redox active particulates to render the fluids conductive. While the carbon black additive provides the necessary electrical, it has a detrimental effect on the flowable electrode's rheological properties. A fundamental understanding of the relationship between viscosity, microstructure, and conductivity is necessary before SSFB electrolytes can be formulated with the desired conductivity and rheological properties. In order to establish these relationships, we have developed a new rheoSANS instrument at the NCNR capable of performing simultaneous dielectric measurements. The combination of these three simultaneous measurements opens up the possibility to not only monitor the DC conductivity of the suspension while performing steady state flow experiments, but also to perform frequency dependent dielectric measurements at the same time as the microstructure is measured via neutron scattering. With appropriate modelling tools, we show it will be possible to relate the rheological and conductivity of these suspensions, measured under flow, to the microstructure.

Wednesday 6:05 Atrium/Harborview

PO122

**Design with rheologically-complex materials via material function design targets**R. E. Corman<sup>1</sup>, Lakshmi Rao<sup>2</sup>, N Ashwin K. Bharadwaj<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, Urbana, IL, United States

Rheologically-complex materials are described by function-valued properties with dependence on a timescale (linear viscoelasticity), input amplitude (nonlinear material behavior), or more generally both (nonlinear viscoelasticity). This complexity presents a difficulty when trying to utilize these material systems in engineering designs. Here, we describe a process to mathematically model and optimize design targets for linear viscoelastic systems, encompassing viscoelastic materials as well as one-dimensional spring-dashpot mechanical systems. We show that simple engineering design assumptions can be relaxed from a conventional spring-dashpot topology to a generalized linear viscoelastic relaxation kernel;  $K(t)$  for an extrinsic force-displacement relation, or the intrinsic stress relaxation modulus  $G(t)$  for viscoelastic material properties. With the relaxation kernel as the design variable, one can identify optimal viscoelastic properties agnostic to any specific material structure or spring-dashpot topology. This approach expands the design space, connecting the system-level performance with optimal material functions. Simplifying the relaxation kernel by the use of specific parameterizations for  $K(t)$  (e.g. Maxwell fluid model, critical gel model), allows for the use of basic optimization techniques. These early-stage design targets allow for broadly creative ideation of possible material solutions, which can then be used for either material-specific selection or later-stage design of novel materials.

Wednesday 6:05 Atrium/Harborview

PO123

**Dynamic mechanical analysis under controlled conditions of temperature and relative humidity**David A. Bohnsack

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Many types of industrially-significant materials exhibit hygroscopic behavior. In many cases, substantial material property changes can occur at ambient temperature and environmental humidity. Most commonly, water acts to plasticize materials, often decreasing the glass transition temperature to near or below ambient temperature. This interaction is particularly important to consumer products such as packaging materials and foodstuffs and may be reversible or irreversible. In other cases, atmospheric water may interact with specific chemistries to drive curing reactions, such as those in silicone sealants and adhesives.

Enhanced environmental control devices coupled with dynamic mechanical analysis allows for viscoelastic property measurements of many classes of materials under well-controlled temperature and humidity. This work demonstrates examples of humidity-controlled testing as applied to foods, packaging materials, and adhesive curing.

Wednesday 6:05 Atrium/Harborview

PO124

**Granular flow in two-dimensional silo with oscillating exit**Kiwing To and Hsiang Ting Tai

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The flow rate of grains out of a silo increases with the exit size  $d$ . If  $d$  is too small, an arch may form and blocks the flow at the exit. To recover from clogging, the arch have to be destroyed. Oscillating the exit mechanically is one simple way of destroying the arch. In this paper, we report the effect of oscillating the exit on the processes of clogging as well as recovery from clogging in two-dimensional silo equipped with movable exit. We measure the flow rate  $Q(d)$  and find that, in the presence of exit oscillation,  $Q(d)$  may remain finite even when  $d$  is only slightly larger than the grain diameter. Transition from continuous flow to intermittent flow occurs by decreasing  $d$  or by reducing the oscillation speed.



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## Plenary Lectures and Award Presentation

- Monday, October 12**  
8:30 AM, Constellation D-F  
**Rheological excursions in flatland: From monolayers to bilayers**  
Jan Vermant  
*Materials Science, ETH Zürich*
- Tuesday, October 13**  
*Bingham Lecture*  
8:30 AM, Constellation D-F  
**Slow dynamics of components in miscible polymer blends**  
Hiroshi Watanabe  
*Institute for Chemical Research, Kyoto University*
- Wednesday, October 14**  
8:30 AM, Constellation D-F  
**Flow in disordered systems: From simple fluids to athermal solids**  
Mark O. Robbins<sup>1</sup>, Joel Clemmer<sup>1</sup>, Vikram Jadhao<sup>1</sup>, and K. M. Salerno<sup>2</sup>  
<sup>1</sup>*Physics, Johns Hopkins University*; <sup>2</sup>*Sandia National Laboratory*
- Thursday, October 15**  
*Metzner Award Presentation*  
8:00 AM, Constellation A  
**The rheology and microstructure of carbon nanotube suspensions**  
Anson Ma  
*Institute of Materials Science, University of Connecticut*

## Social Program

- Sunday, October 11**  
**SoR Outreach Event**  
1:00 PM – 4:00 PM      Maryland Science Center
- ASTM-E37.08 Subcommittee on Rheology**  
3:00 PM – 4:00 PM      Constellation C (Meeting open to all.)
- Student/Industry Forum and Reception: *Careers in Rheology***  
4:00 PM – 6:00 PM      Starting in Constellation F  
*Sponsored by The Dow Chemical Company and American Institute of Physics*
- Welcoming Reception**  
6:30 PM – 8:30 PM      Foyer/Atrium  
*Hosted by TA Instruments*
- Monday, October 12**  
**Baltimore Aquarium Reception**  
7:00 PM – 9:30 PM      National Aquarium
- Tuesday, October 13**  
**Society Business Meeting**  
12:05 PM – 1:30 PM      Constellation C
- Awards Reception**  
7:00 PM – 8:00 PM      Foyer/Atrium  
*Sponsored by Xpansion Instruments*
- Awards Banquet**  
8:00 PM      Constellation D-F
- Wednesday, October 8**  
**Poster Session and Reception**  
6:05 PM – 8:00 PM      Atrium/Harborview  
*Sponsored by Anton-Paar USA*

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