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THE SOCIETY OF RHEOLOGY

92ND ANNUAL MEETING
PROGRAM AND ABSTRACTS

Cross Insurance Center
Bangor, Maine
October 10 - 14, 2021

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Meeting Schedule

Monday, October 11, 2021

	B5	*B7*	*MAB*	*MCD*	*B6*	*B1*	*VR*
8:30	M. J. Solomon (PL1) - *B567*						
9:20	Coffee Break						
9:50	SM1	AR1			SC1	GG1	OP1
10:15	SM2	AR2		AB2	SC2	GG2	OP1
10:40	SM3	AR3		AB3	SC3	GG3	OP1
11:05	SM4	AR4		AB4	SC4	GG4	OP1
11:30				AB5	SC5		OP1
11:55	Monday Boxed Lunch / Student-Industry Forum						
1:30		AR6	FE6	AB6	SC6	GG6	
1:55		AR7	FE7	AB7	SC7	GG7	
2:20		AR8	FE8	AB8	SC8	GG8	
2:45		AR9			SC9	GG9	
3:10	Coffee Break						
3:45	SM10	AR10	FE10	IN1	SC10	MC1	
4:10	SM11	AR11	FE11	IN2	SC11	MC2	
4:35	SM12	AR12	FE12	IN3	SC12	MC3	
5:00	SM13	AR13		IN4	SC13	MC4	
5:25		AR14		IN5	SC14	MC5	
5:50	End						

Tuesday, October 12, 2021

	B5	*B7*	*MAB*	*MCD*	*B6*	*B1*	*VR*
8:30	J. Vermant (PL2) - *B567*						
9:20	Coffee Break						
9:50		AR15	FE15		SC15	GG10	OP2
10:15		AR16	FE16	AB11	SC16	GG11	OP2
10:40	SM17	AR17	FE17	AB12	SC17	GG12	OP2
11:05	SM18	AR18	FE18	AB13	SC18	GG13	OP2
11:30	SM19	AR19		AB14	SC19	GG14	OP2
11:55	Lunch Break / Society Business Meeting						
1:30	SM20	AR20		AB15	SC20	GG15	
1:55	SM21	AR21		AB16	SC21	GG16	
2:20	SM22	AR22	FE22		SC22	GG17	
2:45	SM23	AR23	FE23		SC23		
3:10	Coffee Break						
3:45	SM24	AR24	FE24	IN6	MC6	RI1	
4:10	SM25	AR25	FE25	IN7	MC7	RI2	
4:35	SM26	AR26	FE26	IN8	MC8	RI3	
5:00	SM27	AR27	FE27	IN9	MC9		
5:25	End						
6:00	Awards Reception						
7:00	Awards Banquet						

Wednesday, October 13, 2021

	B5	*B7*	*MAB*	*MCD*	*B6*	*B1*	*VR*
8:30	P. M. Vlahovska (PL3) - *B567*						
9:20	Coffee Break						
9:50	SM29		AM1	IN11	SC24	GG19	OP3
10:15	SM30	AB20	AM2	IN12	SC25	GG20	OP3
10:40	SM31	AB21	AM3	IN13	SC26	GG21	OP3
11:05	SM32	AB22	AM4	IN14	SC27	GG22	OP3
11:30	SM33	AB23		IN15	SC28	GG23	OP3
11:55	Lunch Break						
1:30	SM34	AB24	AM6	IN16	RI6	GG24	
1:55	SM35	AB25	AM7	IN17	RI7	GG25	
2:20	SM36	AB26	AM8	IN18	RI8	GG26	
2:45	SM37	AB27	AM9	IN19	RI9	GG27	
3:10	Coffee Break						
3:45	SM38	AR29	AM10	IN20	SC29		
4:10	SM39	AR30	AM11	IN21	SC30		
4:35	SM40	AR31	AM12	IN22	SC31		
5:00	SM41	AR32	AM13	IN23	SC32		
5:25		AR33	AM14	IN24	SC33		
5:50	End						
6:30	Poster Session & Reception						
6:30	Gallery of Rheology Contest						

Thursday, October 14, 2021

	B5	*B7*	*B2*	*B3*	*B6*	*B1*
8:30	Q. Chen (MP1) - *B567*					
9:10	Transition Remarks - *B567*					
9:20	Coffee Break					
9:50	Gather.Town Networking for In-Person & Virtual Attendees					
11:55	End of Meeting					

Session and Room Codes

AB = Active and Biological Materials
AM = Additive Manufacturing and Composites
AR = Applied Rheology and Rheology Methods
FE = Foams, Emulsions, Surfactants, and Micelles
GG = Arrested Systems: Gels and Glasses
GR = Gallery of Rheology Contest
IN = Flow-induced Instabilities and Non-Newtonian Fluids
MC = Micro- and Nanofluidics and Confined Flows
MP = Metzner Presentation
OP = Online Program
PL = Plenary Lectures
PO = Poster Session
RI = Rheology and Mobility at Interfaces
SC = Suspensions, Colloids, and Granular Materials
SM = Polymers Solutions, Melts, and Blends
VP = Pre-recorded Flash Presentations
B1 = Ballroom 1
B1234 = Ballroom 1-2-3-4
B2 = Ballroom 2
B5 = Ballroom 5
B567 = Ballroom 5-6-7
B6 = Ballroom 6
B7 = Ballroom 7
B3 = Ballroom 3
MAB = Meeting Room A-B
MCD = Meeting Room C-D
VR = Virtual

Contents

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Ballroom 5-6-7 PL1

Manipulating the rheology of colloidal gels with embedded active matter

Michael J. Solomon
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The introduction of strong, short-range attractions between colloidal particles results in the formation of open, space-filling structures - colloidal gels - that have useful mechanical properties, such as elasticity and yield stress. Such gels appear in a broad range of industry sectors - from consumer products to pharmaceuticals. Gel microstructure, particularly at dilute concentrations, is furthermore a fascinating consequence of the interplay between phase separation and dynamical arrest. In these materials, local microscopic dynamics - as driven by thermal fluctuations and determined by the microstructure - are predictive of the gel's linear rheology. Here we address ways to control the rheology of colloidal gels by embedding a small amount of active matter into the gel networks. We investigate dilute gels with fractal cluster microstructure. The active colloids are Janus particles, which can be activated through addition of hydrogen peroxide. This fuel drives self-diffusiophoretic motion of the active colloids; this motion is, however, constrained by their interactions with other passive colloids in the gel network. We characterize the microdynamics and rheology of these gel networks and find that the embedded active matter has a surprisingly large effect on gel linear elasticity and yield stress. We seek explanation for the effects in the dynamical coupling between the embedded active matter and the passive particles of the gel. The results demonstrate how the mechanical properties of gel networks can be autonomously tuned by varying the number and activity of embedded active particles, a function potentially useful in industry applications. It also suggests open research questions about the interaction of the active and passive constituents of soft matter and the potential to exploit these interactions for rheological control and design.

Symposium SM
Polymers Solutions, Melts, and Blends

Organizers: Dimitris Vlassopoulos, Christopher Evans and Poornima Padmanabhan

Monday 9:50 Ballroom 5 SM1

Pressure drop measurements of Newtonian and non-Newtonian fluids in a hyperbolic channel

David F. James[1], Caitlin Roos[2], and Abhishek Tripathi[1]
[1]Mechanical & Industrial Engineering, Univeristy of Toronto, Toronto, Ontario M5S 3G8, Canada; [2]University of Toronto, Toronto, Ontario M5S 3G8, Canada

Measurements of pressure drop versus flow rate were made in a lengthy axisymmetric hyperbolic channel with a 60° conical entrance - the geometry designed to avoid an upstream vortex. Flows exited to the atmosphere. The test liquids were Newtonian fluids, Boger fluids, and concentrated polyethylene oxide solutions. Reynolds numbers were kept below 0.1 so that the only fluid properties were viscosity and elasticity. Measurements were made with two Newtonian fluids, and predictions were carried out analytically and numerically. All three agreed to within several per cent, validating the experimental technique. Measurements with four Boger fluids yielded pressure drops equal to Newtonian values, a result wholly contrary to the literature where measured values reached several times Newtonian values. The free jets at the exit swelled to twice the channel exit diameter, indicating significant elastic stresses in the channel. Why elasticity did not affect the pressure drop measurements is a mystery. Four aqueous solutions of PEO with concentrations of order 1% were prepared, and flow curves revealed ideal power-law characteristics. Pressure drops were predicted, based on viscosity alone, yielding values for inelastic versions of the solutions. The predictions agreed with pressure drop measurements at low flow rates. At a particular flow rate, the measurements for a solution began to rise above its inelastic values, similar to results in the literature for sudden contractions. The onset of die swell started at the same flow rate. Flow visualization with dye drops indicated a secondary motion upstream, which appeared with the onsets in the pressure drop and die swell.

Monday 10:15 Ballroom 5 SM2

Rouse model with fluctuating internal friction

Ramalingam Kailasham[1], Rajarshi Chakrabarti[2], and J. Ravi Prakash[3]
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Macromolecules in solution experience an additional mode of dissipation due to intramolecular interactions, over and above the solvent drag, which resists their conformational reconfiguration. This additional mode of dissipation termed as internal friction [1], has been known to significantly affect the conformational dynamics of chains [2] and the rheology of polymer solutions [3]. Coarse-grained polymer models for internal friction include a dashpot, in parallel with the spring, which captures the resistive force proportional to the time-rate of change of the connector vector between the beads. An exact solution to this model has so far been unavailable, except for the simplest case of a dumbbell, due to the coupling of bead velocities. By expanding the scope of an existing methodology [3] for velocity-decoupling, the exact set of governing stochastic differential equations for a bead-spring-dashpot chain with more than two beads, and its numerical solution using Brownian dynamics, is presented for the first time. This solution is used to: (a) obtain predictions for material functions in simple and oscillatory shear-flow, and (b) address the importance of fluctuations in modeling internal friction, given that the most widely used theoretical framework [4] for interpreting the effects of internal friction in biomolecules relies on a preaveraged treatment of the phenomenon. The inclusion of internal friction results in a non-monotonous variation of the viscosity with shear rate, with the occurrence of continuous shear-thickening following an initial shear-thinning regime. Furthermore, the neglect of fluctuations in internal friction is found to have consequences both at equilibrium and in the presence of a flow-field.

[1] C. W. Manke and M. C. Williams, Macromolecules 18, 2045 (1985).
[2] A. Soranno et al., Proc. Natl. Acad. Sci. U.S.A. 109, 17800 (2012).
[3] C. W. Manke and M. C. Williams, J. Rheol. 31, 495 (1988).
[4] B. S. Khatri and T. C. B. McLeish, Macromolecules 40, 6770 (2007).

Monday 10:40 Ballroom 5 SM3

A thermodynamically consistent model of polymer disentanglement under flow

Dolata E. Benjamin and Peter D. Olmsted
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We formulate a thermodynamically consistent constitutive equation modeling the stretch, orientation, and disentanglement of a polymer melt under flow. Most prior constitutive equations do not explicitly track the evolution of entanglements, rendering them unable to model physical phenomena such as the diffusion of entanglements across the interface during the welding of polymer filaments in additive manufacturing processes. We overcome this limitation by developing explicit coupled evolution equations for the tube conformation and number of entanglements. The conformation kinetic equation is inspired by the Rolie-Poly equation, and accounts for reptation, retraction and convective constraint release. The evolution equation for entanglements contains terms governing shear-induced disentanglement and re-entanglement via reptation. The shear-induced disentanglement is obtained by casting the Ianniruberto and Marrucci disentanglement mechanism into a thermodynamically consistent form. Prior theories assumed that the melt will re-entangle on the reptation time. In contrast, we obtain the re-entanglement mechanism by computing the random walk statistics of a chain in a fixed network of entanglements. We find that the melt will re-entangle faster at the chain ends than the center, leading to a re-entanglement time scale that is shorter than the reptation time. Model predictions for the stress and entanglement evolution are in good agreement with measurements from molecular dynamics simulations, and the computed re-entanglement time is consistent with structural measurements from those same simulations.

Monday 11:05 Ballroom 5 SM4

Revisiting nonlinear flow behavior of rouse chain: Roles of FENE, friction-reduction, and Brownian force intensity variation

Hiroshi Watanabe, Yumi Matsumiya, and Takeshi Sato
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The local elastic strength k, segmental friction coefficient z, and the Brownian force intensity B of polymer chains in melt are expected to change under fast flow. This study examined effects of those changes on rheological and structural properties of the Rouse model, the most frequently utilized model for unentangled melts. Specifically, Langevin equation of the Rouse model was solved with the decoupling and pre-averaging approximations to derive analytical expressions of nonlinear rheological properties and end-to-end stretch ratio of the chain under steady shear and extension. The expressions explicitly included non-equilibrium parameters rk, rz, and rB defined as the ratios of k, z, and B under flow to those at equilibrium, thereby offering a method of evaluating each of rk, rz, and rB from rheological and structural data under flow within the framework of those approximations. Data of extensional viscosity eta-E and relaxation rate of tensile stress decay coefficient d{etaE(-)}/dt reported for unentangled polystyrene melt (PS-27k; M =27.1k) and data of shear viscosity eta and first normal stress difference coefficient Y1 reported for PS-14k melt (M = 13.7k) were analyzed with this method to evaluate a rz/rk ratio under respective flow conditions. The rz/rk ratios thus obtained under extension and shear were found to exhibit the same dependence on the Weissenberg number Wi, given that Wi was reduced to an iso-local stretch state wherein the local elastic unit of the chain (Rouse spring) is stretched to the same extent under the extension and shear. The analytical expressions of the rheological properties also enabled a preliminary test of the behavior of rB of unentangled PS melts. This test posed a serious question about the relationships under fast flow often assumed in molecular models, rB = rz (proportionality between B and z not affected by flow) and rB = 1 (no flow effect on B).

Symposium AR
Applied Rheology and Rheology Methods

Organizers: Mubashir Ansari, Ruel Mckenzie and Jörg Läuger

Monday 9:50 Ballroom 7 AR1

The dynamics of parallel-plate and cone–plate flows

David C. Venerus and Anand U. Oza
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Rotational rheometers are the most commonly used devices to investigate the rheological behavior of liquids in shear flows. These devices are used to measure rheological properties of both Newtonian and non-Newtonian, or complex, fluids. Two of the most widely used geometries are flow between parallel plates and flow between a cone and a plate. A time-dependent rotation of the plate or cone is often used to study the time-dependent response of the fluid. In practice, the time dependence of the flow field is ignored, that is, a steady-state velocity field is assumed to exist throughout the measurement. In this study, we examine the dynamics of the velocity field for parallel-plate and cone-plate flows of Newtonian fluids by finding analytical solutions of the Navier-Stokes equation in the creeping flow limit. The time-dependent solution for parallel-plate flow is relatively simple as it requires the velocity to have a linear dependence on radial position. Interestingly, the time-dependent solution for cone-plate flow does not allow the velocity to have a linear dependence on radial position, which it must have at the steady state. Here, we examine the time-dependent velocity fields for these two flows, and we present results showing the time dependence of the torque exerted on both the stationary and rotating fixtures. We also examine the time dependence of spatial non-homogeneities of the strain rate. Finally, we speculate on the possible implications of our results in the context of shear banding, which is often observed in parallel-plate and cone-plate flows of complex fluids.

Monday 10:15 Ballroom 7 AR2

Probing 3D molecular orientation and alignment of flowing fluids by small-angle scattering

Peter H. Gilbert, Jack Rooks, Paul Butler, and Yun Liu
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Rheological properties of complex fluids depend on the orientation of macromolecules in solution. Thus, constructing the 3D molecular orientation distribution of macromolecules during shear allows for deeper understanding of the fluid's rheology. It is possible to view molecular and micelle orientation within a fluid by combining rheological methods with small-angle scattering (SAS) techniques, which has gained popularity in the past decade. In the case of small-angle neutron scattering (SANS), this combined-mode measurement is called RheoSANS. RheoSANS yields information on the traditional rheological properties of a fluid, while simultaneously providing data on the orientation and structure of macromolecules. This study aims to improve current RheoSANS analysis and measurement methods. Scattering patterns at different positions relative to the flow direction are used to create the 3D reciprocal space of scattering generated by oriented molecules. These are analyzed to extract orientation information. In addition, quantitative analysis methods of alignment, such as the commonly reported alignment factor, are investigated to understand their relationship with molecular orientation. Several different methods for determining this alignment factor are systematically evaluated and quantified. This work provides a framework to deepen our understanding of the quantitative meaning of alignment and the 3D orientation of flowing macromolecules.

Monday 10:40 Ballroom 7 AR3

A rheometer for high-solids, heterogeneous soils

Benjamin A. Appleby[1], Muhammad Ishaq[2], Jamal Rostami[2], and Joseph R. Samaniuk[1]
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In geotechnical engineering the movement and fluidization of soils is a challenge to study from a rheological perspective because soils are typically composed of highly heterogenous particle sizes, include large particles, and have exceptionally large moduli. Standard shear rheometers are capable of measuring fluids and soft solids but are impractical when viscosities exceed 100 Pa·s due to the need for either geometries with smaller surface areas, or torque transducers of a much larger capacity. This is a problem for soil materials like sands and clays that have effective viscosities surpassing 1000 Pa·s. Soil materials also include particle sizes at the millimeter scale and larger, that can match or exceed the measuring gaps of traditional geometries. Indexing-type mixing devices have been fabricated to measure torque-rotation rate relationships for soil rheological properties, but generally those devices are not calibrated to obtain rheological material functions such as viscosity and yield stress. In this presentation we describe the calibration of a custom-built soil mixer by obtaining an effective inner radius of the inner rotating geometry. With torque and rotation rate measured with a calibration fluid, the effective inner radius of the various mixing-impeller geometries can be calculated. These calibrations can then be used to estimate rheological material functions for soils. We will present the calibration of a single-flight auger geometry using calibration fluids of bentonite mud, and silicone oil, over shear-rates of 1 - 400 1/s. Details of the calibration, the rheological data of soils previously uncharacterized, and the significance for the geotechnical engineering community will be discussed.

Monday 11:05 Ballroom 7 AR4

Advancing towards thermal nonequilibrium rheometry

Ruel McKenzie
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Temperature fields can spatially modulate the hydrodynamics of complex fluids. Conductive heat flows by way of molecular motion. Heat and fluid flow properties are coupled through the temperature sensitivity of viscosity and the fluid susceptibility to viscously dissipate heat. We recently developed a tool that superimposes temperature fields unto shear fields to map the space of reciprocal effects in the presence of the two fields in a stress-controlled rheometer. The simultaneous action of momentum and heat flux is a widely found scenario in the processing and application of complex fluids. These fluxes are generally treated separately but their simultaneous occurrence can lead to fluid instabilities, fluctuations, time periodic or time evolutionary behavior. We are interested in the role of entropy production on the thermal nonequilibrium rheological behavior of complex fluids. Using our first-generation temperature superposition tool, we have begun to explore the capabilities of this system by investigating the thermal nonequilibrium rheological dynamics of a catanionic solution of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) in a deep eutectic solvent of choline chloride and glycerol. Here we present a preliminary understanding of our results thus far in terms of predicted models for the rheological behavior, scaling of the entropy production with regards to the Marangoni number (Ma), determining the heat flux susceptibility and conduction timescale with regards to the thermorheologically derived coefficients.

Symposium AB
Active and Biological Materials

Organizers: Sujit Datta and Danielle Mai

Monday 10:15 Meeting Room C-D AB2

Excess entropy scaling in active matter systems

S.Arman Ghaffarizadeh[1] and Gerald J. Wang[2]
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Active matter systems feature discrete particles that can convert stored or ambient free energy into motion. In order to realize the engineering potential of active matter, there is a strong need for predictive and theoretically grounded techniques to describe transport in these systems. In this work, we perform molecular-dynamics (MD) simulations of a model active matter system, in which we vary the total fraction of active particles ($0.2\le \phi \le0.9$) as well as the active particles' degree of activity. These simulations reveal a fascinating array of transport phenomena, including activity-enhanced diffusion coefficients. By adapting an existing result for binary (inactive) fluids, we demonstrate the existence of an excess entropy scaling relation in an active system. This relationship is well supported by our MD results, and establishes a new connection between transport (dynamics) and structure (statics) in active matter, a promising step for predictive and generalizable models of other transport phenomena in such systems.

Monday 10:40 Meeting Room C-D AB3

A front-back flow asymmetry controls locomotion dynamics in viscoelastic fluids

Shijian Wu[1], Kourosh Shoele[2], and Hadi Mohammadigoushki[1]
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Locomotion in viscoelastic fluids is critical for biological functions. Recent theoretical studies by multiple research groups have suggested that depending on the shape and flexibility of the swimmer, swimming in viscoelastic fluids can be enhanced or reduced compared to that of the Newtonian fluids. In this work, we provide a systematic experimental investigation on the effects of the helical swimmer shape (i.e., the pitch angle and tail thickness) on swimming dynamics in a Boger fluid using a combination of experiments and 3D simulations of the FENE-P model. The 3D printed helical swimmer is actuated in a magnetic field using a custom-built Helmholtz coil, and swimming speed and the detailed form of flow structure around the swimmer is obtained by particle tracking and particle image velocimetry. Our results indicate that at low pitch angles (i.e., p/11), the swimming speed is slower than the Newtonian fluid consistent with theoretical predictions. However, increasing the pitch angle beyond a critical threshold (>2p/9) leads to swimming speed enhancement in the Boger fluid. In addition, increasing the tail thickness gives rise to enhancement in the swimming speed, in apparent disagreement with the existing predictions. Furthermore, we have resolved the detailed form of flow structure around the helical swimmer. Interestingly, for the Newtonian fluid, the flow is characterized by front-back flow symmetry. However, for the viscoelastic fluid we observe a strong front-back flow asymmetry that is characterized by formation of a negative wake in the rear of the swimmer both in the experiments and 3D simulations of the FENE model. Our analysis indicates that for a swimmer that swims faster than the Newtonian fluid, the normalized front velocity is stronger than the flow in the wake (downstream) of the swimmer. Our results illustrate the importance of elasticity and the feedback loop that exists between the flow structure around the swimmer and the swimming dynamics.

Monday 11:05 Meeting Room C-D AB4

Self-propulsion of a freely suspended swimmer by a swirling tail in a viscoelastic fluid

Jeremy P. Binagia[1], Laurel Kroo[2], Manu Prakash[3], and Eric Shaqfeh[1]

[1]Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States; [2]Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, United States; [3]Department of Bioengineering, Stanford Univeristy, Stanford, CA 94305, United States

There has recently been a great deal of interest in developing novel propulsion methods that take advantage of non-Newtonian fluid behavior. In this talk, we present one such method that consists of two counter-rotating bodies of revolution of unequal size; while this swimmer shows no net translation in a Newtonian fluid under Stokes flow, it swims in the direction of the "larger" body or the "head" (suitably defined) when placed in a viscoelastic fluid. Because our proposed swimmer is both force- and torque-free, it is ideally suited for studying the motility of microorganisms swimming in complex biological fluids since many of these fluids are indeed elastic. Using a combination of numerical simulations and analytical theory, we make predictions for the swimmer's speed as a function of its geometry and the fluid's rheology. In particular, we find that in the limit of small Deborah (De) number (i.e. the relevant measure of how fluid elasticity), the speed is linear in De and in the concentration of polymer in the fluid. In regard to geometry, we show detailed results if the bodies are two unequal-size spheres and demonstrate that the swim speed is a non-monotonic function of the relative size of the two spheres, with speed being maximized for a size ratio of 0.75. Through an analysis of the forces acting on each sphere, we conclude that the swimmer generates thrust from a pressure imbalance across its body, created from fluid being convected radially inward by elastic hoop stresses. We then construct a mechanical swimmer with this geometry where the spheres are linked magnetically, and the motor in the "head" imposes a relative rotation velocity between the head and the tail. Indeed, the swimmer demonstrates no visible propulsion in a Newtonian fluid, but does indeed demonstrate propulsion in a highly elastic fluid. We conclude with comparisons of the numerically simulated propulsion speed and the experimental measurements.

Monday 11:30 Meeting Room C-D AB5

Life in a tight spot: How bacteria swim, disperse, and grow in complex spaces

Tapomoy Bhattacharjee, Daniel B. Amchin, Ricard Alert, Jenna A. Ott, and Sujit S. Datta

Princeton University, Princeton, NJ 08544, United States

Bacterial motility is central to processes in agriculture, the environment, and medicine. While motility is typically studied in bulk liquid or on flat surfaces, many bacterial habitats -- e.g., soils, sediments, and biological gels/tissues -- are complex porous media. Here, we use studies of E. coli in transparent 3D porous media to demonstrate how confinement in a heterogenous medium fundamentally alters motility. In particular, we show how the paradigm of run-and-tumble motility is dramatically altered by pore-scale confinement, both for cells performing undirected motion and those performing chemotaxis, directed motion in response to a chemical stimulus. Our porous media also enable precisely structured multi-cellular communities to be 3D printed. Using this capability, we show how spatial variations in the ability of cells to perform chemotaxis enable populations to autonomously stabilize large-scale perturbations in their overall morphology. Finally, we show how when the pores are small enough to prevent cells from swimming through the pore space, expansion of a community via cellular growth and division gives rise to distinct, highly-complex, large-scale community morphologies. Together, our work thus reveals new principles to predict and control the behavior of bacteria, and active matter in general, in complex environments.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Marie-Claude Heuzey, Sara Hashmi and Rahul Pandey

Monday 9:50 Ballroom 6 SC1

Linear viscoelastic properties of adhesive soft particle glasses

Ali Shahmohammadi and Roger T. Bonnecaze

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A model is presented to predict the linear viscoelastic rheology of hydrophobically modified adhesive soft particle glasses in an aqueous solution. The hydrophobes on the surfaces of particles in contact preferentially associate with each other creating an adhesive force between particles. The extent of this adhesive force depends on the number of associating or physically bonded hydrophobes and the strain on the bonds. The model is first presented for two horizontal surfaces with hydrophobes attached to them. The force required for oscillatory movement between these adhesive surfaces exhibits a Maxwellian behavior with a single relaxation time that is about the time for hydrophobe dissociation. The model is extended to predict the storage and loss moduli of adhesive soft particle glasses in ordered cubic lattices. In addition to the adhesive force, the particles also exhibit repulsive elastic and elastohydrodynamic interparticle forces. For situations where there is no adhesive force between particles, the storage modulus is independent of frequency, and the loss modulus is a linear function of frequency. The storage and loss moduli as functions of frequency are richer with adhesive forces. The storage modulus exhibits two plateaus, one at low and one at high frequency. The loss modulus exhibits a local maximum in frequency that occurs at approximately the dissociation rate of the hydrophobes.

Monday 10:15 Ballroom 6 SC2

Rheology of colloids bridged by telechelic polymers: Dynamics of transitions between loops and bridges

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In waterborne coatings consisting of colloids and rheology-modifying telechelic polymers, the polymer's hydrophobic endcaps, or "stickers," temporarily adsorb to the colloids' surfaces, forming loops (both endcaps on the same colloid) and bridges (endcaps on adjacent colloids). The rates at which the polymers transition between bridge and loop configurations influence the dynamic properties of the waterborne coatings. We predict the bridge-to-loop and loop-to-bridge transition times of telechelic polymers by approximating the colloids as flat surfaces and combining Brownian dynamics (BD) simulations and self-consistent field theory (SCFT). We show that the equilibrium information from SCFT can be used to obtain the ratio of the two transition times, so that only the faster bridge-to-loop time needs be calculated by BD simulations. This allows for investigation of rates ove a wider range of experimentally-relevant parameter spaces. BD simulations suggest that a common assumption, that the bridge-to-loop transition time is approximately equal to the time for a lone hydrophobic particle to desorb from a surface, is only valid for a combination of strongly binding stickers, and shorter chains, while in the opposite situation the transition time is dominated by the polymer relaxation time. The results obtained can be combined with colloidal particle simulations to predict the rheology of latex paint formulations.

Monday 10:40 Ballroom 6 SC3

Responsive yielding in soft capsule suspensions

Ryan Poling-Skutvik[1], Abhishek Dhand[2], Daniel Keane[1], and Chinedum Osuji[2]
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Control over the yield stress dictates the performance of complex fluids in applications ranging from 3D printing to therapeutics to consumer products. Here, we investigate the behavior of two different classes of soft colloids - porous microcapsules and emulsion droplets - and demonstrate control over the yield transition through the addition of polymers. The porous microcapsules are formed through the association of TEMPO-modified cellulose nanofibrils (CNF) and oleylamine at an oil-water interface under shear to encapsulate an aqueous internal phase. These capsules are then suspended in a density-matched solvent mixture consisting of toluene and chloroform. We incorporate poly(acrylic acid) (PAA) to the internal phase of these capsules, which leads to sticky interactions between the capsules. The emulsion system consists of cyclohexane droplets in water and stabilized by nonionic surfactants. To the emulsion suspension, we add a long-chain triblock polystyrene-polyethylene oxide-polystyrene (SEOS) polymer that bridges between droplets to form an elastic network. Both systems exhibit pronounced yield stresses that we control by changing the polymer concentration, volume fraction, and temperature. By comparing the different yielding behavior, we identify how the polymers induce a yield stress and control the recovery behavior of these systems. Additionally, we comment on the difference between physically (capsules) and chemically (emulsions) stabilized droplets on suspension rheology.

Monday 11:05 Ballroom 6 SC4

Rheological properties of phase transitions in polydisperse and monodisperse colloidal rod systems

Shiqin He[1], Dominic R. Pascucci[1], Marco Caggioni[2], Seth Lindberg[3], and Kelly M. Schultz[1]
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During manufacturing processes and product end-use, rheological modifiers can induce phase transitions. To design materials that undergo phase transitions, understanding the dynamic changes in rheology and microstructure is crucial. Colloidal rods are desirable rheological modifiers because they can tune rheology with small amounts of material. In this study, we characterize the rheological properties and microstructural changes of two colloidal rod systems used as rheological modifiers, polydisperse polyamide (PA) and monodisperse hydrogenated castor oil (HCO), during their phase transitions using multiple particle tracking microrheology (MPT). In MPT, Brownian motion of probes embedded in a sample is measured and related to rheological properties. Our systems consist of a colloid (PA or HCO), a surfactant (linear alkylbenzene sulfonate, LAS), and a non-absorbing polymer (polyethylene oxide, PEO) used to induce depletion interaction to drive gelation. Samples are characterized at different LAS:colloid. Measurement of probe diffusivity indicates that there is a change in microstructure when LAS:colloid is varied. Time-cure superposition (TCS) is then used to determine the critical values at different LAS:colloid. The critical relaxation exponent, n, is a measure of the material structure at the phase transition and is also dependent on LAS:colloid. n is higher for LAS:colloid>16, indicating loosely associated networks, than LAS:colloid=16, which indicates tightly associated networks. This is because the strength of the electrostatic force changes when LAS:colloid is varied. This changes the starting material structure and leads to different gel evolution. Our characterization determines that the rheology and microstructure at the phase transition of both systems depend on LAS:colloid. In addition, monodispersity and polydispersity does not affect gelation evolution. This work will inform future product design by providing guidance to specify desired rheology and minimize trial-and-error experiments.

Monday 11:30 Ballroom 6 SC5

High shear capillary rheology and flow birefringence of rod-like viruses

Steve Kuei[1], Paul Salipante[1], Ryan Murphy[2], Katie Weigandt[2], and Steve Hudson[1]
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Rod-like particles are commonly found in a variety of biologically and industrially relevant solutions, from biofilaments to worm-like surfactant solutions. Such solutions display complex thinning behavior after the application of shear, and there is an ongoing effort to understand the microstructural changes of these fluids and how these changes manifest in the resulting rheology. Using semi-dilute solutions of Fd bacteriophage as a model rod fluid, we use capillary microrheology and flow birefringence as platforms with which to capture high-shear rheological behavior while simultaneously measuring the fluid's microstructural state. We find that orientational order climbs across six decades of shear, reaching regions of shear thinning and rod alignment that surpass previously theorized limits, and are best described by dilute theories.

Symposium GG
Arrested Systems: Gels and Glasses

Organizers: Emanuela del Gado and Jyoti Seth

Monday 9:50 Ballroom 1 GG1

Time–connectivity superposition and the gel/glass duality of weak colloidal gels

Bavand Keshavarz[1], Donatien Gomes Rodrigues[2], Jean-Baptiste Champenois[2], Matt Frith[3], Jan Ilavsky[3], Michela Geri[1], Thibaut Divoux[4], Gareth H. McKinley[1], and Arnaud Poulesquen[2]
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Colloidal gels result from the aggregation of Brownian particles suspended in a solvent. Gelation is induced by attractive interactions between individual particles that drive the formation of clusters, which in turn aggregate to form a space-spanning structure. We study this process in aluminosilicate colloidal gels through time-resolved structural and mechanical spectroscopy. Using the time-connectivity superposition principle a series of rapidly acquired linear viscoelastic spectra, measured throughout the gelation process by applying an exponential chirp protocol, are rescaled onto a universal master curve that spans over eight orders of magnitude in reduced frequency. This analysis reveals that the underlying relaxation time spectrum of the colloidal gel is symmetric in time with power-law tails characterized by a single exponent that is set at the gel point. The microstructural mechanical network has a dual character; at short length scales and fast times it appears glassy, whereas at longer times and larger scales it is gel-like. These results can be captured by a simple three-parameter constitutive model and demonstrate that the microstructure of a mature colloidal gel bears the residual skeleton of the original sample-spanning network that is created at the gel point. Our conclusions are confirmed by applying the same technique to another well-known colloidal gel system composed of attractive silica nanoparticles. The results illustrate the power of the time-connectivity superposition principle for this class of soft glassy materials and provide a compact description for the dichotomous viscoelastic nature of weak colloidal gels.

Monday 10:15 Ballroom 1 GG2

State behavior and kinetics of alkali-activated aluminosilicate gels

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Cement production and use is one of the leading contributors to anthropogenic CO_2 emissions. Alkali-activated binders (AABs) present opportunities for significant reduction in CO_2 emissions, as well as in-situ resource utilization for lunar and Martian construction in support of human space exploration [1]. The chemical composition of these binders impacts macroscopic properties such as workability and strength, but further work is required to connect to the 'geopolymer' formation reaction and microstructure development. The rheological development with time and concentration is crucial for applications including traditional construction processes (pumping, pouring, setting) as well as additive manufacturing. A mechanistic and quantitative understanding of the chemical kinetics and dynamics of microstructure formation and associated rheology development in model AABs will facilitate the universal engineering of construction materials from a variety of aluminosilicate materials. The structure-property relationships of these gels have been characterized based on the equilibrium storage modulus, which scales as a function of chemical composition consistent across multiple formulations. Complementary scattering and NMR measurements give further insight to microstructural differences in these states [2]. Additionally, the evolution of the storage modulus over time is fit to kinetic models which give insight to the reaction mechanism and quantify the kinetics with respect to the chemical composition. These experimental findings are summarized via a new pseudo-ternary state diagram, which provides a composition roadmap for rheological properties of aluminosilicate gels and AABs in the literature [3].

1. M. Katzarova, J.N. Mills, N.J. Wagner. Adv. Sp. Res. 2021. In Review.
2. J.N. Mills, N.J. Wagner, P. Mondal, J. Am. Ceram. Soc. 104 (2021) 572-583. https://doi.org/10.1111/jace.17459.
3. J.N. Mills, P. Mondal, N.J. Wagner. Cem. Conc. Res. 2021. Submitted.

Monday 10:40 Ballroom 1 GG3

Gel and glassy states in macro- and nano-emulsions in the presence of micellar depletion attraction

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In this work, we measure the rheological properties of oil-in-water emulsions with different droplet sizes from macro- to nanoscale and within 35%-65% volume fractions in the presence of depletion attraction. The experimental results have been discussed by considering the available theoretical models for the van der Waals, electrostatic, and depletion interdroplet interactions. At constant surfactant concentration, the depth of attractive potential is much higher than kT for macroemulsions, whereas it is on the order of thermal energy for nanoemulsions. Thus, as the droplet size decreases in systems with considerable yield stress below jamming transition, the emulsions undergo a gel-to-glass transition. A model is proposed to describe the yield stress in attractive glass and gel regimes by considering contributions from Brownian motion and interaction between droplets.

Monday 11:05 Ballroom 1 GG4

Multi-staged progression of the viscoelastic moduli during gelation of Aiyu pectin

Yeng-Long Chen[1], Fan-Wei Wang[1], Michela Geri[2], Yun-Ru Chen[1], Jung-Ren Huang[1], and Gareth H. McKinley[2]
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Aiyu is an edible gel dessert made from the extract obtained by washing the seeds of Ficus Pumila var. Awkeotsong, uniquely cultivated in Taiwan. Water is the only component needed in order to make the gel at room temperature. The main gelation components are ions, low methoxyl pectin, and methoxylesterase enzyme. The multivalent ions, in particular calcium, crosslink with pectin polymers to form an elastic network.

During gelation, we observed an inflection point in the storage modulus together with a corresponding frequency-dependent maximum and subsequent plateau in the loss modulus. We characterized the rheological and microstructural evolution with Optimal Window Chirp rheometry (OwCh) and conventional oscillatory shear time sweeps, as well as microstructural characterization with cryo scanning electron microscopy.

Many calcium pectate systems have crosslinks formed by consecutively bonded calcium junction zones, but the length of the junction zones vary from system to system. By considering the reaction kinetics model of a microstructural transformation from transient, short junction zones to longer, more stable junction zones, we developed an ideal rubber network model that captures the characteristics of the viscoelastic moduli progression and their dependence on salt and calcium concentration.

Symposium OP
Online Program

Organizers: Anne M. Grillet and Marie-Claude Heuzey

Monday 9:50 Virtual OP1

Online discussion: Session 1

Anne M. Grillet[1] and Marie-Claude Heuzey[2]
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Online discussions will be broken up into two topics each day. Each group will start with a full-length (20 minute) virtual keynote presentation then authors of flash presentations will be allowed 10 minutes to provide a quick (3 minute) overviews of their key findings followed by questions and discussion with the audience.

Monday:
- Polymer: melts, composites and AM
- Glasses, gels and networks

Lists of each discussion group, keynote and list of flash presentation authors as well as zoom links will be provided by October 1st.

Monday Afternoon

Symposium SM
Polymers Solutions, Melts, and Blends

Organizers: Dimitris Vlassopoulos, Christopher Evans and Poornima Padmanabhan

Monday 3:45 Ballroom 5 SM10

Dynamic dilution in bidipserse ring polymer melts

Thomas C. O'Connor[1], Jan Smrek[2], and Gary S. Grest[3]
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Ring polymers exhibit many unique linear and nonlinear rheological behaviors that could enable new material applications. However, most knowledge of ring polymer rheology is limited to monodisperse melts, while the most scalable methods for making ring polymers produce melts with high dispersity. Here, we begin to explore the rheology of disperse rings with molecular simulations of bidisperse melts of unconcatenated ring polymers. We characterize the linear viscoelasticity and polymer diffusion of an ensemble of melts with 50-50 volume fractions of long rings (N/Ne=14) and short rings of various molecular weights. We observe that all rings contribute similarly to the stress relaxation at times shorter than the short-ring relaxation time. At longer times, the diffusing short rings act as a solvent, dynamically diluting long rings. This is verified by direct comparison of simulated ring-ring blends to simulated ring-oligomer solutions. We show that the viscoelasticity of long rings can be described by Fractal-Loopy-Globule dynamics with a fundamental loop size that swells dynamically as short rings diffuse.

Monday 4:10 Ballroom 5 SM11

Entanglement kinetics during interrupted orthogonal shear flow

Peter D. Olmsted[1], Marco Galvani Cuhna[2], and Mark O. Robbins[3]
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Both entangled and unentangled polymer melts exhibit stress overshoots when subject to shearing flow. The size of the overshoot depends on the applied shear rate and is related to relaxation mechanisms such as reptation, chain stretch and convective constraint release. Previous experimental work shows that melts subjected to interrupted shear flows exhibit a smaller overshoot when sheared after some relaxation. The time scale for recovery of the maxima is about the timescale for relaxation of the stress for unentangled chains but is significantly longer for entangled chains. This is attributed to changes in the entanglement structure of the melt due to the applied flow, and the Rolie-Poly model (among others) has been used to show this behavior is consistent with tube theory. Here, we show results of molecular dynamics simulations of interrupted shear of polymer melts where the shear flow after the relaxation stage is orthogonal to the original applied flow. We observe that the size of the stress overshoot is larger than predictions by the Rolie-Poly model, and larger than observed during a second shear in the same direction as the original for the same relaxation time. Differences in maxima are also observed for overshoots in the first normal stress and chain end-to-end distance, as well as in minima for undershoots in the second normal stress and in the number of entanglements per chain as measured with standard computational tools.

Monday 4:35 Ballroom 5 SM12

Diffusion of thin nanorods in polymer melts

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The diffusion of monomerically thin nanorods in polymer melts are studied by molecular dynamics simulations. We focus on the systems where chains are long enough to screen the hydrodynamic interactions such that the diffusion coefficient D_{parallel} for the direction parallel to the rod decreases linearly with increasing rod length L. In unentangled polymers, the diffusion coefficient for the direction normal to the rod exhibits a crossover from $D_{\mathrm{perpendicular}} \sim L^{-2}$ to $D_{\mathrm{perpendicular}} \sim L^{-1}$ with increasing L, corresponding to a progressive coupling of nanorod motion to the polymers. Accordingly, the rotational diffusion coefficient $D_R \approx D_{\mathrm{perpendicular}} L^{-2} \sim L^{-4}$ and then $D_R \sim L^{-3}$ as L increases. In entangled polymers, $D_{\mathrm{perpendicular}}$ and D_R are suppressed for L larger than the entanglement mesh size *a*. $D_{\mathrm{perpendicular}} \sim L^{-3}$ and $D_R \sim L^{-5}$ for L sufficiently above *a* in agreement with de Gennes' rod reptation model.

Monday 5:00 Ballroom 5 SM13

Exploring the origins of the distinct relaxation times measured in shear and extensional rheometry for concentrated polymer solutions

Jianyi Du[1], Hiroko Ohtani[2], Kevin Ellwood[2], and Gareth H. McKinley[1]
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Concentrated polymer solutions exhibit distinct rheological properties from their dilute counterparts, due to the enhanced importance of inter- and intramolecular interactions. A number of previous experimental studies have reported notably lower extensional relaxation times obtained from capillary breakup extensional rheometry than those from steady or oscillatory shearing flows. However, the origin of such differences has not been considered in depth, and a physical model that incorporates the structural complexity of entangled polymer systems is absent, hampering the extraction of accurate constitutive parameters from experiments. To address this limitation, we analyze the capillarity-driven thinning dynamics of entangled polymer solutions described by the Doi-Edwards-Marrucci-Grizzuti model and the Rolie-Poly model. Both models incorporate the key features of polymer reptation and contour length fluctuation, while differing slightly due to convective constraint release. Numerical calculation of the filament thinning profiles for parameters representative of entangled systems reveals three distinct regimes of dynamics: a long initial tube-reorientation regime, followed by a brief intermediate elasto-capillary regime, and finally a finite-extensibility regime very close to the pinch-off singularity. An apparent extensional relaxation time obtained from fitting the elasto-capillary regime using an exponential-thinning formula gives values close to half the Rouse time of the entangled chains. By contrast, the much longer disengagement time controlled by the tube reorientation dynamics sets the filament lifetime, as well as the rheological responses in shear flow. Finally, we develop a universal expression with no additional fitting parameters for the ratio of the shear and extensional relaxation times. This formula, expressed as a function of the number of entanglements and the polymer concentration, agrees well with available experimental data from previous studies for a range of entangled polymer solutions.

Symposium AR
Applied Rheology and Rheology Methods

Organizers: Mubashir Ansari, Ruel Mckenzie and Jörg Läuger

Monday 1:30 Ballroom 7 AR6

In-vitro cell-on-cell dry eye model incorporating normal stress control

Philipp Baumli, Chunzi Liu, Maggie Braunreuther, and Gerald G. Fuller
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On the human ocular surface epithelium, significant friction and shear forces occur due to eyelid blinking and contact lens wear. As a result, protein-deficiency-caused dry eye conditions lead to frictional damage, discomfort, visual disturbance, and damage to the ocular surface. We aim to contribute to the understanding of protein-deficiency-caused, more specifically mucin-deficiency-caused, dry eyes. We have developed a refined in-vitro cell-on-cell dry eye model that considers and can actively tune variation in the normal load encountered by corneal epithelial cells and conjunctival cells during the blinking movement. We have developed a new instrument based on the Live Cell Rheometer (LCR) to subject stratified cell layers of corneal epithelial cells in contact with layers of conjunctival cells to varying physiologically relevant normal loads. The normal stress modes which we work with are steady-state compression, step compressions, and oscillatory compression. The feature of varying normal load is essential since the normal loads and stresses encountered in the eye differ from patient to patient. Protein-deficiency-caused dry eye conditions are mimicked by inducing mucin-deficiency of corneal and conjunctival cells via treatment with mucin-selective protease. This new instrument provides averaged compression properties of cell layers. We quantify the effect of mucin-deficiency on layers of corneal epithelial and conjunctival cells in-situ and benchmark our results against more severe conditions such as actin knockout conditions, which more strongly impair the integrity of the cell layers.

Monday 1:55 Ballroom 7 AR7

Gaborheometry: Applications of the Gabor transform to time-resolved oscillatory rheometry

Joshua David John Rathinaraj and Gareth H. McKinley
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Oscillatory rheometric techniques are widely used for rheological characterization of the viscoelastic properties of complex fluids. However, in a mutating material the evolution of microstructure is commonly both time- and shear-rate dependent, and thixotropic phenomena are observed in many complex fluids. Application of the Fourier transform for analyzing oscillatory data assumes the signals are *time-translation invariant* which constrains the mutation number of the sample to be extremely small. This constraint makes it difficult to accurately study shear-induced microstructural changes in thixotropic and gelling materials. In this work, we explore applications of the Gabor transform (a Short Time Fourier Transform (STFT) combined with a Gaussian window) for providing optimal time-frequency resolution of the viscoelastic properties of a mutating material. First, we show using simple models that application of the STFT enables extraction of useful data from the initial transient response following the inception of oscillatory flow. Secondly, using measurements on a Bentonite clay, we show that a Gabor transform enables us to more accurately measure rapid changes in the complex modulus and also extract a characteristic thixotropic/aging time scale for the material. Finally, we consider extension of the Gabor transform to non-linear oscillatory deformations using an amplitude-modulated input signal, in order

to track the evolution of the Fourier-Tschebyshev coefficients characterizing a thixotropic fluid. We refer to the resulting test protocol as Gaborheometry and construct an operability diagram in terms of the imposed ramp rate and the mutation time of the material. We show that there is a trade-off between frequency and time resolution (effectively a rheological uncertainty principle!). This unconventional, but easily implemented, rheometric approach facilitates both SAOS and LAOS studies of time-evolving materials, reducing the number of experiments and the data post-processing time significantly.

Monday 2:20 Ballroom 7 AR8

High throughput microrheology: A path to rapid phase diagram and formulation mapping

Yimin Luo[1], Mengyang Gu[2], Yue He[2], Chelsea Edwards[1], Matthew E. Helgeson[1], and Megan Valentine[3]
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Differential dynamic microscopy (DDM) combines the real-space resolution of microscopy and the ensemble sensitivity of scattering and has emerged as a promising tool to track the dynamic evolution of complex fluids. In DDM, image pair differences are ensemble averaged and analyzed in Fourier space through the image structure function D(q,?t), which encodes material functions including the intermediate scattering function and mean-squared displacement, without the need for particle tracking. The method boasts easy experimental setup, sensitivity to weakly scattering samples, applicability to scenarios where tracking is onerous or impossible, and offers a path to fully automated analysis. However, DDM analysis currently suffers from drawbacks associated with slow computation, lack of error quantification and robustness issues. We present a statistical approach by rigorously deriving the noise term, which arises due to imaging artifacts, and resampling through Gaussian Process Regression. As a result, a mere 1% of the original computation needs to be carried out at strategically selected design points, greatly improving the computational efficiency to near real time. We further extend DDM microrheology to more rigid materials where small displacement of probes limits the resolution of DDM relative to multiple particle tracking. These advances make possible truly automated microrheology characterization of material systems over a wide formulation space, which we demonstrate using a case study involving mixed polyelectrolyte solutions that undergo liquid-liquid phase separation (coacervation) at different polymer and salt concentrations. We show how coupling DDM microrheology with imaging in situ during phase separation enables identification of phase boundaries, partitioning of salt and polymer in the emerging phases, and rheological measurements of dense phase droplets. The high throughput measurements and analysis enabled by this method serve as a critical link for the materials discovery and inverse design.

Monday 2:45 Ballroom 7 AR9

In-situ microrheology of drying paint

Maria C. Roffin[1], Christopher L. Wirth[2], Steven V. Barancyk[3], Reza M. Rock[3], Andy Surface[3], and James F. Gilchrist[1]
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Paint formulation and drying conditions have a strong influence on the final performances of the coating, yet there are few measurable variables between the formulation stage to the final film performance. The fast drying of thin films of paint, such as those used in automotive coatings, results in higher potential for fluid instabilities that often lead to defect formation in the final coating. The rheological properties of paint prior to and during drying is key in understanding the transition from a fluid coating to a solid film and is necessary for defining the connection between formulation and drying conditions, defect formation, and consequently the final paint performance. Passive microrheology, tracking the Brownian motion of passive tracers in the fluid, is used to characterize the properties of coating formulations in both quiescent liquids and during drying where the evaporative flux can cause partitioning and even strong Marangoni stresses that result in internal convection, leading to superimposition of the fluid kinematics on the random fluctuations of the probe particles. In this work, we implement a de-drifting algorithm to subtract the substantial influence of convection, allowing us to probe the time-evolved rheological properties of a drying film, by removal of the convective component of the initial measured particle Mean Square Displacements. We test thin films of model automotive paints in both the quiescent state and during drying in a range of different conditions, such as composition, molecular weight and polymer concentration. The local shear thinning resulting from drying-induced convection directly influences the local rheology and final behavior of the final coating.

Monday 3:45 Ballroom 7 AR10

Practical rheological investigation of industrial soft solids

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Soft solids may be defined as materials that flow after yielding. Industry uses various practical tests for classifying soft solids such as greases and numerous foods. Some provide simple quality control or quality assurance screening. Methods often are meant to simulate actual use conditions. There are variations in rheological techniques used to analyze these typically highly non-Newtonian materials. Rotational and oscillatory rheometry, as well as texture analysis - often involving compressive and/or tensile deformation modes - provide different insights into the product behavior. Data are presented and discussed herein for a few different methods used to test commercial materials.

Monday 4:10 Ballroom 7 AR11

Three-dimensional technique for measuring sag in drying coatings

Marola W. Issa[1], Hairou Yu[1], Maria C. Roffin[2], James F. Gilchrist[2], Steven V. Barancyk[3], Reza M. Rock[3], and Christopher L. Wirth[1]

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Coatings are found in nearly every aspect of modern society including architectural, automotive, and consumer goods applications. Undesired coating defects often arise during the flash stage of the coating application process which constitutes the roughly 10-minute interval immediately following spray application for automotive coatings. Fundamental understanding of the transient rheology of these systems is essential for predicting and avoiding defects such as sag. Sag refers to excessive gravity-driven flow that can occur following coating application, resulting in a nonuniform surface texture and visually undesirable appearance. We used a new technique, called Variable Angle Inspection Microscopy (VAIM), to non-invasively measure flow through the volume of an arbitrarily oriented thin film. Initial benchmarking measurements in the absence of drying tracked the velocity of silica probe particles in ~140 µm thick films of known viscosity, much greater than water, at incline angles between 5° and 10°. Probe particles were tracked at speeds as high as ~100 µm/s deep into the film. The sag flow field was well-resolved in ~10 µm thick slabs and in general the VAIM measurements were highly reproducible. Complementary profilometer measurements of film thinning were utilized to predict sag velocities with a known model. The model predictions show excellent agreement with our measurements, which validates the effectiveness of this new method in relating material properties and flow regimes. Thereby, this work will assist in accelerating formulation efforts including the development of energy efficient coating systems for automotive applications.

Monday 4:35 Ballroom 7 AR12

Active probe rheology simulations: General formalism and applications

Pouria Nourian, Rafikul Islam, Dinesh Sundaravadivelu Devarajan, and Rajesh Khare

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We have developed a molecular simulation analogue of the experimental active bead microrheology technique. In the first part of the presentation, the governing equations of the technique will be presented along with a dimensionless formalism [1] that discusses the relative importance of the different physical effects that dictate the viability of the technique. Eight conditions are identified that must be satisfied for the success of the technique, some of these conditions are applicable to both experimental and computational implementations of probe rheology, while others are specific to simulations. The formalism is illustrated by application to determining the viscoelastic properties of a weakly entangled polymer melt system.

A potential advantage of probe rheology over bulk rheology is its ability to measure the local values of the rheological properties. The second part of the presentation will focus on the application of the active probe rheology technique for the evaluation of the local viscoelastic properties of complex materials. Results will be presented for two systems: a polymer melt system with a gradient in temperature and a colloidal suspension system with a gradient in volume fraction. Our results demonstrate that probe rheology can successfully determine the local values of the viscoelastic moduli of the two systems. The results will be discussed in terms of the interplay of the different length scales involved in these systems.

References:

[1] Nourian, P.; Islam, R.; Khare, R.; "Implementation of active probe rheology simulation technique for determining the viscoelastic moduli of soft matter", Journal of Rheology, in press.

Monday 5:00 Ballroom 7 AR13

Volatile dripping-onto-substrate (vDoS) extensional rheometry of polymeric fluids

Benjamin P. Robertson and Michelle A. Calabrese

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Extensional flows of volatile, low-viscosity polymeric fluids are important in applications from spraying and roll-coating processes to fuel injection. Traditional extensional rheometers like the capillary breakup extensional rheometer (CaBER) are severely limited in their capability to study these fluids, due to their rapid breakup on the order of the plate separation time, inertial effects from pre-deformation, and solvent evaporation.[1] The recently-developed dripping-onto-substrate (DoS) rheometry[2] technique allows for measurement of lower viscosity samples in a single drop, reducing the use of expensive sample components and minimizing pre-deformation. However, the small drop volume exacerbates evaporation effects when volatile solvents are used, limiting the efficacy of DoS for measuring polymeric fluids formed in organic solvents. To address these challenges, we developed an environmental control chamber to substantially reduce the rate of evaporation in volatile DoS (vDoS) extensional rheometry. Using this system, we measure the extension of dilute solutions of high molecular weight PEO in several solvents of varying volatility and quality. By comparing parameters extracted from vDoS, including extensional relaxation time, at varying rates of evaporation, we validate this promising rheometric technique for use in a wider range of systems of interest.

[1] Rodd, L. et al. Appl Rheol, 15.1 (2005): 12-27. [2] Dinic, J. et al. ACS Macro Lett, 4 (2015): 804-808.

Monday 5:25 Ballroom 7 AR14

Macromolecular engineering of rheology and pinching dynamics of formulations

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The current state-of-the-art practice in macromolecular engineering of formulations is to rely on the characterization of response to shear flow, with velocity gradients perpendicular to flow direction, for evaluating and understanding the influence of macromolecules on stability, rheology and processability, and applications. Understanding shear rheology response has direct relevance to control of flows through channels as well as drag flows near moving solid surfaces. However, streamwise velocity gradients associated with extensional flows often arise during processing of formulations, but unlike shear rheology, measurement of extensional rheology response has remained a longstanding challenge. In particular, dispensing and liquid transfer to substrates by dripping, jetting, or spraying involve capillarity-driven pinching of liquid necks with strong extensional flows, and most conventional techniques fail to emulate the deformation history and strain rates, or are unsuitable for characterizing low viscosity, low elasticity fluids. In this contribution, we show dripping-onto-substrate (DoS) rheometry protocols help to address these characterization challenges. We demonstrate that characterization of pinching dynamics and extensional rheology response allows a comprehensive examination of interactions between macromolecules in presence of associative groups/molecules or particles, and consequently better understanding of material properties that must be controlled or optimized for macromolecular engineering of formulations.

Symposium FE
Foams, Emulsions, Surfactants, and Micelles

Organizers: Ruth Cardinaels, Anniina Salonen and Sachin Velankar

Monday 1:30 Meeting Room A-B FE6

Mixing dynamics of bilgewater emulsions in Taylor Couette flows

Vishal Panwar and Cari Dutcher
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Taylor-Couette flows between two concentric, rotating cylinders, is ideal for studying the mixing dynamics and stability of emulsions due to the availability of wide variation of hydrodynamic flow states. The requirement to control the concentration of oil discharge at sea from the marine vessels require a better understanding of the stability and formation of Navy standard bilge mix emulsions (50% marine diesel fuel, 25% steam lube oil, 25% Diesel lube oil) onboard these ships. In this study, a pre-prepared (IKA: T-25 digital Ultra-Turrax) concentrated oil-water emulsion is directly injected into the annulus of the Taylor-Couette cell containing surfactant-water solution at varied flow conditions to determine the intermixing rate or dispersion rate of the emulsion. The optical properties of the Tayler-couette cell enables us to visually study the mixing and spread of the emulsion in the solution. It was observed that the dispersion coefficient showed an approximately linear response to increasing inner cylinder speed of Taylor-couette cell. Samples were collected at different mixing stages from the TC cell and laser diffraction particle analyzer was used to characterize droplet size distribution for the mixing stages. The measurements indicate an initial droplet breakup followed by shear induced coalescence to form a larger median droplet size with time at lower mixing speed. Whereas as the mixing speed increases, the droplets continues to break under increased shear rate and a delay in droplet coalescence was observed.

Monday 1:55 Meeting Room A-B FE7

Mesoscale simulation approach for dynamics and assembly of deformable objects

Toluwanimi Bello, Sangwoo Lee, and Patrick T. Underhill
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In dilute suspensions, surfactant micelles and emulsion droplets often take spherical shapes. But at high enough concentrations, contact among the micelles or droplets leads to nonspherical shapes. In this limit, the dynamics and assembly of the suspension depend more on the interfaces between objects than the bulk objects themselves. This has similarities with foams and biological tissues in which the interfaces between deformable objects (gas bubbles or cells) play a critical role. We have adapted a mesoscale approach (called vertex models) in order to apply it to the dynamics and assembly of small deformable objects where thermal fluctuations are important. In particular, we have quantified the phase diagram of assembly and kinetics of assembly when a system is quenched into an ordered region of the phase diagram. A unique feature of 3D materials is that multiple ordered states are possible. We have quantified the meta-stability of these ordered states and found a "diffusionless transformation" between ordered states. These transformations are well-known in metallic systems, but have only more recently been found in experiments with soft materials. Exchange of material and volume between objects also plays an important role in determining the ideal packing structures.

Monday 2:20 Meeting Room A-B FE8

Toward a biological toolkit: Systematic characterization of double emulsions for screening applications

Suzanne G. Calhoun[1], Kara K. Brower[2], Gaeun Kim[2], Vineeth Chandran Suja[1], Rochelle Radzyminski[3], Margarita Khariton[2], Polly M. Fordyce[2], and Gerald G. Fuller[1]
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In the past ten years, droplet microfluidic techniques have enabled novel biological investigation at unprecedented scale, with applications ranging from disease diagnosis, synthetic biology, fundamental biochemical characterization, and single cell analysis. Recently, double emulsions (DEs), droplets with a W/O/W architecture, have generated significant interest in the field due to their unique compatibility with fluorescence-activated cell sorting (FACS), allowing droplets to be be screened and sorted by a phenotype-of-interest to expand cellular analysis capabilities. However, producing stable double emulsion droplets of predictable size for optimized reactions, especially under complex biologically-relevant surfactant conditions, remains prohibitively challenging and largely inaccessible to non-microfluidic specialists. To address this need, we conducted extensive systematic size parameterization of DE droplets in a microfluidic dual flow-focuser device in a 'dripping-dripping' flow regime, building upon our prior development of an open-source microfluidic DE generation platform, Dropception. With the goal of creating a easy-to-use toolkit for biological researchers, we characterized monodisperse droplets with <5% CV across >100 flow conditions and a broad range of 6 biologically relevant aqueous solutions for applications such as cellular lysis, microbial growth, and drug delivery. In parallel, we performed extensive rheological investigation of these aqueous and oil phase components, to quantify previously unexplored multi-surfactant stabilization of complex droplet architectures. We observe that size variation is dominantly explained by simple flow-based volume conservation, whereas surfactant variation influences DE stability ranges. We apply these findings to optimize FACS analysis of different size double emulsions. This interdisciplinary work importantly enables new screening-based biological applications of DEs by lowering the barrier of entry to new researchers.

Monday 3:45 Meeting Room A-B FE10

Drainage via stratification in foam films made with polymer-surfactant complexes

Chenxian Xu, Carina Martinez, and Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States

Freestanding films of soft matter exhibit stratification due to confinement-induced structuring and layering of supramolecular structures like micelles. In many cosmetics, foods, pharmaceutical, and petrochemical applications, often polymers are added to surfactant solutions as rheology modifiers. Interaction between neutral polymer like PEO and monomers and micelles of anionic surfactant like SDS results in the formation of polymer-surfactant complexes and changes both interfacial properties and bulk shear rheology response. The influence of such polymer-surfactant complexes on foam formation, stability, drainage, and lifetime are not well-understood and motivate this study. In this contribution, we show foams formed with PEO-SDS mixtures exhibit three features of stratification: step-wise thinning, co-existence of thick thin regions, and formation of nanoscopic topological features like nanoridges and mesas. The nanoscopic thickness variations and transitions in foam films are characterized using interferometry, digital imaging, and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). We characterize the variation in surface tension, shear viscosity and extensional relaxation time as a function of surfactant concentration at fixed polymer concentration. By complementing with tensiometry and rheometry measurements, we seek an understanding of the influence of added polymer on forces, flows and fluxes that drive drainage via stratification, and model drainage via thin film equation amended with thickness-dependent disjoining pressure.

Monday 4:10 Meeting Room A-B FE11

The impact of viscous stress and Marangoni stress on the micro-scale droplet film drainage time

Yun Chen and Cari Dutcher
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Liquid-liquid droplet emulsions are widely observed in various applications such as bilgewater, food processing, and water-entrained diesel fuels. The dispersed droplets are usually stabilized by the surfactant molecules that are adsorbed onto the droplet interfaces. The presence of the surfactant molecules usually causes the reduction of droplet interfacial tension, and therefore, inhibits the droplet coalescence. Despite the impact of interfacial tension on the droplet coalescence, other factors will also affect the droplet stability. When two droplets are moving close to each other, a thin film forms between the two droplets and must drain before they can coalesce. In this scenario, the time scale for the film drainage is significant to quantify the emulsion stability. Studies have shown that this film drainage time can be influenced by the viscous stress and Marangoni stress at the droplet interface. The viscous stress at the interface is determined by the viscosity ratio between the dispersed and continuous phases, while the Marangoni stress is induced by the gradient of the adsorbed surfactant molecules along the interface. For different liquid-liquid systems, both viscous stress and Marangoni stress can affect the film drainage to a certain extent, which will be the focus of this work. In this presentation, systematic droplet coalescence experiments will be presented. In particular, systems with different viscosity ratios between the dispersed and continuous phases are studied to understand the impact of viscous stress. In addition, the film drainage time is also characterized for surfactants with different concentrations to understand the impact of the Marangoni stress on the droplet coalescence.

Monday 4:35 Meeting Room A-B FE12

Drainage kinetics of sodium caseinate foam films

Lena Hassan[1], Chenxian Xu[1], Michael Boehm[2], Stefan Baier[2], and Vivek Sharma[1]
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Many food,cosmetic and pharmaceutical foams contain proteins that influence both the interfacial and bulk properties of formulations. In this study, we characterize the drainage of protein-based foams as well as single foam films, and contrast their behavior with micellar foams formed with small molecular surfactants above the critical micelle concentration. Micellar foam films undergo drainage via stratification manifested as step-wise thinning in the plots of average film thickness over time. Stratification in micellar foam films is accompanied by formation of coexisting thick-thin regions visualized in reflected light microscopy as exhibiting distinct grey regions as intensity is correlated with thin film interference. We critically examine the drainage of protein foam films to determine how and when stratification can be observed, and evaluate the connection between drainage of single foam films and bulk foams.

Symposium AB
Active and Biological Materials

Organizers: Sujit Datta and Danielle Mai

Monday 1:30 Meeting Room C-D AB6

The colloidal nature of complex fluids leads to enhanced motility of flagellated bacteria

Shashank Kamdar[1], Seunghwan Shin[1], Lorraine F. Francis[1], Xinliang Xu[2], and Xiang Cheng[1]
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The natural habitats of microorganisms in human microbiome and ocean and soil ecosystems are full of colloids and macromolecules, which impart non-Newtonian flow properties drastically affecting the locomotion of swimming microorganisms. Although the low-Reynolds-number hydrodynamics of the swimming of flagellated bacteria in simple Newtonian fluids has been well developed, our understanding of bacterial motility in complex non-Newtonian fluids is still primitive. Even after six decades of research, fundamental questions about the nature and origin of bacterial motility enhancement in polymer solutions are still under debate. Here, we study the motility of flagellated bacteria in colloidal suspensions of varying sizes and volume fractions. We find that bacteria in dilute colloidal suspensions display quantitatively the same motile behaviors as those in dilute polymer solutions, where a universal particle-size-dependent motility enhancement up to 80% is uncovered, accompanied by a strong suppression of bacterial wobbling. By virtue of the well-controlled size and the hard-sphere nature of colloids, the finding not only resolves the long-standing controversy over bacterial motility enhancement in complex fluids, but also challenges all the existing theories using polymer dynamics to address the swimming of flagellated bacteria in dilute polymer solutions. We further develop a simple physical model incorporating the colloidal nature of complex fluids, which quantitatively explains bacterial wobbling dynamics and mobility enhancement in both colloidal and polymeric fluids. Our study sheds light on the puzzling motile behaviors of bacteria in complex fluids relevant to a wide range of microbiological processes, and provides a cornerstone in engineering bacterial swimming in complex environments.

Monday 1:55 Meeting Room C-D AB7

Opto-rheology of biologically derived active gels

Daniel L. Blair[1], Claudia Dessi[2], and David A. Gagnon[1]
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In this talk we will discuss our recent results on the microscopic physical origins of shear thickening in active microtubule based gels. Active matter is inherently out-of-equilibrium and can possess anomalous bulk rheological properties. Previous experimental and numerical studies suggest organisms with extensile swimming behavior (e.g. Escherichia coli) can decrease the apparent viscosity of a fluid, while those with contractile swimming behavior (e.g. Chlamydomonas reinhardtii) can increase the apparent viscosity of a fluid. However, these "swimmers" couple to the fluid through purely hydrodynamic interactions, whereas active gels contain transient percolated structures that provide a short-lived elastic response that resist the applied deformation. To explore this, we use a custom-built confocal rheometer platform that provides simultaneous macroscale rheological measurements and fluorescent imaging of the local microtubule dynamics. We find increasing ATP concentration, and therefore increasing activity, yields a significant increase in the apparent viscosity of the suspension to an ATP and shear rate dependent maximum. Simultaneously, using velocimetry techniques, we find significant increases in local velocity fluctuations and deformation rates, suggesting underlying microscale mechanisms for the observed macroscale rheology. We will present a model that captures the connection between the local mechanics and the global viscoelasticity.

Monday 2:20 Meeting Room C-D AB8

Effects of collagen on viscoelasticity of Pseudomonas aeruginosa biofilms grown in mouse wound beds

Gordon F. Christopher and Minhaz Ur Rahman
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Bacterial biofilms are viscoelastic, surface-attached aggregates that are found in chronic wound sites, causing persistent and often deadly infections. Pseudomonas aeruginosa biofilms are infamous for resistance to immune response, environmental conditions, antibiotic treatment, and physical removal. Although several biological mechanisms enable these properties, viscoelasticity plays an important role in virulence and resistance of P. aeruginosa. Understanding the mechanisms causing biofilm viscoelasticity and how the wound bed host proteins, such as collagen, affect viscoelasticity can aid in designing novel anti-microbial treatments.

We first explore how collagen affects biofilm viscoelasticity using particle tracking microrheology in an in-vitro wound like model. To understand how collagen interacts with the biofilms, we study a range mutant strains of PAO1 P. aeruginosa that lack major components of the biofilm matrix in the presence of collagen. Collagen is seen to universally create more elastic and stiffer biofilms that exhibit less heterogeneity. Data indicates that the free collagen incorporates into the biofilm through non-specific physical entanglement and/or through adhesion to bacteria themselves, which results in the changes to the biofilm viscoelasticity.

These results suggest in-vivo biofilms will have significantly different viscoelastic behavior in comparison to typical in-vitro results. To confirm this, in-vivo microrheology experiments should be conducted, but this extremely challenging. Therefore, we developed a novel ex-vivo technique that allows similar measurements to be conducted on unmanipulated biofilms grown in mouse wound beds. Our ex-vivo biofilms exhibit viscoelastic behavior similar to the in-vitro films grown in the presence of collagen, confirming our hypothesis and indicating that in-vitro viscoelasticity is not an ideal representation of in-vivo conditions.

Symposium IN
Flow-induced Instabilities and Non-Newtonian Fluids

Organizers: Dana Grecov, Irmgard Bischofberger and Antonio Perazzo

Monday 3:45 Meeting Room C-D IN1

How much of the transient rheological behavior of geological shear zones can be explained using granular physics alone?

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The transient rheology of Earth materials in geological shear zones (e.g., earthquake fault zones, the basal shear zones of glaciers) controls the nucleation and modes of instabilities. Mathematical models that can accurately predict this transient behavior are therefore necessary for predicting the response of Earth's near-surface and subsurface to perturbations. One such modeling framework, commonly used in the fault and glacier mechanics communities, is that of Rate-and-State-dependent Friction (RSF). The RSF framework is empirical and in its current state, is developed based on contact mechanics observations. However, decades of research by rock friction experimentalists and geologists shows that current RSF formulations cannot accurately predict the transient response of shear zones as observed in the lab. In this talk, I will first briefly describe the main macro- and micro-scale observations that form the basis of RSF. I will then present a model of shear zone constructed from granular materials with time independent contact-scale properties (realized using the discrete element method) and show that such a model can reproduce many observations relevant to the transient rheology of geologic shear zones, and over-perform existing RSF formulations. I further show that a measure of the normalized temperature of the granular layer can predict the magnitude of its immediate response to perturbations in sliding velocity. In majority of work presented here, we use a Hertzian contact law for grain-grain interactions and such a model produces steady-state rate strengthening friction in the (quasi-static) range of shear rates explored. However, we find that a model with Hookean contacts shows a transition from rate-weakening to rate-strengthening at some intermediate shear rates. In the rate-weakening regime, the model also produces stick-slip instabilities as expected in the RSF framework. However, the critical stiffness at which the instabilities emerge is an order of magnitude larger than that predicted by RSF.

Monday 4:10 Meeting Room C-D IN2

Computational models and experimental studies of mold filling in thin channels with yield stress fluids

Rekha R. Rao[1], Joshua T. McConnell[1], Anne M. Grillet[1], Weston Ortiz[2], Bikash Dey[3], Pania Newell[3], and Christine C. Roberts[1]
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Materials that behave as both fluids and solids can be seen in a wide variety of applications from pouring concrete to lava flows and food processing. Yield stress is a useful concept for developing models that demonstrate both fluid and solid behavior depending on the local state of the fluid. In this talk, we will discuss an ongoing project to use elastoviscoplastic models to understand the complex flow profiles of a model yield stress fluid, Carbopol, as it evolves in time in a free surface flow. We use a Saramito model to describe the rheology of the fluid (Saramito, "A

new constitutive equation for elastoviscoplastic fluid flows." Journal of Non-Newtonian Fluid Mechanics 145.1 (2007): 1-14). This model describes the material as a Maxwell fluid above yield and an elastic solid below yield, with a yield criterion based on the von Mises stress. Conservation equations for momentum and mass and the Saramito constitutive equations for stress are solved using the finite element method coupled to a free-surface moving mesh algorithm. We verify our implementation by comparing our results to benchmarks in the literature such as flow past a sphere and a ball falling in a tube full of yield stress fluid. Furthermore, we compare results from mold filling simulations to validation flow visualization experiments in a quasi-two-dimensional flow where fluid fills a thin gap between transparent plates. The experiments show regions of low strain where the fluid displaces as a solid body and high strain regions where the Carbopol is fluidized. The computational model matches qualitatively for the yield stress fluid. Extensions to fully three-dimensional flows using a level set method will also be discussed. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Monday 4:35 Meeting Room C-D IN3

Microphase separation and flow-induced crystallization in entangled polymeric solutions in extensional flows

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Flow-induced phenomena in entangled solutions of linear C1000H2002 polyethylene dissolved in n-hexadecane and benzene solvents were simulated via nonequilibrium molecular dynamics at concentrations of 14.5C* and 13.5C*, respectively, of the coil overlap concentration, C*. The simulations revealed that both solutions undergo a chemical phase separation when subject to planar extensional flow at extension rates faster than the inverse Rouse time of the solution. The onset of phase separation initiated after roughly two Hencky strain units of deformation for both solutions and attained a stationary state at about ten Hencky strain units. Furthermore, the simulations revealed that at very high extension rates the polymer phase forms semicrystalline domains regardless of the solvent; however, the critical extension rate for flow-induced crystallization appeared to be affected by a number of variables, including solution temperature and the chemical nature of the solvent.

Monday 5:00 Meeting Room C-D IN4

An experimental study on vortex-induced vibrations of a cylinder in shear thinning flow

Pieter R. Boersma, Jonathan P. Rothstein, and Yahya Modarres-Sadeghi
Department of Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States

Traditional vortex-induced vibration (VIV) experiments subject a flexible or flexibly-mounted cylinder to Newtonian flow. In this work, we present experimental results on VIV of a one-degree-of-freedom cylinder placed in shear-thinning flows. These experiments were conducted in a rotating water channel using a cylinder with a diameter of 2 mm. In each series of experiments, we kept the characteristic Reynolds number, defined based on the characteristic viscosity using the Carreau model constant and varied the reduced velocity. The mass ratio was smaller than 10. For experiments at constant characteristic Reynolds numbers, we observed a lock-in region in a reduced velocity range of approximately 6 to 9 with a maximum amplitude of oscillations of approximately 0.2D. The amplitude of oscillations and the width of the lock-in region decreased with decreasing characteristic Reynolds number and at characteristic Reynolds numbers lower than 18, VIV was completely suppressed.

Monday 5:25 Meeting Room C-D IN5

Numerical study of vortex-induced vibrations of a cylinder in shear-thinning and shear-thickening power-law fluids

Umang N. Patel, Jonathan P. Rothstein, and Yahya Modarres-Sadeghi
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Vortex-Induced Vibration (VIV) of a cylinder in Newtonian fluid has been widely studied due to its widespread applications. In this work, we study the influence of shear-thinning and shear-thickening fluids on the VIV response. We have considered a one degree-of-freedom flexibly-mounted cylinder with a mass-ratio of $m^* = 2$ and zero structural damping in shear-thinning and shear-thickening power-law fluids at $Re_0 = 15$ and $Re_0 = 200$, respectively, defined based on the zero-shear-rate viscosity of the fluids. We investigate how the VIV amplitude and frequency, flow forces, and the vorticity contours change as the reduced velocity, U^*, and fluid's time-constant, λ, change. We have observed that at a constant reduced velocity, the amplitude of oscillations increases in shear-thinning fluids as the time constant is increased until it reaches a plateau. For shear-thickening fluids, the amplitude of oscillations decreases with increasing time constant and at large values of time constants VIV is completely suppressed. We have found that at a constant characteristic Reynolds number, Re_{char}, defined based on a viscosity evaluated at the characteristic shear-rate, U/D, the amplitude of oscillations remains the same for shear-thinning, shear-thickening and Newtonian fluids, while their wakes are significantly different. At the same Re_{char}, shear thinning amplifies the generation of vorticity and reduces the extent of the wake, whereas shear thickening limits the generation of vorticity and extends the wake.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Marie-Claude Heuzey, Sara Hashmi and Rahul Pandey

Monday 1:30 Ballroom 6 SC6

Effect of geometric frustration on the linear viscoelasticity of dense colloidal suspensions

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In dense suspensions that comprise of colloids which interact via a hard sphere potential, the elastic and viscous components of the stress response is determined by the excluded volume effects and the hydrodynamics. The near-equilibrium structure of suspensions with smooth and rough colloids is probed to decouple the effect of surface roughness-induced geometric frustration on the storage and the loss moduli. We perform small oscillatory shear experiments in the linear viscoelastic regime on suspensions containing smooth and rough poly(methylmethacrylate) colloids (particle diameters: $2a = 1.50\ \mu m \pm 6\%$ and $2a_{eff} = 1.55\ \mu m \pm 5\%$, respectively) in a refractive index-matched solvent, squalene, at various volume fractions (φ). Changes in the scaled moduli are studied as a function of the distance to the glass transition volume fraction $\varphi^* = (\varphi_g - \varphi)/\varphi_g$, where φ_g is the glass transition point. Between φ_g and the maximum packing (φ_{max}), the frequency-sweep rheometry show that smooth particle suspensions exhibit a scaled modulus ~10 Pa while rough particle suspensions exhibit a modulus ~ 10^5 Pa. We generate a master Maxwell curve fitting the linear viscoelastic response of our data and earlier works from the literature through the shift parameters α and β with respect to scaled frequency and moduli, respectively. Divergence of the ratio α/β at $\varphi^* = 0$ gives an initial estimate of φ_g ˜ 0.57 for smooth and 0.54 for rough particle suspensions considered in our studies. Furthermore, we capture the effect of surface roughness on local microstructure response through a functional form of φ^* and storage modulus (G') through scaling of the form, $G' \sim f(\varphi^*)/a^3$. The data suggest that there is a direct link between the energy dissipation and the geometric frustration of particles that exhibit rotational constraints due to surface roughness.

Monday 1:55 Ballroom 6 SC7

Contact mechanics between colloidal particles

Furst M. Eric
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The rheology of a colloidal suspension depends sensitively on the interaction forces between particles. At high volume fractions, particles are separated by a fraction of their size, which may be on the order of nanometers. Dispersion, electrostatic, steric, depletion, and hydrodynamic interactions, as well as geometrical characteristics such as shape, roughness, and the presence of asperities, all potentially contribute to interparticle forces. I will present experiments that use laser tweezers to measure the contact and sliding mechanics between micrometer-size colloidal particles. The purpose of this talk is to describe recent experiments on the contact mechanics of silica and polymer latex particles that are strongly bound by cohesion. [1] I will discuss the nature of the cohesion and contact, the aging of contacts, and their mechanics, including the existence of a critical bending moment, stick slip motion, particle rolling, and the ability to tune these forces by reducing the interfacial energy of the particles. Such measurements of colloidal-scale interactions and mechanics should be informative for developing models of suspension rheology, including the elasticity and modulus of colloidal gels and the contact mechanics underlying discontinuous shear thickening.

[1] Francesco Bonacci, Xavier Chateau, Eric M. Furst, Jennifer Fusier, Julie Goyon and Anaël Lemaître., Nat. Mater., 1-8 (2020).

Monday 2:20 Ballroom 6 SC8

Coupling between attractions and repulsions in flow of colloidal suspensions

Sabitoj Virk and Patrick T. Underhill
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Theories and simulations of colloidal suspensions have been successful in capturing many important features found in flow experiments. This includes systems with strong repulsions to stabilize the suspension or with strong attractions that lead to phase separation or gel formation. Less attention has been paid to suspensions with simultaneous weaker attractions and repulsions. This is particularly important for designing suspensions by manipulating the colloidal interactions and in the flow properties of biological materials. In this talk we will focus on how the coupling between the attractions and repulsions alters the zero-shear-rate viscosity. We will show how two systems can have the same effective interaction while also having very different viscosities. We will also show how repulsions can be used to either increase or decrease the viscosity. These both have implications for designing suspensions and understanding experimental observations.

Monday 2:45 Ballroom 6 SC9

Network physics analysis of short-range attractive

Mohammad Nabizadeh, Nasirian Farzaneh, Ravandi Babak, and Safa Jamali
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Colloidal gels exhbit a range of rate- and time-dependent rheological behavior that are classified as thixotropic elaso-visco-plastic. This complex rheology arises from the colloidal phase dynamics, and specifically, the evolution of a particulate microstructure that forms due to attractive interactions between different particles. These forces result in thermoreversible bonds, which in turn result in space-spanning networks that govern the mechanics of colloidal gels. What is clear is that particle-level bonds give rise to clusters at the mesoscale, and that elasticity in these gels arises from a percolated network at the macroscale. Thus understanding the physics of this particulate network is key to controlling and designing gels with desirable properties. Thus, we borrow well-established concepts from network science to interrogate and characterize the particulate network in attractive colloidal gels. We associate each colloidal particle to a vertex, and each inter-particle bond to an edge; we then proceed to the analysis of the networks of bonds, completely unaware of the spatial coordination of the particles, and to reveal structural signatures both in local and bulk scales. Our results indicate that network science is able to identify locally glassy structures, elastically active bonds, and other microstructural features of gels that are formed at different conditions. In particular, employment of the Gaussian Mixture Models (GMM) on the network of the inter-particle bonds, leads to the identification of the locally rigid clusters, coarse grained to single rigid beads, the inter-cluster connections, and eventually to reveal the rather glassy structure of the coarse-grained system. Finally, the clusters that we obtain through this method, when fed into the Cauchy-Born theory, yield elastic moduli quantitatively similar to those in glassy systems.

Monday 3:45 Ballroom 6 SC10

Relationships among structure, memory, and flow in sheared disordered materials

Larry Galloway[1], Erin Teich[2], Max Ma[3], Christoph Kammer[1], Ian Graham[3], Nathan Keim[4], Celia Reina[1], Doug Jerolmack[5], Arjun Yodh[3], and Paulo Arratia[1]

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How soft materials yield is a question of fundamental interest to material engineers and rheologists alike. Often, we model complex fluids from observations of the bulk response alone. However, it may be possible to predict material response by understanding the constituent particle interactions and their arrangements. This possibility is investigated here via experiments with a custom built Interfacial Stress Rheometer and densely packed monolayers of repulsive particles and simulations of granular and atomic scale systems. The bulk rheology (G', G") is measured while simultaneously tracking the positions of up to 50,000 particles. We quantify particle microstructure using excess entropy. Results reveal a direct relation between excess entropy and energy dissipation, that is insensitive to the nature of interactions among particles. We use this relation to build a physically-informed model that connects rheology to microstructure. Our findings suggest a framework for tailoring the rheological response of disordered materials by tuning microstructural properties.

Monday 4:10 Ballroom 6 SC11

Shear induced geometry and jamming in sphere packings

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Rigidity or jamming in amorphous sphere assemblies can be induced by compression or by shear deformation. In frictionless sphere packings,jamming occurs at the packing fraction of 64%, also known as random close packing density (RCP). In the presence of friction, jamming can occur below RCP when subjected to compression or shear deformation. Here, we show shear deformation leads to geometrical features that are characteristic of jammed packings at RCP for a wide range of densities below RCP in frictionless packings. We test the mechanical stability of shear deformed frictionless packings, with and without the inclusion of frictional forces, to understand the distinct roles played by shear deformation & friction in shear jamming phenomenology. Unique to shear jamming is the geometric criterion on the contact number Z for jamming, i.e., the average contact number $Z = D + 1$, where D is the spatial dimensionality. This condition is independent of friction coefficient, spatial dimensions, and jamming protocols. In two dimensions, Using rigidity percolation analysis, we identified that the percolation of over-constrained (or rigid+stress or self-stress) regions corresponds to the shear jamming transition. These regions transmit stress across the packing.

Monday 4:35 Ballroom 6 SC12

Irreversible aggregation in sheared non-Brownian suspensions of clathrate hydrates

Michela Geri and Gareth H. McKinley

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In colloidal suspensions, the aggregation of constituent particles is governed primarily by the contrasting role of thermal agitation and shear break-up. The equilibrium between these two processes determines the effective volume fraction of dispersed solids and hence the suspension material properties, such as its shear viscosity. For non-Brownian particles thermal agitation is not important, but it has been shown that irreversible aggregation is possible for large shear rates (above 100 1/s) even for relatively dilute solutions (volume fractions as low as 10%). In these systems agglomeration is completely controlled by the shear rate, proving that hydrodynamic forces are important to overcome the energy barrier preventing particle aggregation. In this talk, we show that a different process can also control the irreversible aggregation in systems where bonds between particles are physically permanent due to sintering. The suspensions investigated are made of synthetic clathrate hydrate particles dispersed in an oil phase, which are of great interest to the energy sector due to their enormous potential for transport and storage of gases such as methane, carbon dioxide and hydrogen. First, we introduce a novel method that allows us to reliably control hydrate formation starting from a dispersion of ice particles. By monitoring the evolution of the suspension viscosity over time, we can follow the phase-transformation from ice to

hydrate over many different water/ice volume fractions and applied shear rates. Combining rheometry and microscopy, we show that the hydrate particles inevitably sinter over time, producing an exponentially divergent viscosity increase that can be accelerated or delayed only by the addition of surface-active agents, which can control or even fully suppress the sintering process. We propose an analytical model that captures all our experimental observations with a single unknown parameter representing the characteristic sintering time.

Monday 5:00 Ballroom 6 SC13

Going with the flow: Multiscale dynamics of colloidal deposition, erosion, and interactions with immiscible fluids

Joanna Schneider[1], Navid Bizmark[2], Rodney D. Priestley[1], and Sujit S. Datta[1]
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Transport of colloidal particles underlies diverse processes, including environmental pollution, groundwater remediation, and oil recovery. These processes frequently involve deposition of colloidal particles on a solid surface and their subsequent interactions with an immiscible fluid. Using confocal microscopy, we identify the fundamental mechanisms of particle deposition and erosion in porous media at various injection conditions. These key insights into the multi-scale interactions between fluid, particles, and the solid matrix allow us to understand how particles distribute in a porous medium. Furthermore, we find that we can harness deposition and erosion processes for immiscible fluid mobilization. While most studies focus on accomplishing this goal using particles that can localize at the immiscible fluid interface, we demonstrate that deposition of non-surface active particles can, surprisingly, promote mobilization of a trapped fluid from a porous medium without requiring any surface activity. We unravel the underlying physics by analyzing the extent of deposition, as well as the geometry of trapped fluid droplets, at the pore scale. Finally, we look at the complexities that arise between colloidal interactions, hydrodynamics, and capillarity when an immiscible fluid interacts with dense, multi-particle aggregates. Here, we directly visualize the interactions between multilayer colloidal particle deposits and moving immiscible fluid droplets in microchannels. As the immiscible fluid interface passes over particles, we observe that they strongly adsorb to it, despite not being surface active under quiescent conditions. Taken together, our work reveals new ways by which colloids can be harnessed to mobilize trapped fluid from a porous medium and help guide the development of more accurate models that describe how deposited particles, bacteria, and viruses can be transported by immiscible fluid interfaces (e.g., wetting/drying cycles) in the environment.

Monday 5:25 Ballroom 6 SC14

Virtual mass of an oscillating sphere

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Virtual mass or added mass describes the inertia of the fluid around a submerged body that acts to resist a relative acceleration between the body and the fluid. When the body is a sphere, this mass was determined to be 1/2 of the mass of the displaced fluid from the inviscid flow theory, under the condition that the relative acceleration is slow and the radius of the sphere is small such that the sphere develops a steady response to the acceleration. This result since then became a broadly accepted term in the equation of motion for spherical particles submerged in fluids. Not all flows satisfy the condition of this classical result. In this study, we report that for a sphere performing small-amplitude oscillations in gases, its virtual mass is not surprisingly at odds with the classical expression. We triggered oscillation of the sphere magnetically in dense gases, and then measured the frequency of free oscillation, from which the virtual mass of the sphere was extracted. We found that for three gases CO2, N2 and CH4 at pressures up to 96 bar virtual masses were consistently greater than that from the classical correlation by 30-40%. Simulations of oscillatory flow around sphere show strong vortex shedding, which explains that the observed virtual masses were proportional to the cross-section area rather than the volume / mass of the sphere. We did not experiment oscillations in liquids or with high frequencies, which could be of potential for revealing fluid's elasticity.

Symposium GG
Arrested Systems: Gels and Glasses

Organizers: Emanuela del Gado and Jyoti Seth

Monday 1:30 Ballroom 1 GG6

Colloidal vitrification is a spontaneous non-equilibrium transition driven by osmotic pressure

Roseanna N. Zia and Jialun Wang
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Persistent dynamics in colloidal glasses suggest the existence of a non-equilibrium driving force for structural relaxation during glassy aging. But the implicit assumption in the literature that colloidal glasses form within the metastable state bypasses the search for a driving force for vitrification and glassy aging and its connection with a metastable state. The natural relation of osmotic pressure to number-density gradients motivates us to investigate the osmotic pressure as this driving force. We use dynamic simulation to quench a polydipserse hard-sphere colloidal liquid into the putative glass region while monitoring structural relaxation and osmotic pressure. Following quenches to various depths in volume fraction f (where f_{RCP} ˜ 0.678 for 7% polydispersity), the osmotic pressure overshoots its metastable value, then decreases with age toward the metastable pressure, driving redistribution of coordination number and interparticle voids that smooths structural heterogeneity with age. Overall,

the osmotic pressure drives structural rearrangements responsible for both vitrification and glassy age-relaxation. We leverage the connection of osmotic pressure to energy density to put forth the mechanistic view that relaxation of structural heterogeneity in colloidal glasses occurs via individual particle motion driven by osmotic pressure, and is a spontaneous energy minimization process that drives the glass off and back to the metastable state. This connection of energy, pressure, and structure identify the glass transition, $0.63<f_g=0.64$.

Monday 1:55 Ballroom 1 GG7

Bijels: 2D glasses or 3D gels?

Herman Ching and Ali Mohraz
Chemical and Biomolecular Engineering, University of California, Irvine, CA 92697, United States

Bicontinuous interfacially jammed emulsion gels (bijels) are a unique class of soft materials that spontaneously form when spinodal decomposition in a liquid mixture is arrested by colloidal jamming at the fluid interfaces. The result is a mechanically stable mixture where independently percolating fluid domains are separated by a sample-spanning monolayer of colloidal particles. In this talk, we report the rheology of bijels, motivated from both scientific and technological perspectives. Bijel rheology is directly linked to the ability to process them into functional materials with applications ranging from electrochemical energy storage to tissue engineering. Fundamentally, bijel rheology presents an intriguing, nontrivial case: a jammed colloidal monolayer trapped at a continuous fluid interface percolates throughout the mixture, resulting in gel-like viscoelasticity, while the inherently negative Gaussian curvature of the fluid interface can induce volume-fraction-dependent attractive capillary forces between the particles. These attributes result in rich rheological behavior that, to date, has not been fully explored. In addition, while the jammed particle monolayer can be viewed as a 2D colloidal glass, the system as a whole may be considered a dilute colloidal gel, posing a fundamental question about the nature of arrested dynamics and viscoelasticity in bijels. To investigate these problems, we have developed a new bijel chemistry comprised of the nonvolatile liquid pair propylene carbonate and 1,4-butanediol, enabling a set of long-duration experiments necessary for full quantification of bijel rheology in the linear and nonlinear regimes. We present a systematic set of experiments at different colloid volume fractions, temperatures (interfacial tensions), and strain amplitudes. We apply an adaptation of the Mode Coupling Theory formulism developed to describe the dynamics of hard spheres near glass transition, to interpret the rheology of bijels, and address the fundamental questions posed above.

Monday 2:20 Ballroom 1 GG8

Relaxation processes in partially arrested soft matter

Henning Winter
Chemical Engineering and PS&E, UMass Amherst, Amherst, MA 01002, United States

Soft solid matter typically contains a substantial fraction of mobile constituents besides the "arrested" components. While the arrested fraction dominates the long-time behavior and is characterized by an equilibrium modulus Ge, the "un-arrested" mobile fraction softens the overall behavior and gives rise to transient viscoelastic phenomena. The longest relaxation time, tau,max, associated with the mobile phase can be quite large, large enough to prevent a direct measurement of Ge. The relaxation of the mobile phase is constrained by the presence of the arrested constituents. An attempt will be made to extract the relaxation time spectrum of the mobile phase from experimental data of soft solids and express its properties separately from Ge.

Monday 2:45 Ballroom 1 GG9

Microscopic origins of non-exponential stress relaxations in arrested soft materials

Jake Song[1], Qingteng Zhang[2], Felipe de Quesada[1], Mehedi H. Rizvi[3], Jan Ilavsky[2], Joseph B. Tracy[3], Suresh Narayanan[2], Robert L. Leheny[4], Emanuela Del Gado[5], Niels Holten-Andersen[1], and Gareth H. McKinley[1]
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Non-exponential stress relaxation processes occur ubiquitously in arrested soft materials such as glasses, colloidal suspensions, and biological networks. Despite this ubiquity, the microscopic origins of such relaxation processes remain unclear. Here, we directly study this phenomenon through a combination of rheology and x-ray photon correlation spectroscopy on a model arrested gel. By investigating the microscopic relaxation processes in the gel in quiescent and in driven conditions, we find that these slow relaxation processes are governed by an interplay of microscopic fluctuations in the elastic stresses accrued during arrest, and of the elastic avalanches generated by small mechanical perturbations onto the system. We thus show that non-exponential stress relaxations in strongly arrested materials are a signature of non-linear relaxation processes governed by internal stress heterogeneities, and a manifestation of the fractal potential energy landscapes underlying such materials.

Symposium MC
Micro- and Nanofluidics and Confined Flows

Organizers: Xiaolong Yin and Amanda Marciel

Monday 3:45 Ballroom 1 MC1

Let's set the (error) bar high: Quantifying uncertainties in MD simulations of transport under nanoscale confinement

Yuanhao Li and Gerald J. Wang
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Ergodicity (or at least the tantalizing promise of it) is a core animating principle of molecular-dynamics (MD) simulations: Put simply, sample for long enough (in time), and you will make representative visits to the states of a system throughout phase space consistent with the desired statistical ensemble. Although the assumption of ergodicity is not (in general) the most dangerous assumption made in a typical MD simulation, one is nevertheless never guaranteed a priori that the chosen window of sampling in a production run is sufficiently long to avoid problematically non-ergodic observations. In this talk, we demonstrate several particularly striking and troublesome examples of this phenomenon in MD simulations of nanoconfined fluids, with implications for the quantification of uncertainty in computed transport properties. In particular, we demonstrate that commonly used sampling strategies can lead to significantly overconfident estimates of fluid self-diffusion. We introduce a simple scheme that ameliorates these issues and enables improved confidence in MD measurements of nanoconfined fluid transport properties.

Monday 4:10 Ballroom 1 MC2

Diffusion into dead-end pores of non-uniform cross-section

Francesca Bernardi[1], Jessica P. Remeis[2], Emma Abele[2], Garam Lee[3], Abigail W. Taylor[4], and Daniel M. Harris[2]
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Understanding micron-scale fluid flows is critical to perfecting the manufacturing and use of microfluidic technologies for medical and engineering applications. In particular, microchannels with dead-end pores are ubiquitous in natural and industrial settings, and ongoing research focuses on fluid and chemical transport in and out of these pores. In the present work, we detail a repeatable and accessible experimental protocol developed to study the passive diffusion process of a dissolved solute into dead-end pores of rectangular and trapezoidal geometries. Custom microchannels with pores of specified geometries are rapidly produced using inexpensive materials and a commercial craft cutter. The experimental data is compared directly to both detailed 3D numerical simulations as well as to analytical solutions of an effective 1D diffusion equation: the Fick-Jacobs equation. The role of the pore geometry on the passive diffusion process will be highlighted. Ongoing and future directions will be discussed. This work is supported by the National Science Foundation through grants CBET-1902484 and CBET-1902512.

Monday 4:35 Ballroom 1 MC3

Flow rate–pressure drop relation for complex fluids in narrow geometries

Evgeniy Boyko and Howard A. Stone
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Pressure-driven flows of non-Newtonian fluids in narrow and confined geometries are ubiquitous in natural processes and technological applications. For such confined flows, one theme is understanding the relationship between the flow rate and pressure drop for a given geometry. Conventionally, obtaining the flow rate-pressure drop relation requires solving the equations for the distribution of the velocity and pressure fields, which may involve cumbersome calculations for non-Newtonian flows even in simple geometries. Here, we show that these detailed calculations of the non-Newtonian flow problem can be bypassed by applying the Lorentz reciprocal theorem. We derive a closed-form expression for the flow rate-pressure drop relation of complex fluids in such geometries, which holds for a wide class of shear-thinning and viscoelastic constitutive models. For the weakly non-Newtonian limit, our theory provides an analytical expression for the first-order non-Newtonian correction solely using the corresponding Newtonian solution, eliminating the need to solve the non-Newtonian flow problem. In particular, for the flow-rate-controlled situation, we find that the first-order non-Newtonian pressure drop correction may increase, decrease, or not change the total pressure drop for a viscoelastic second-order fluid, depending on the geometry, but always decreases it for a shear-thinning Carreau fluid. Our method can be used to determine the pressure drop at higher orders only with the knowledge of the velocity and stress fields at the previous orders. Given the inability of numerical simulations using the elastic dumbbell models such as the Oldroyd-B and FENE-CR models to predict the experimental flow rate-pressure drop behavior of viscoelastic fluids in some cases, we believe that our approach may be useful in providing insight into the cause of this disagreement.

Monday 5:00 Ballroom 1 MC4

High-pressure microfluidics identifies homogeneous bubble nucleation in polymer foams

Andrew S. Ylitalo[1], Huikuan Chao[2], Thomas C. Fitzgibbons[3], Weijun Zhou[3], Sriteja Mantha[1], Ernesto Di Maio[4], Richard C. Flagan[1], Zhen-Gang Wang[1], and Julia A. Kornfield[1]

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Homogeneous nucleation is challenging to study due to the high supersaturation required, fast and unpredictable dynamics, and competition with heterogeneous nucleation. High-pressure microfluidic hydrodynamic focusing, a technique in which a stream of gas-saturated liquid is focused to a small (10s um) diameter and ensheathed by a stream of pure liquid, uniquely overcomes these challenges by reaching high supersaturation quickly, continuously probing millisecond dynamics, and isolating the nucleating stream from surfaces. Here, we study homogeneous nucleation of carbon dioxide bubbles in polyol undergoing rapid (100s ms) depressurization from as much as 100 bar (10 MPa) to atmosphere with a custom-built, high-pressure microfluidic hydrodynamic-focusing channel. While isolated from the channel walls, the nucleating inner stream may still undergo heterogeneous nucleation due to trace contaminants. To distinguish homogeneous from heterogeneous nucleation, we estimate the time of nucleation for a representative sample of bubbles by first tracking bubbles with high-speed microscopy and image-processing, then extrapolating their growth back to nucleation using a diffusion model with parameters measured in the Di Maio lab (U Naples). The resulting distribution of nucleation times can be compared to the uncorrelated, Poisson-like distribution that is characteristic of homogeneous nucleation events. Confident identification of homogeneous nucleation allows for meaningful evaluation of the effects of supersaturation, temperature, and additives (surfactants, cosolvents) on the nucleation rate and comparison to theoretical predictions.

Monday 5:25 Ballroom 1 MC5

Growth and coalescence of nanoscopic mesas in stratifying, ultrathin freestanding films

Chenxian Xu[1], Subinuer Yilixiati[2], Yiran Zhang[3], and Vivek Sharma[1]

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Ultrathin (thickness < 100 nm) freestanding films of soft matter exhibit stratification due to confinement-induced structuring and layering of supramolecular structures like micelles and nanoparticles. Stratification in micellar films proceeds by the growth of thinner domains at the expense of surrounding thicker film, and local volume conservation leads to the formation of nanoscopic ridges at the moving front. The ridge often undergoes instability leading to the nucleation of nanoscopic mesas, that grow and coalesce over time. The shape and size of ridges and mesas in stratifying films are visualized and analyzed using interferometry, digital imaging, and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). In this contribution, we analyze the shape evolution and coalescence of mesas in an effort to develop a comprehensive understanding of drainage by stratification in micellar foam films, including the role played by the contribution of supramolecular oscillatory structural forces to disjoining pressure. We present the theoretical analysis of flows under confinement using a thin film equation amended with oscillatory structural disjoining pressure and discuss how the interplay of hydrodynamics and thermodynamics dictates the drainage flows in foam and soap films.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Ballroom 5-6-7 PL2

Do interfaces matter in rheology?

Jan Vermant
Materials Departement, ETH Zurich, Zurich 8093, Switzerland

Dealing with interfaces in rheology and fluid mechanics is usually achieved using the Gibbs sharp interface approach, with the stress boundary condition being the way in which we can efficiently describe its effects. This works, even when interfaces become structured and have their own intrinsic rheological response. However, understanding the rheological response of an interface can be challenging due to the unavoidable coupling with the surrounding bulk phases (which act as sinks for momentum) and the fact that interfaces can be compressible, rendering their response more complicated. Our ability to measure the interfacial rheological properties has progressed much over the last years, and we also have a better understanding of its - sometimes subtle - effects, e.g. during the thinning of of liquid films, by using an interplay of experiments and computational interfacial rheology. Understanding how the material functions influence thin film stability we can engineer these properties, building in for example a yield stress, strong elastic reponses into the interface, using many of the ideas and elements of the toolbox that we have in bulk rheology. These can be used to impart stability to multiphase systems in unusual manners However, we also may want to try to a chieve the opposite, e.g. keeping interfaces fluid even when they become crowded such as in cell membranes. In this talk I hope to take you on a journey from fundamentals to applications, coming back to the open questions concerning a simple boundary condition.

Symposium SM
Polymers Solutions, Melts, and Blends

Organizers: Dimitris Vlassopoulos, Christopher Evans and Poornima Padmanabhan

Tuesday 10:40 Ballroom 5 SM17

Probing nonequilibrium dynamics of entangled polymers using orthogonal superposition rheometry

Jiamin Zhang[1], Andres Jurzyk[1], Andres Jurzyk[2], Matthew E. Helgeson[1], and L. Gary Leal[1]
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Understanding changes to microstructural dynamics under nonlinear deformations is critical for designing flow processes of entangled polymeric fluids, motivating the development of experimental methods to probe strain- and rate- dependent modifications to relaxation mechanisms. Although orthogonal superposition rheometry (OSR) holds promise as such a probe, the ability to interpret the superposition moduli accessible by OSR in the context of entangled polymer dynamics remains an open question. To fill this gap, we report model OSR predictions using detailed microstructural models for both monodisperse and polydisperse entangled polymers, i.e., the Rolie-Poly and the Rolie-Double-Poly models, respectively, which account for reptation, chain retraction, and convective constraint release. By combining numerical calculations with a perturbation analysis, we demonstrate that for polymers that can be described by a single-mode model the OSR superposition moduli at different shear rates and frequencies can generally be collapsed onto a single master curve, with rate-dependent shift factors that depend on the nonlinear rate-dependent modification of polymer conformation and relaxation rates without changing the dominant relaxation mechanisms. We systematically study how the OSR moduli are sensitive to the shape and dispersity of the molecular weight distribution. We discuss the generality of our results for a broad class of constitutive models and suggest an analogy to Laun's rule to relate OSR moduli to the first normal stress difference. Our results provide a foundation to guide the design and interpretation of future experiments and demonstrate that orthogonal superposition rheometry often probes features in nonlinear dynamics more directly than conventional rheometry techniques.

Tuesday 11:05 Ballroom 5 SM18

Flow-induced crystallization of a polyethylene liquid above the melting temperature and its nonequilibrium phase diagram

Mohammad H. Nafar Sefiddashti, Brian J. Edwards, and Bamin Khomami
Chemical and Biomolecular Engineering, University of Tennessee-Knoxville, Knoxville, TN 37996, United States

Nonequilibrium molecular dynamics (NEMD) simulations have been performed to study flow-induced crystallization (FIC) of linear entangled $C_{1000}H_{2002}$ polyethylene (PE) melt under planar elongational flow at 450K; well above the quiescent melting temperature of PE. These simulations reveal that the PE entangled melt undergoes a reversible FIC at extension rates roughly higher than 15 τ_R^{-1}, where τ_R is the Rouse relaxation time of the melt. The melting point of the flow-induced crystallized PE is ~415K, which indicates a 15-30K melting point elevation due to FIC. Furthermore, a nonequilibrium phase diagram is developed in the local molecular order parameter (q) vs. stress (σ) space, which depicts a reversible transition from coiled, biphasic, stretched, pretransitional, and crystalline phases under applied stress generated by the elongational flow.

Tuesday 11:30 Ballroom 5 SM19

A thermodynamically inspired method for quantifying phase transitions in polymeric liquids with application to flow-induced crystallization of a polyethylene melt

Brian J. Edwards, Mohammad H. Nafar Sefiddashti, and Bamin Khomami
Chemical and Biomolecular Engineering, University of Tennessee-Knoxville, Knoxville, TN 37996, United States

Thermodynamic-like local atomistic entropy and enthalpy variables are introduced as a means to delineate and quantify phase transitions in atomistic simulations of extensional flow of an entangled polyethylene melt. These variables measure the local ordering and energetics at the monomer level, as opposed to the global system, and hence can be used to detect and quantify flow-enhanced nucleation events at small length and time scales that lead to flow-induced crystallization. The kinetics of the nucleating localized crystals can also be tracked using an atomistic Gibbs free energy composite variable. Based on the assumption that the global crystallization process followed a first-order reversible kinetic rate expression with a lag time, kinetic rate constants were calculated as functions of Deborah number that allowed quantification of the flow-induced crystallization phenomenon exhibited by the simulated system under planar elongational flow at a temperature high above its quiescent melting point.

Symposium AR
Applied Rheology and Rheology Methods

Organizers: Mubashir Ansari, Ruel Mckenzie and Jörg Läuger

Tuesday 9:50 Ballroom 7 AR15

Rheology of aluminum copper alloys in the solidification region

Lakshmi Ravi Narayan and Rainer J. Hebert
Department of Materials Science and Engineering, University of Connecticut, Storrs, CT 06269, United States

Metal alloys solidify over a range of temperatures. Characterizing the properties of the liquid and solid fractions in this range is important for understanding solidification processing methods such as casting, welding and additive manufacturing. The viscosity of the liquid fraction is important for the modelling and simulation of the hot cracking phenomenon experienced by metal alloys during solidification. The rheology of binary aluminum-copper alloys has been investigated in the liquid-solid two-phase region. Oscillatory measurements have been made at temperatures within the solidification range, and both oscillatory and rotational measurements have been made in the fully liquid region. For each alloy, the viscosity has been measured for temperatures within the solidification region from fully liquid to near that at which it is fully solid. The composition of the liquid fraction at each of these temperatures has been determined using computational thermodynamics. The viscosity of an alloy with this composition in the fully liquid state has been measured for comparison. There is a sharp rise in the viscosity at temperatures that correspond to the coherency point for these alloys. This data is required for the modelling of the hot cracking phenomena that limits the processing of metal alloys and will furthermore help alloy development efforts.

Tuesday 10:15 Ballroom 7 AR16

The kitchen pot thickens, drop by drop

Karthika Suresh[1], Lena Hassan[1], Carina Martínez Narváez[1], Michael Boehm[2], Stefan Baier[2], and Vivek Sharma[1]
[1]Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States; [2]Motif FoodWorks, Inc., Boston, MA, United States

Many food formulations contain sugars and polysaccharides as thickeners that influence flow behavior, stability, processability, texture, and mouthfeel. Interfacial and rheological properties of key ingredients including polysaccharides influence production and processing of various foods, as well as the consumer perception and bioprocessing that begin with every bite. Typically, chefs, formulators and regular cooks in kitchens judge stickiness, stringiness, spinnability, ropiness, and flowability by dripping a sauce or a mixture from a ladle, stretching a liquid bridge between finger and thumb, or by dispensing from a nozzle/bottle onto a substrate. Stream-wise velocity gradients associated with extensional flows spontaneously arise during these operations associated with dripping, dispensing or stretching liquid bridges. In spite of great advances in quantitative characterization of shear rheology response, elucidating, measuring and harnessing the extensional rheology, there remain well-known challenges associated with robust, reliable and affordable measurement of extensional rheology response. In this contribution, we present a range of experiments that emulate the kitchen flows and survey the influence of typical thickeners by quantitative studies relying on visualization and analysis of pinching flows encountered in dripping, dispensing, and stretched liquid bridges. In addition to dripping, we rely on dripping-onto-substrate (DoS) rheometry protocols that we developed that rely on analysis of capillary-driven thinning and break-up of liquid necks created by releasing a finite volume of fluid onto a substrate. Additionally, we devise a portable stretched liquid bridge that emulates the commercially available capillary break-up extensional rheometer (CaBER). Finally, we describe our efforts to experimentally examine and characterize the flow behavior of sugar and polysaccharide-based recipes considered desirable by chefs and sweet makers.

Tuesday 10:40 Ballroom 7 AR17

Fingerprints of thixotropy, anti-thixotropy, and viscoelasticity: A comparison of protocols

Yilin Wang and Randy H. Ewoldt
Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

We explore different ways to distinguish between thixotropy, anti-thixotropy, and viscoelasticity. A step shear rate test is typically used to differentiate between thixotropic and viscoelastic fluids; however, it cannot differentiate between anti-thixotropy and viscoelasticity. Orthogonal superposition (OSP) combined with a step change in shear rate can uniquely identify anti-thixotropy, but cannot distinguish thixotropic and viscoelastic signatures. Here we show that hysteresis loops, which are obtained by continuously ramping shear rate up-then-down, or down-then-up, are another promising way to contrast the three dynamics. While there is no universal model for each of the three dynamics, we explore signatures of the most basic thixotropic, anti-thixotropic, and viscoelastic fluid models: a thixotropic visco-plastic kinetic model, an anti-thixotropic visco-plastic kinetic model, and the viscoelastic Jeffreys model. We describe first how establishing an equilibrium at high shear rates, then ramping down-then-up, simplifies features of the hysteresis loops. From these, we identify two distinguishing features. The first is a binary feature of clockwise versus counterclockwise loops: clockwise for thixotropy, but counterclockwise for viscoelasticity and anti-thixotropy. A second feature is therefore required to distinguish the latter two dynamics, and this is achieved at high ramping rates, which we interpret as either a high viscoelastic Deborah number for which elastic stress does not have time to relax, or a high thixotropic Deborah number for which the thixotropic structure does not have time to change. The distinguishing fingerprint features are observed independent of the model details. We establish further evidence for these hysteresis loop signatures by experimentally measuring different materials covering the range of behavior. The protocols explored here can be used to distinguish thixotropic, anti-thixotropic, and viscoelastic dynamics under shear, which have different microstructural origins.

Tuesday 11:05 Ballroom 7 AR18

Using hydrogel autofluorescence to determine elastic modulus in spatially nonuniform hydrogels

John A. McGlynn and Kelly M. Schultz
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Hydrogels are designed as implantable scaffolds to promote tissue regeneration by delivering additional human mesenchymal stem cells (hMSCs) to a wound because hMSCs are involved in all stages of regeneration and improve healing outcomes. Many areas of the body have spatial variations in elastic modulus, G', such as where tendon meets bone. To use hMSC-laden hydrogels in wound repair, spatial variation in implant G' must match the tissue. Unfortunately, traditional measurement techniques are unsuitable for characterizing nonuniform materials. For example, bulk rheology averages over the sample and cannot measure the spatial properties of these materials. Microrheological techniques measure low moduli regimes limiting their ability to characterize tissue mimics. Finally, atomic force microscopy is affected by tip geometry, probe stiffness and often relies on assumptions of infinitesimal strain theory, which can be violated in biological materials. We present a new method for measuring spatial variation in G' by relating G' to gel autofluorescence. We demonstrate this techniques efficacy using a well-studied hydrogel for hMSC delivery. Our gels consist of 4-arm poly(ethylene glycol)-norbornene which cross-links with a peptide upon exposure to UV light. Uniform gels with different G' are made by controlling extent of reaction by changing UV exposure time. G' is measured with a frequency sweep on a bulk rheometer. Gels from the same solution are then made and autofluorescence is measured as a function of extent of reaction. We measure a linear relationship between G' and brightness, enabling measurements of brightness to be used to accurately determine G'. We then prepare hydrogels with a step-change in G' by varying UV light exposure spatially using a photomask and measure the resulting spatial variation in brightness and calculate G'. This work introduces a technique for measuring spatial variations in G' in nonuniform materials, providing a new way to characterize hydrogels designed for use in wound healing.

Tuesday 11:30 Ballroom 7 AR19

Rheology empowered failure analysis of insulating glass unit performance enables a more accurate prediction of sustainability and resiliency to a changing climate

Christopher White, Michael Dimitriou, and Hossein Nejad
Exponent Inc, Bowie, MD 20715, United States

Insulating glass units (IGUs) are clear assembles that comprise most modern building envelopes. These massive factory-made assemblies of double or triple lites of glass are filled with inert gas and sealed prior to being installed onto the building envelope, thus separating the inside from the outside of a building. The insulating glass units have two seals: a weather seal, typically silicone sealant (secondary sealant), and an interior gas pressure seal primarily composed of polyisobutylene (primary sealant). IGUs, although generally reliable, they experience a range of failure mechanisms. Diagnosing the root cause of the failures involves understanding the rheological changes to either the primary weather seal or secondary gas seal. The presentation will showcase the use of rheology to uncover the failure mechanism in a series of IGU failures. These failures are related to weather exposure, primarily Ultra-Violet radiation. Correlating the known environmental exposure to the rheological properties enables estimating the residual capacity of the building envelope. Assessing the resiliency of the building to environmental hazards follows from the estimate of the building's performance reserve. The resiliency calculation for a company's physical facilities is a critical component of compliance with the Scope 31 sustainability or Task Force of Climate-related Financial Disclosures (TCFD).2 Investors, shareholders, and

regulators increasingly require accurate Scope 3 sustainability calculations and TCFD disclosures. A United Nations Environmental Program report identified quantifying the response of physical facilities to changing environmental stress as an unmet critical need.3 Quantifying the performance of the IGUs with rheology enables more accurate predictions of the risks associated with a changing climate. 1. https://www.epa.gov/climateleadership/scope-3-inventory-guidance. 2. https://www.fsb-tcfd.org/. 3. Connell, R.; Hamaker-Taylor, R.; Khosa, B.; Firth, J.; Rycerz, A.; Turner, S.;

Symposium FE
Foams, Emulsions, Surfactants, and Micelles

Organizers: Ruth Cardinaels, Anniina Salonen and Sachin Velankar

Tuesday 9:50 Meeting Room A-B FE15

Factors governing rod formation and growth in polymer micelles

Patrick J. McCauley, Satish Kumar, and Michelle A. Calabrese
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Wormlike micelles (WLMs) are elongated, flexible self-assembled structures used in drag reduction and cosmetic applications. While typically studied in small molecule surfactants, WLMs also form in amphiphilic block polymer solutions, where self-assembly can be tuned via block composition and molecular weight. Previous work on polymer WLMs examined limited block polymer compositions or primarily one solution condition like temperature or additive concentration; thus, a holistic picture of the role of these factors on polymer WLM formation and growth is lacking. Here, a series triblock poloxamers with polyethylene oxide (PEO) end blocks and polypropylene oxide (PPO) midblocks are examined comprehensively to determine the role of amphiphile characteristics (molecular weight, block molecular weight, PPO fraction) and solution conditions (temperature, inorganic salt concentration) on WLM formation and growth. In these systems, micelles undergo a sphere-to-rod transition and growth into WLMs with increasing temperature, eventually phase separating at the cloud point temperature. Salt addition reduces these transition temperatures, with most pronounced effects for poloxamers with high PEO molecular weights and PEO fractions. The local micelle structure determined via small-angle neutron scattering (SANS) is then connected with bulk rheological properties. Interestingly, the local microstructure is similar across poloxamers and sodium chloride (NaCl) and sodium fluoride (NaF) content. However, the growth of WLMs varies significantly, where bulk properties such as viscosity and relaxation time increase by orders of magnitude with increasing PPO and decreasing PEO block size. Increasing NaCl content dramatically increases micelle growth whereas NaF content has little impact, attributed to different anion-specific interactions with the micelle. These studies reveal key parameters dictating rod formation and growth in poloxamer micelles, providing a comprehensive dataset for developing or refining computational models.

Tuesday 10:15 Meeting Room A-B FE16

In situ rheodielectric investigation of alignment of lyotropic liquid crystal mesophases under large amplitude oscillatory shear

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

Lyotropic liquid crystal (LLC) mesophases can be formed through the self-assembly of amphiphilic block copolymers in the presence of selective solvent(s). By altering the temperature and concentration, a variety of nanostructures, such as cubic, lamellar, and hexagonal structures can be obtained. LLC structures are of high interest in applications such as scaffolds for catalysis and separation, templating, encapsulation of molecules as drug delivery agents, and nanocarriers. However, self-assembly usually leads to a polydomain structure with locally anisotropic ordered domains (grains) that are randomly orientated throughout the whole sample. By applying an external stimulus (e.g., electrical or mechanical), the randomly oriented macrodomains can be macroscopically aligned, resulting in long-range order of the hierarchically ordered structure. In this study, the macroscopic alignment of LLCs is investigated under large amplitude oscillatory shear (LAOS). We follow the development of the overall orientation of the lamellar microstructure using the time progression of the dielectric loss modulus e"(t) and conductivity of the samples. We show that different formulations can achieve perpendicular and parallel alignments under LAOS.

Tuesday 10:40 Meeting Room A-B FE17

Magneto-rheology and field-induced ordering in polymer solutions via a mechanism alternate to phase alignment

Karthika Suresh, Grace V. Kresge, and Michelle A. Calabrese
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55414, United States

While block copolymers (BCPs) are promising materials due to their tunable structure and functionality, practical methods for processing BCPs with controlled grain size and orientation remain challenging. We recently discovered anomalous rheology and assembly behavior in homopolymer, diblock BCP, and triblock BCP solutions exposed to low intensity (B <0.5 T) magnetic fields, which undergo a disorder-to-order transition after a critical induction time. Prior to magnetization, these solutions are composed of coiled polymers or spherical micelles with no inherent structural anisotropy; we thus attribute this field-induced ordering to a mechanism other than phase alignment, as is traditionally observed in magnetized BCPs. Using magneto-rheology, a three-to-six order of magnitude increase in the suspension modulus is observed upon field application, where the induction time is inversely related to amphiphile molecular weight. Small angle x-ray scattering (SAXS) measurements

following magnetization indicate that the observed field-induced phase formation depends on polymer characteristics. Homopolymer solutions like polyethylene oxide and polypropylene oxide exhibit field-induced crystallization, but require long magnetization times (~18 h). Conversely, both diblock and triblock BCPs order rapidly, forming ordered phases including hexagonally-packed cylinders and cubic packings. Unlike in homopolymers, BCPs do not exhibit any signatures of field-induced crystallization. Followup studies using Fourier transform infrared spectroscopy (FTIR) suggest that instead of inducing phase alignment, low intensity magnetic fields alter polymer-solvent interactions in these systems to facilitate structural transitions. Understanding these directed-assembly mechanisms is of significant scientific interest for its potential to enhance assembly with minimal input from external fields, and the potential to discover new structures not accessible through traditional self-assembly routes.

Tuesday 11:05 Meeting Room A-B FE18

Why can we measure interfacial rheology for some polymers at the A/W interface and not for others?

Daniel Ashkenazi[1], Stelios Alexandris[2], Dimitris Vlassopoulos[2], and Moshe Gottlieb[1]
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Polymer laden fluid interfaces play a crucial role in many biological and industrial process. Exploration of the still poorly understood interplay between polymer molecular characteristics, polymer organization at the interface, and their effect on the mechanical properties of the interface is a prerequisite for a proper design for multitude of interface dominated processes. Several instruments have been developed over the year for the measurement of the interfacial shear rheology. The magnetic needle device, the double wall ring, and the bicone are the most frequently used. Detailed studies have been carried out concerning the operation of these devices (e.g., D. Renggli et al. J. Rheol. 2020, 64, 141). Taking advantage of the understanding that has been developed over the years it is possible to characterize the interfacial rheology of some polymer-loaded interfaces while it is not accessible for others. In this talk we would like to identify the characteristics that prevent the measurement of interfacial rheology of some polymers and make it possible for others. A combination of classical rectangular Langmuir-Pockels trough, Brewster's angle microscopy for morphology and layer thickness determination, and different shear interfacial rheometers have been employed in the attempt to resolve this question.

Symposium AB
Active and Biological Materials

Organizers: Sujit Datta and Danielle Mai

Tuesday 10:15 Meeting Room C-D AB11

Rheological characterization of covalent adaptable thioester networks

Shivani Desai[1], Benjamin Carberry[2], Kristi Anseth[2], and Kelly M. Schultz[1]
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Different types of cells have been shown to play an important role in repairing tissues during processes such as wound healing and tissue regeneration. Synthetic scaffolds are being developed as 3D cell culture platforms, which can be implanted into the body to deliver additional cells and enhance natural repair. Covalent adaptable networks have emerged as promising candidates for 3D cell culture platforms. These networks have adaptable cross-links that can break and reform in response to external stimuli, such as pH and shear. The ability to rearrange cross-links enables these networks to relax stress when encapsulated cells apply force to the network. This dynamic rearrangement mimics the native extracellular matrix (ECM) and permits complex cell functions including differentiation, spreading and proliferation. In this study, adaptable thioester networks are formed by photopolymerizing 8-arm PEG-thiol and PEGthioester di-norbornene. These thioester networks undergo rearrangement when excess thiols are available in the network. To design thioester networks for cell delivery applications, we first vary the amount of excess thiol in the network and use bulk rheology to measure stress relaxation of the networks. We then characterize network degradation with 100% excess thiol at physiological pH with multiple particle tracking microrheology (MPT). MPT measures Brownian motion of fluorescent probe particles embedded in the material and characterizes microstructural changes in the material. Using time-cure superposition we determine the critical relaxation exponent, n, which defines the sol-gel phase transition and also provides information about network connectivity. These results indicate that rearrangement causes phase transitions in the network over time. This work quantifies dynamic structural properties of thioester networks which informs the design of these scaffolds for specific tissue engineering applications and enhanced cell delivery.

Tuesday 10:40 Meeting Room C-D AB12

Blood thixotropy and rheological hysteresis under shear

Elahe Javadi and Safa Jamali
Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States

Blood as a suspension of red blood cells (RBCs) and plasma with a low volume concentration of white blood cells and platelets is known as a thixotropic fluid with non-newtonian, viscoelastic, and shear thinning characteristics. At low shear rates, the bridging of fibrinogen proteins results in the formation of rouleaux structures manifesting in a large increase of overall viscosity and measurable yield stress. These internal flocculated mesostructures are however broken down under sufficient shear forces in a dynamical fashion giving rise to thermokinematic memory formation and thixotropic behavior of the blood. We apply an in silico flow sequence in which blood is subject to a rate-decaying flow from an initial high

deformation rate (ramp down) followed by increasing to the initial high shear rate (ramp-up) upon reaching a minimum deformation rate to probe the origins and characteristics of this thixotropic behavior. The shear stress response of the blood under these flow protocols in the shape of well-characterized hysteresis loops can be directly used to quantify a thixotropic timescale. The hysteresis areas measured show a strong dependence on the flow time intervals, hematocrit level in the system as well as the concentration of fibrinogen and other large proteins. Employing such protocols, we present a full investigation of blood's intrinsic thixotropic timescale at different conditions and the structural origin of such thermokinematic memory.

Tuesday 11:05 Meeting Room C-D AB13

Effects of sustained low-dosage aspirin consumption on the thixotropic behavior, microstructure and rheology of human blood

Matthew J. Armstrong[1], Trevor Corrigan[2], Erin Milner[3], Dorian Bailey[3], Andre Pincot[3], and Thomas Brown[3]
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The leading cause of death globally is cardiovascular disease. The cost of this disease as measured by both financial loss and loss of lives has increased dramatically over the last two decades. The scale of this problem necessitates development of as many solutions as practicable. One of the most common preventative measures over the last several decades has been the prophylactic use of sustained, low dosage, acetylsalicylic acid (Aspirin). Even though this approach has been heavily utilized, few if any rheological studies validating the change in physical, mechanical properties of human blood such as viscosity and yield stress at varied shear rates exist in the literature. This is a rheological study of human blood from multiple donors before and after taking a daily 81mg dose of Aspirin for 14 days. The viscosity and yield stress both demonstrate a statistically relevant aggregated decrease across the entire study population. The advancement and evolution of blood modeling to incorporate more thixo-elasto-visco-plastic (TEVP) features to accurately capture transient flow now allows for the use of these models to characterize blood. With recently collected steady state and oscillatory shear flow rheological data from a DHR3 using human we show 'best-fit' modeling efforts with the contemporary enhanced thixo-elasto-visco-plastic (TEVP) model. Best fit rheological model parameters are then used to determine values for normal, healthy blood, determine the 95% confidence interval and corroborate correlations with physiological parameters (HDL, LDL, hematocrit, etc.) from literature. Series of physical processes (SPP) analysis is incorporated to illustrate how mechanical properties are tied to the transient, evolving microstructure of human blood and physiological parameters under large amplitude and uni-directional oscillatory shear flow both before and after the 14 day aspirin protocol. LAOS with human blood is then used to build an aggregated mechanical contour map of 'solid-like' and 'liquid like' properties.

Tuesday 11:30 Meeting Room C-D AB14

Effect of excipient addition on the extensional flow of protein solutions

Kathleen T. Lauser, Amy Rueter, Isabelle Jones, and Michelle A. Calabrese
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55414, United States

With global sales of over $288 billion in 2016, solution-based protein medications represent a sizable portion of the pharmaceutical industry.[1] Subcutaneous injection of these medications exposes proteins to strong shear and extensional forces, which can cause conformational changes such as protein denaturation and aggregation, leading to loss of function.[2] We developed a dripping-onto-substrate (DoS) instrument[3] optimized for small-volume measurements on proteins, to link the spatiotemporal decay of a liquid bridge radius to extensional rheological properties. Our experiments with model albumin proteins have shown that even dilute, low viscosity formulations demonstrate differences in thinning behavior that is distinct from water controls. Additionally, we compared DoS experiments with proteins alone to measurements with added excipients, such as poloxamers and polysorbates, that preferentially diffuse to interfaces and protect proteins structure.[4] While these excipients have been found to be stabilizing to protein solutions in shear[4], in extensional flows and at higher concentrations, excipients can lengthen the total time or magnitude of extensional deformation, which can ultimately be destabilizing. This work quantifies the effect of extensional flows on protein behavior both with and without excipients, and identifies optimal ranges of excipients that prevent interface aggregation without introducing additional extensional destabilization.

References: 1. Moorkens, E. et. al. Front Pharmacol,11 (2017) 1-12 2. Bekard, I. et al. Biopolymers, 95 (2011): 733-745. 3. Dinic, J. et al. ACS Macro Lett, 4.7 (2015): 804-808. 4. Lee, H. et. al. Adv. Drug Deliver. Rev. (2011) 1160-1171.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Marie-Claude Heuzey, Sara Hashmi and Rahul Pandey

Tuesday 9:50 Ballroom 6 SC15

Two-step relaxation of shear-thickening dense suspensions

Andrew Griese[1], Jae Hyung Cho[1], Ivo Peters[2], and Irmgard Bischofberger[1]

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While the steady-state rheological properties of dense suspensions exhibiting discontinuous shear thickening (DST) have been studied extensively, the transient responses of these systems remain largely unexplored. We investigate the two-step exponential stress relaxation of shear-thickening aqueous cornstarch suspensions upon flow cessation. We reach a steady-state flow before the flow cessation by imposing a constant stress, rather than a constant shear rate, to enable access to the system at or near the critical shear rate at which DST is observed. Our experiments show that the characteristic timescale of the first relaxation step varies linearly with the apparent viscosity of the suspension in the steady state, which indicates that the system relaxes like a Maxwellian viscoelastic fluid. The characteristic timescale of the second relaxation step, in contrast, varies linearly with the reciprocal of the critical shear rate, which hints at the breakdown of the frictional contact network due to interparticle repulsions. We compare these results in stress-controlled experiments with those in rate-controlled experiments to further verify our hypotheses.

Tuesday 10:15 Ballroom 6 SC16

Scaling of the viscosity in discontinuously shear-thickening suspensions

Bulbul Chakraborty[1] and Jeffrey F. Morris[2]

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We consider the scaling behavior of the viscosity of simulated shear thickening suspension within the context of a theoretical framework developed by Wyart & Cates [1], in which the jamming volume fraction is reduced due to stress-induced frictional contacts between particles. The simulation is based on the same essential physics and the transition to the frictional state results in a dramatic increase in viscosity and magnitude of the normal stresses [2]. The WC mean-field theory captures many important features of the simulated rheology in DST, but is unable to capture certain features; we explore the rheological response in a more general crossover scaling theory of jamming that includes both the frictionless and frictional limits. Wyart-Cates fits into this framework, with the influence of friction viewed as a perturbation on the frictionless jamming point. The jamming packing fraction as a function of stress (at which the viscosity diverges) is a line of critical points. In mean-field theory, the only effect of the relevant perturbation is to change the jamming packing fraction, while in the more general framework, there are distinct critical exponents at frictional and frictionless jamming. The effect of friction appears to depend on network characteristics such as the anisotropy of the frictional network that depend both on packing fraction and the applied stress. We describe the scaling form of the viscosity, and determine the exponents and the scaling function by performing data collapse.

[1] Wyart, M. and Cates, M.E., 2014. Discontinuous shear thickening without inertia in dense non-Brownian suspensions. Phys. Rev. Lett. 112, p.098302. [2] Singh, A., Mari, R., Denn, M.M. and Morris, J.F., 2018. A constitutive model for simple shear of dense frictional suspensions. J. Rheol. 62, pp.457-468.

Tuesday 10:40 Ballroom 6 SC17

A first-principles approach toward characterizing the rheology of starch granules during granule swelling

Vivek Narsimhan[1], Gnana P. Desam[2], Jinsha Li[3], Nader L. Dehghani[1], and Ganesan Narsimhan[2]

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Starch pasting is the process by which starch granules swell irreversibly in hot water and thicken. This process confers texture to many foods, and controls the flow behavior of starches in pharmaceuticals, biomaterials, and consumer products. Currently, the bioprocess industry spends considerable resources to chemically modify starches for the sole purpose of tailoring their swelling in order to control their flow behavior. Despite the importance of starch swelling, there is a surprising lack of first-principles theories that can offer physical guidance on how to design these processes given the chemical makeup of starch and the heating profile. In this talk, we will discuss our recent developments in first-principles modeling to describe starch rheology during the initial stages of swelling. The first part of the talk will discuss a recently-developed polymer swelling model based on Flory-Rehner theory that predicts how the size distribution of starch granules change during swelling, given the physical properties of the granule (gelatinization temperature and enthalpy, fraction of network that is cross-linked, and second virial coefficient between water and starch). In the second part of the talk, we will discuss how to connect the volume fraction from this theory to the linear viscoelasticity of the starch dispersion. For volume fractions ?<0.5, we show through experiments and Stokesian dynamics simulations that the starch rheology behaves similarly to a rigid particle dispersion. For volume fractions above this limit, the rheology depends on the granule contact mechanics. In particular, we find that the storage modulus G' vs volume fraction ? fall onto a master curve when G' is normalized by ?/R, where ? is the granule-

solvent interfacial energy and R is the average swollen granule size. We demonstrate that both the swelling and rheology theories discussed here allow one to forecast the time dependent storage modulus for many starches and certain food products under arbitrary heating profiles.

Tuesday 11:05 Ballroom 6 SC18

Understanding granular clogging of porous media and continuum flow in rapid underground tunneling

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In underground tunneling, drilling fluid is typically pumped underground to be mixed with excavated solids and conveyed back to the surface, thus cleaning the hole of debris. This critical function of drilling fluid can fail if tunnel walls fracture, or if a porous formation is encountered, since fluid becomes "lost" to the ground. Loss of drilling fluid is a major technical challenge in rapid underground tunneling since the high drilling speed increases the risk of losing the entire drilling assembly including the drill bit, motor, and drill string. Although tunnel wall fracture can be avoided with decreased flow rates, fluid loss to porous media such as gravel and cobble with large pore sizes is difficult to predict or control. Drilling muds alone are made of colloidal clay suspensions that will not clog such porous media at high flow rates, but granular solids picked up from soil cuttings can clog at high flow rates because the flow drives suspension interaction and contact resulting in accumulation at appropriate particle to orifice ratios. The length-scales between suspensions and porous media ultimately determine the time-scale to initiate clogging in porous media. We have fabricated an experimental system to investigate strategies for mitigating drilling fluid losses when encountering seams of porous formation during high-speed tunneling. The system includes chambers of various diameters composed of clear PVC filled with porous media. Flow rate and pressure drop across the chambers are measured to determine the flow regime and permeability of the system over time. Flow in the laminar and inertial regimes will be investigated to characterize clogging by colloidal clays and granular sands to ascertain the relevant length and time scales to instigate clogging and reduce fluid loss. We will present the differences between granular and colloidal clogging on porous media permeability over time and its impact on flow.

Tuesday 11:30 Ballroom 6 SC19

Rheo-small angle neutron scattering measurements of shear-thickening colloidal suspensions with varying interparticle friction

Yu-Fan Lee[1], Brown C. Scott[2], and Wagner J. Norman[1]
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Shear thickening of colloidal suspensions is an active area of research aimed to understand the abrupt increase of viscosity under various high shear flow conditions. As efforts in theoretical models and simulations seek to examine the fundamental physics for strong to discontinuous shear thickening, the current consensus reveals the key role of tangential constraint controlled by nanometric inter-particle interactions, such as enhanced lubrication hydrodynamics or frictional contact forces. However, experimental tests of these latest theories are lacking especially in microstructure at particle level. In this work, we seek to understand the relationship between microstructure and rheology of colloidal suspensions with varying surface friction level. Microstructures are measured via small angle neutron scattering in both velocity-gradient and velocity-vorticity plane. The results illustrate that, no matter the friction level of particles or the projection of plane, structures formations is always observed with a characteristic length scale of a few particle diameters. Meanwhile, it is found that opposite trend in first normal stress differences for two model suspensions with different friction level can distinguish between these micromechanical mechanisms for shear thickening, and this difference is reflected in the shear-induced anisotropic microstructures measured in the velocity-gradient plane [1]. Statistical comparison of experiments with simulations indicates that better resolution of microstructures in simulation models are required to be validated by the experimental data presented. In general, investigation of rheology and microstructure provide quantitative information valuable to understand the mechanistic role of lubrication hydrodynamics and frictional contact in shear thickening.

[1] Y.-F. Lee, Y. Luo, T. Bai, C. Velez, S. C. Brown, and N. J. Wagner, Physics of Fluids 33, 033316 (2021).

Symposium GG
Arrested Systems: Gels and Glasses

Organizers: Emanuela del Gado and Jyoti Seth

Tuesday 9:50 Ballroom 1 GG10

Crazing reveals entanglement network in glassy ring polymers

Jiuling Wang and Ting Ge
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Molecular simulations are used to show that an entanglement network exists in non-concatenated ring polymers of sufficiently long contour length when they are cooled down well below the glass transition temperature. The entanglement network consists of only a fraction of the topological constraints that force ring polymers to be in self-similar globular conformations. The entanglement network can support stable craze formation in ring polymer glass under tensile loading. The structural features of the ring polymer craze and the drawing stress during the craze formation are related to the underlying entanglement network by generalizing traditional models for the crazing in linear polymer glass. The computer

simulations and theoretical analysis demonstrate tuning polymer topology as a promising way to manipulate the mechanical properties of traditional plastic materials.

Tuesday 10:15 Ballroom 1 GG11

Microscopic interactions and emerging elasticity in model soft particulate gels

Minaspi Bantawa, Wayan A. Fontaine-Seiler, Peter D. Olmsted, and Emanuela Del Gado
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We discuss a class of numerical models for particulate gels in which the particle contacts are described by an effective interaction combining a two-body attraction and a three-body angular repulsion. Using molecular dynamics, we show how varying the model parameters allows us to sample, for a given gelation protocol, a variety of gel morphologies. For a specific set of the model parameters, we identify the local elastic structures that get interlocked in the gel network. Using the analytical expression of their elastic energy from the microscopic interactions, we can estimate their contribution to the emergent elasticity of the gel and gain new insight into its origin.

Tuesday 10:40 Ballroom 1 GG12

Elasticity in gels of discoidal colloids

Mahesh Ganesan, Peng-Kai Kao, and Michael J. Solomon
University of Michigan, Ann Arbor, MI, United States

Producing colloidal gels of tailored rheology using minimal amount of constituent particles is an active material design problem in a number of industries. Navigating this challenge in the dilute limit is hampered by the universality of the arrested spinodal decomposition mechanism of colloidal gelation which leads to universal, invariant microstructures. Consequently, volume fraction and interparticle bond strength are the limited tools available for formulators to control gel rheology, which themselves are however, typically constrained by functional requirements of the formulation. Here, we demonstrate that manipulating particle shape anisotropy is a highly effective means to expand the rheological design space for dilute colloidal gels. Using discoidal particles of varying aspect ratios as a model anisometric system, we show that the volume fraction dependence of elastic modulus in discoidal gels exhibits a remarkable shift towards lower concentrations - by as much as a factor of 20 - from the universal curve of sphere gels. Relatedly, discoid gels also exhibit 10^1 - 10^2-fold higher elastic modulus than sphere gels at fixed volume fraction. We apply a well-known model of elasticity in fractal networks and through independent characterization of the model parameters, rationalize this efficient generation of elasticity in terms of the multiplicative contributions of particle shape induced changes to network fractal dimension, backbone topology and anisotropy in interparticle interactions.

Tuesday 11:05 Ballroom 1 GG13

Colloidal bond kinetics govern the rheology of weakly attractive gels

Mohammad Nabizadeh and Safa Jamali
Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States

Colloidal gels are ubiquitous in industrial and natural settings alike. Apart from this practical relevance, the complexity and variety of the rheological responses of colloidal gels under an applied deformation make their far-from-equilibrium structure-rheology coupling of great interest. These gels show strict rate- and time dependent rheologies, with strict thermokinematic memory built into the material due to lively and dynamic nature of microstructure evolution in gels under flow. This complex rheology is believed to be determined by the dynamic and continuously forming/breaking inter-particle bonds under different applied deformation regimes. Here, we employ detailed computer simulations to study the origins of the mechanical and rheological features in short-range attractive colloidal gels at intermediate volume fractions, with respect to multiple characteristics of the particulate network. We decouple the role of different forces on particles, and also interrogate the evolution of the colloidal structure at different rates, quantified by a non-dimensional group called Mason number, as ratio of shearing to attractive forces. We show that by increasing the Mason number the micromechanics of interparticle interactions changes from attractive to hydrodynamic dominated, accompanied by an intermediate transition regime where the competition between the two results in dynamical heterogeneities. We then present an analysis of the life and death mechanism of bonds where at small Mason numbers the old bonds are dominantly responsible for the mechanics of the gel, while at large Masons, it is the young ones that determine the rheological response. Finally, we present visual mapping of particle bond numbers, their lifetimes and the stress response under different conditions.

Tuesday 11:30 Ballroom 1 GG14

Tuning viscoelastic behavior of vitrimers via crosslinker and backbone control

Laura E. Porath and Christopher M. Evans
Materials Science and Engineering, University of Illinois Urbana Champaign, Urbana, IL 61802, United States

Vitrimers are a class of dynamic polymer network that can combine the mechanical response of permanent networks with the reprocessability of thermoplastics. We first designed silicone-based vitrimers that can be easily tuned in terms of the molecular weight between crosslinks and the type of dynamic bond acting as the crosslinker. Viscoelastic properties of the silicone vitrimers are analyzed using oscillatory shear rheology to determine the plateau modulus, zero-shear viscosity, and characteristic relaxation time from the crossover of storage and loss moduli. The vitrimers show faster relaxation times and lower viscosity upon heating, but also demonstrate entropic elasticity, where the modulus increases with temperature, just as permanent networks do. Upon switching from a trifunctional crosslinker to a tetrafunctional crosslinker, the modulus increased while the relaxation time decreased, which can be attributed to the local chemistry of the crosslinkers accelerating exchange reactions. Our findings

provide a path for designing materials where static and dynamic properties can be pseudo-independently controlled. We also find that mixtures of dynamic bonds do not result in additive properties. In addition, we have investigated the role of polymer strand chemistry in networks with the exact same dynamic bond density and find orders of magnitude differences in relaxation time, pointing to the critical role of the backbone in vitrimers.

Symposium OP
Online Program

Organizers: Anne M. Grillet and Marie-Claude Heuzey

Tuesday 9:50 Virtual OP2

Online discussion: Session 2

Anne M. Grillet[1] and Marie-Claude Heuzey[2]
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Online discussions will be broken up into two topics each day. Each group will start with a full-length (20 minute) virtual keynote presentation then authors of flash presentations will be allowed 10 minutes to provide a quick (3 minute) overviews of their key findings followed by questions and discussion with the audience.

Tuesday:
- Polymer: solutions, structure and modeling
- Methods and applied rheology

Lists of each discussion group, keynote and list of flash presentation authors as well as zoom links will be provided by October 1st.

Tuesday Afternoon

Symposium SM
Polymers Solutions, Melts, and Blends

Organizers: Dimitris Vlassopoulos, Christopher Evans and Poornima Padmanabhan

Tuesday 1:30 Ballroom 5 SM20

Polypropylene ionomers: Extensional strain-hardening and extensional-flow-induced crystallization

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Ionomers are polymers containing small amounts of ionic groups attached to the backbone. These ionic groups aggregate into nanometer-size ionic clusters, which act as physical crosslinks, resulting in substantial increase in both melt strength and extensional strain hardening (SH). These two are desirable rheological properties for several processing operations (e.g., thermoforming, blow film molding and foaming). We measured the response to uniaxial extensional flow of a series of polypropylene (PP) ionomers and quantified the SH level as a function of the ion content. We performed ex-situ X-ray scattering measurements on melt-stretched samples to elucidate the mechanisms of chain stretching and concomitant SH behavior. We found that the level of SH directly correlates with lamellar and crystal orientation developed after deformation and quenching. Moreover, we observed that the crystallization is significantly accelerated after a pulse of extensional flow is applied on the PP ionomers at a temperature above the quiescent crystallization temperature, producing highly oriented crystal structures. Such extensional flow-induced crystallization effect also operates in the non-ionomer polyolefins, albeit at a much lower level.

Tuesday 1:55 Ballroom 5 SM21

Short-chain branching and rheology of crystallizing LLDPEs

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The semi-crystalline nature gives rise to unique superior mechanical properties and optical properties of everyday plastic products. The material designers manipulate the structure and arrangement of crystalline domains through molecular weight distribution and short-chain branching (SCB) of constituting polymers. However, they also modify numerous other properties in the process, such as rheology during crystallization. Therefore, the changes in relaxation times and the magnitudes of viscous and elastic modulus during crystallization can be linked to the structure of developing crystalline domains. Additionally, the rheology during crystallization is crucial for polymer manufacturing optimization studies. Previously we showed that SCB distribution determines the rheology of polymer melts during crystallization qualitatively. In this work, we combine detailed information from molecular weight distribution, comonomer content distribution, and cross molecular weight/comonomer content distribution with rheo-Raman measurements. The interpretation of experimental data through the slip-link model allows us to gain insights into crystalline structures. Our study focuses on several industrial-grade LLDPEs, and we present a model that connects the SCB distribution to the rheology of crystallizing LLDPEs quantitatively. This model is useful for the designing future LLDPEs materials and final products

Tuesday 2:20 Ballroom 5 SM22

Rheology during crystallization of mixed polyolefins

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The processing of mixed waste-stream polyolefins influences their crystallization kinetics and material properties, with implications for manufacturing useful products from recycled plastics. Blends of polyethylene and isotactic polypropylene have been studied due to their prevalence in the waste stream, including work on improving properties through processing and compatibilization. However, little is known about the interplay of processing, domain structure, rheology and crystallization in immiscible blends with two crystallizing species. We employ the rheo-Raman microscope, phase contrast microscopy, and differential scanning calorimetry to study the crystallization and the associated rheology in immiscible blends of polyethylene and isotactic polypropylene. We find that the crystallization kinetics and rheology are a strong function of domain structure and composition. In particular, we examine the continuity of the iPP domain and its impact on the crystallization kinetics. Our results indicate the importance of rheology and processing on the structure and properties of mixed waste-stream crystallizing polymers.

Tuesday 2:45 Ballroom 5 SM23

Attraction and indifference in the flow and crystallization of poly(L-lactide) with tungsten disulfide inorganic nanotubes (PLLA/WS2NT)

Lison Rocher[1], Andrew S. Ylitalo[2], Tiziana Di Luccio[2], Riccardo Miscioscia[3], Giovanni De Filippo[4], Giuseppe Pandolfi[3], Fulvia Villani[3], Alla Zak[5], Gary H. Menary[1], Alex B. Lennon[1], and Julia A. Kornfield[2]
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In situ synchrotron X-ray scattering was used to reveal the transient microstructure of poly(L-lactide) (PLLA)/tungsten disulfide inorganic nanotubes (WS2NTs) nanocomposites. This microstructure is formed during the blow molding process ("tube expansion") of an extruded polymer tube, an important step in the manufacturing of PLLA-based bioresorbable vascular scaffolds (BVS). A fundamental understanding of how such a microstructure develops during processing is relevant to two unmet needs in PLLA-based BVS: increasing strength to enable thinner devices and improving radiopacity to enable imaging during implantation. Here, we focus on how the flow generated during tube expansion affects the orientation of the WS2NTs and the formation of polymer crystals by comparing neat PLLA and nanocomposite tubes under different expansion conditions. Surprisingly, the WS2NTs remain oriented along the extrusion direction despite significant strain in the transverse direction while the PLLA crystals (c-axis) form along the circumferential direction of the tube. Although WS2NTs promote the nucleation of PLLA crystals in nanocomposite tubes, crystallization proceeds with largely the same orientation as in neat PLLA tubes. We suggest that the reason for the unusual independence of the orientations of the nanotubes and polymer crystals stems from the favorable interaction between PLLA and WS2NTs. This favorable interaction leads WS2NTs to disperse well in PLLA and strongly orient along the axis of the PLLA tube during extrusion. As a consequence, the nanotubes are aligned orthogonally to the circumferential stretching direction, which appears to decouple the orientations of PLLA crystals and WS2NTs.

Tuesday 3:45 Ballroom 5 SM24

Effect of flow on the rheology-crystallinity relationship in crystallizing polyethylenes

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Polymer crystallization from the melt is characterized by dramatic changes in structure and rheology that affect the processing conditions used to generate industrially relevant products. Although relationships between crystallinity and rheology are necessary to simulate and monitor the effect of processing on final part properties, direct measurement of these relationships is often complicated by the respective measurement techniques that are used to quantify crystallinity and rheology. Here, simultaneous Raman spectroscopy and rheology measurements are performed in polyethylenes to better understand the modulus-crystallinity relationship. Chemometric methods are used to measure the relative crystallinity in the Raman spectra to avoid uncertainties in more common peak fitting techniques. The modulus-crystallinity relationship measured during isothermal crystallization is well-described by a generalized effective medium (GEM) model that treats the semicrystalline domains growing from the melt as viscoelastic solid inclusions dispersed in the melt phase. The semicrystalline domains grow and impinge upon each other to form superstructures that eventually generate a stress-supporting network that spans the measurement geometry. At this percolation, the model predicts a critical gel-type response with power law relaxation dynamics at low frequencies. These suspension-based concepts can also be applied to isothermal crystallization processes with constant stress or strain to measure the intrinsic viscosity of semicrystalline domains dispersed in the melt. Increasing shear rates drive the intrinsic viscosity to much higher values, indicating highly anisotropic domains are generated in flow.

Tuesday 4:10 Ballroom 5 SM25

Shear-induced nematic phase in entangled rod-like PEEK melts

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We present novel rheo-optical evidence for a shear-induced isotropic-nematic transition exhibited by poly(ether ether ketone) (PEEK) melts of various chain lengths. The key factor is the significant rigidity of the PEEK chain that makes it a rod-like polymer. At low shear rates PEEK is an isotropic rodlike polymer with viscosity scaling as the sixth power of Mw, as predicted by Doi and Edwards. At high shear rates PEEK is fully nematic and at intermediate shear rates there is a biphase. The shear rate at which the longest chains start to form the nematic coincides with the critical shear rate that needs to be exceeded for shear flow to accelerate crystallization kinetics. Consequences of this nematic alignment on crystallization and mechanical properties will be discussed.

Tuesday 4:35 Ballroom 5 SM26

Relating the entanglement of semiflexible polymer melts to their local inter- and intra-chain structure

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Predicting the rheological properties of polymer melts from their microscopic structure has been a longstanding challenge. Several theories developed over the past 50 years accurately predict how quantities such as the plateau modulus G_N^0 scale with dimensionless parameters such as the ratio of Kuhn length to packing length (l_K/p). However, these theories have limited ranges of validity and are mutually incompatible. We will discuss our efforts to resolve this issue by developing a unified theory for polymer entanglement that reduces to three previous scaling theories (Lin/Noolandi, Edwards/de Gennes, and Morse) in the regimes for which they were designed. Our theory also treats the crossovers between these regimes, and has been made quantitative by obtaining the relevant chemistry-independent prefactors using molecular dynamics simulations and topological analyses. It is consistent with the theory developed simultaneously and independently by Milner and Bobbili; the two theories are complementary in the sense that each explains things that the other does not. Finally, it agrees well with experiment, and is applicable to recently developed conjugated polymers which possess a melt rheology that cannot be explained by either the L/N model or the Morse model.

Tuesday 5:00 Ballroom 5 SM27

Predicting the plateau modulus from molecular parameters of conjugated polymers

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The relationship between Kuhn length b, Kuhn monomer volume v0, and plateau modulus GN° initially proposed by Graessley and Edwards and experimentally investigated by Everaers, while well-studied for flexible and stiff polymers, has a large gap in experimental data between the flexible and stiff regimes. This gap prevents the validation of the crossover between flexible and stiff polymers and therefore, the prediction of mechanical properties from chain structure of any polymer in this region. Given the chain architecture, including a semiflexible backbone and side chains, conjugated polymers are an ideal class of material to study this cross-over region. Using small angle neutron scattering, oscillatory shear rheology, in-situ polarized optical rheology, along with the freely rotating chain model, we have shown that twelve polymers with aromatic backbones, including conjugated polymers, populate a large part of this gap. We also have shown that a few of these polymers exhibit nematic ordering, which explains a lower experimental GN° than predicted using Everaers' plot, as nematic polymers have fewer entanglements than isotropic polymers. Nevertheless, when 50 ? above the nematic to isotropic transition, these polymers follow the proposed relationship between b, v0, and GN°.

Symposium AR
Applied Rheology and Rheology Methods

Organizers: Mubashir Ansari, Ruel Mckenzie and Jörg Läuger

Tuesday 1:30 Ballroom 7 AR20

Materials that alter the interfacial liquid film in soft tribology

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The interfacial film thickness between two soft surfaces strongly influence the elastohydrodynamic lubrication (EHL) friction coefficient because of its contribution to the shear and normal forces in lubrication analysis. We use a tribology accessory on a stress-controlled rheometer to examine how the fluid film, comprising a mixture of water and glycerol, separates two solid surfaces in tribological sliding conditions. Specifically, we investigate how the film thickness is modified by the surface pattern, wettability, and porosity of the bulk substrates. Poly(dimethyl siloxane) (PDMS) materials are patterned using photolithography and replica molding, their wettability is engineered by incorporating poly(ethylene oxide)-PDMS copolymers into the liquid precursor, and porosity is generated through the use of a sacrificial foaming agent, citric acid monohydrate. For patterned surfaces, we combine Reynolds' equations with linear elasticity to model the tribological behavior of many soft materials, including that of robotic and human fingertips. Softer patterns bend more easily during applied deformation, which consequently decrease the EHL friction. A large wetting energy difference between the elastomer and liquid cause air bubbles to form and thus increase lift between the two surfaces, as predicted by the Cassie-Baxter equations. Porous substrates act as an effective fluid buffer that further controls the interfacial film thickness between tribopairs. Our results collectively show that the liquid film is a key parameter in the rheotribology of soft materials, and furthermore enables the design of friction in realistic environments.

Tuesday 1:55 Ballroom 7 AR21

Defluidization of cohesive particles on an air-bearing rheometer for estimation of particle-level cohesion

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Granular media which includes cohesive powders and bulk solids have to be handled on a regular basis in a variety of industrial applications. Characterization of the flow properties of these powders are of paramount importance when it comes to efficient design and optimization of many industrial operations. Given the abundance of cohesive particles in various industrial applications, accurate prediction of inter-particle cohesion is very important. Inter-particle cohesion plays an important role in various industrial unit operations. However, predicting particle-level cohesion is non-trivial at best. An attractive alternative is bulk measurements from which cohesion can be easily estimated. Recently, particle defluidization was identified as a bulk measurement that can be used to extract inter-particle cohesion (Liu et al., 2018). This method requires direct-coupling of experimental, "standard" defluidization curves (pressure-drop vs. gas velocity) with discrete-element-method (DEM) simulations; "standard" refers to defluidization without channeling. Hence, the method is not readily applicable to highly-cohesive (Group C) particles that exhibit channeling. In this work, we obtain standard-defluidization-curves for Group C particles using a rheometer with a rotating impeller. Then, we confirm that the measurements from the rheometer are system-size-independent, thereby ensuring the feasibility of direct-coupling of the experiments with smaller DEM simulations. Furthermore, we show that the torque required to rotate the impeller may provide an alternative to the pressure-drop to characterize particle defluidization. Finally, we show that the extracted characteristic-velocities from these experiments may provide a relative-gauge for particle-level cohesion.

Tuesday 2:20 Ballroom 7 AR22

A new rapid DSR separation method for polymer modified asphalt

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The goal of this study was to develop a rapid test method on the Dynamic Shear Rheometer (DSR) to measure polymer modified asphalt (PMA) separation. Unlike the traditional aluminum tube test, this new method allows separation to occur while measurements are recorded on the DSR at the same time. Results could be reported within 1 hour. There are two main reasons why the aluminum tube test takes days. First, separation in PMA is a slow process. Second, if separation occurs, all the measurement methods, including Penetration, Softening Point, and DSR, require a sufficient amount of separation between the top and bottom of the tube due to the detection sensitivity and limit. Indeed, the DSR can perform extremely precise measurement and detect small changes in rheological properties caused by separation. Meanwhile, separation temperature can be controlled with strict precision. In this new DSR separation test, a regular DSR sample size (25 mm diameter) PMA was loaded and heated to 182.2ºC (360ºF) for 15 min. The complex modulus (G*) and phase angle (d) at 60ºC (140ºF) before and after heating were recorded. The difference of the phase angles has a linear correlation to the separation results measured by the aluminum tube method.

Tuesday 2:45 Ballroom 7 AR23

RhIGNets: Rheology-informed graph neural networks for learning hidden rheology of complex fluids

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Precise and dependable property prediction for complex and structured fluids is of great interest across industrial and academic settings alike. Thus over many decades, constitutive models with different levels of complexity have been developed in order to recover different sets of rheological properties in complex fluids under various flow protocols. To do so, the central goal is to solve non-trivial time and rate-dependent constitutive equations in form of differential equations. We present a data-driven approach, Rheology-Informed Graph Neural Networks (RhIGNets), for solving systems of coupled Ordinary Differential Equations (ODEs) adopted for complex fluids modeling. Using the graph mode of Tensor Flow, the suggested RhIGNets are used to learn and recover the hidden rheology of complex constitutive models with multiple coupled ODEs. In practice, identifying model parameters for a multi-variant thixotropic or viscoelastic constitutive model generally necessitates a long list of experimental testing. RhIGNets are found to be capable of learning these non-trivial model parameters for a complex material using only a handful of data points from a single flow procedure, allowing for accurate modeling with a small number of experiments. We also show that proposed RhIGNets are not restricted by the choice of constitutive model and can be used to reconstruct complicated manifestations of thixotropic-elasto-visco-plastic (TEVP) fluids by extending to incorporate multiple constitutive relations of choice.

Tuesday 3:45 Ballroom 7 AR24

Rheology and texture of dairy and alternative cheeses using fractional calculus

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Cheese is a complex fabricated food gel that gets its unique physical properties from coagulated milk protein, casein, that entraps fat and moisture. Cheese rheology has been widely studied and applied effectively to explain texture. Recently, Faber et. al (2017) showed that fractional calculus can be used to quantify the linear viscoelastic properties of full-fat, low-fat, and zero-fat semi-hard cheeses over a range of temperatures and water/protein ratios, and derived equations for the firmness F, springiness S, and rubberiness R (FSR attributes). Plant-based (non-dairy) cheese alternative sales are growing at 28% CAGR in the last 4 years. However, these alternative products lack the desired textural properties of dairy cheese due to the different chemistries and structures, mostly due to bound globular plant proteins. In this research, we compare the rheological properties of plant-based cheese alternatives and dairy cheeses, and quantify FSR attributes in terms of two material parameters (i.e. the quasi-property G and the fractional exponent B). We test the applicability of the Scott-Blair model on plant-based alternative cheeses and show that the model describes both the dynamic shear moduli and the creep compliance well. With the creation of contour plots, we are able to directionally show the effect of different ingredients on cheese texture. As we move to better understand the rheology of plant-based alternative foods, such as non-dairy alternative cheeses, we can create food structures that provide desired textures and functions through tailored rheological fingerprints. The goal of this work is to build an understanding of the impact of ingredients on plant-based cheese alternative texture and create rheological predictive models to easily overcome current textural and functional limitations of plant proteins.

Tuesday 4:10 Ballroom 7 AR25

Pseudo-linear large-amplitude oscillatory shear stress (LAOStress): A delicious gift from Afuega'l Pitu Spanish cheese

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We describe dimensionality reduction and feature selection from nonlinear rheology for the purpose of human cognition and sample comparison. Specifically, we consider stress-controlled amplitude sweeps in large-amplitude oscillatory shear (LAOStress) for the Spanish acid-coagulated cheese Afuega'l Pitu. Being a food product enables routes of human perception unavailable with inedible materials, and this in part guides our feature selection hypotheses. The dataset consists of two variations (Blancu and Roxu) each from nine different manufacturers, totaling 18 different samples each tested at three different temperatures (25, 50, 75 °C) each at three different frequencies. These 162 different conditions each experience a LAOStress amplitude sweep that generates a nonlinear strain waveform at each stress amplitude covering a range of 10 - 10,000 Pa. We developed data processing software to analyze this large dataset which allowed us to test different summarizing metrics (low-dimensional descriptions) that highlight the similarities and differences between the cheeses. Key features include the linear viscoelastic compliance (modulus) and the critical stress for significant nonlinearity (either 15% or 100% increase in compliance). The data reduction was simple because the material revealed a distinct response that we call "pseudo-linear" LAOS, wherein some metrics of nonlinearity are small, while others are dramatic. This is geometrically interpreted with Lissajous curve rotation and distortion. For these samples, we generally observe significant rotation (change of first-harmonic compliance) with minimal distortion (as captured by local LAOS measures within a Lissajous curve and higher harmonics). We introduce a map for quantitatively assessing pseudo-linear signatures which can be used across a wide range of soft matter microstructures and constitutive models to help identify and assess low-dimensional features of LAOS datasets.

Tuesday 4:35 Ballroom 7 AR26

Liquid sheet breakup and droplet evaporation in agricultural sprays

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Spraying is a common process in everyday life with applications in agriculture, drug administration, printing, and painting. For agriculture purposes, small droplets are needed to enhance coverage of agricultural sprays, but not so small that they cause drift of the sprayed pesticides. Spray drift can cause the deposition of chemicals to undesired areas with a negative impact on livestock, ecosystems, and human health. In this work, different factors influencing spray breakup and droplet size distributions are discussed. Herein we experimentally measure the droplet size distribution of sprays from agricultural spray nozzles. The sprays were both homogeneous as well as emulsion containing, and the dynamic surface and interfacial tensions were varied to identify their influence on spray volume fraction below 150 µm, which is correlated with the spray drift risk, and on the volume median diameter, which is correlated with the spray deposition. The results of this work will help to understand the factors affecting a droplet size during a spraying process, towards increased efficacy of spraying pesticides.

Tuesday 5:00 Ballroom 7 AR27

The effects of pH and ionic strength on the extensional relaxation time of agricultural sprays

Minghuan Xu, Andrew Riseman, and John Frostad
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Agricultural spraying is widely employed for crop fertilizing and pest management. Recent work from our group has shown that rheologically modifying these agricultural solutions can reduce the required chemical load and subsequent impact on the environment. Specifically, adding small amounts of long-chain polymers to increase the extensional rheology can reduce the loss of droplets from plant surfaces due to bouncing and splashing. However, the pH and ionic strength of these agricultural solutions can vary enormously from one application to another, which presents a challenge to proper formulation. Here we systemically vary the pH and ionic strength of dilute aqueous polyethylene oxide solutions and evaluate the effect on the extensional relaxation time.

Symposium FE
Foams, Emulsions, Surfactants, and Micelles

Organizers: Ruth Cardinaels, Anniina Salonen and Sachin Velankar

Tuesday 2:20 Meeting Room A-B FE22

Tuning the thermoresponsive assembly and gelation of ABA/BAB triblock polymers for targeted antibiotic delivery to treat middle ear infections

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Middle ear infections are prevalent among young children and frequently recur. The standard oral antibiotic treatment method relies heavily upon parental compliance for optimal dosing and results in systemic exposure that can have numerous adverse side-effects. To minimize these effects, we are developing a non-invasive targeted delivery system based on poloxamer 407 (P407), a commercially-available FDA-approved ABA triblock polymer, antibiotic ciprofloxacin, and three chemical permeation enhancers. The system is liquid at room temperature so that it can be syringed into the ear canal and forms a gel comprised of FCC-packed spherical micelles upon contact with the warm tympanic membrane (TM), allowing for extended antibiotic diffusion into the middle ear. Our prior work showed that chemical modification of P407, which resulted in bridged micelles, was required for effective delivery in a chinchilla model; however this compound was novel and its degradation products are of unknown toxicity, potentially impeding rapid translation of the technology into clinical practice. To avoid this complication, we have incorporated reverse poloxamers (RPs), containing the same blocks as poloxamers but organized in a BAB fashion, into the P407 formulation to induce bridging and tune the transition temperature and rheological properties of the hydrogel. At constant poloxamer content, RP addition shifts thermal disorder-to-order transition to higher temperatures regardless of RP identity, which improves the syringeability of the hydrogels. At constant P407 content, RP addition in low concentrations does not markedly change the FCC structure or mechanical properties. However, higher RP content leads to formation of both new spherical packings and ordered phases, depending on the RP hydrophobe content and molecular weight. Understanding and controlling these self-assembled structures will enable creation of antibiotic-loaded hydrogel systems with targeted gelation temperatures and optimal diffusion across the TM.

Tuesday 2:45 Meeting Room A-B FE23

Constitutive modeling of dilute wormlike micelle solutions: Shear-induced structure, transient dynamics, and inhomogeneous flows

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We present a reformulation of the 'reactive rod model' (RRM) of Dutta and Graham [Dutta, Sarit and Graham, Michael D., JNNFM 251 (2018)], a constitutive model for describing the behavior of dilute wormlike micelle (WLM) solutions that treats WLMs as dilute suspensions of rigid Brownian rods undergoing reversible scission and growth in flow. Evolution equations for micelle orientation and stress contribution are coupled to a kinetic reaction equation for a collective micelle length, producing dynamic variations in the length and rotational diffusivity of the rods. We improve on the previous framework by reformulating the kinetic equation for micelle growth on a more microstructural (though still highly idealized) basis, in particular by allowing for micelle growth associated with strong alignment of rods and breakage due to tensile stresses along the micelles. We show that this model is able to capture many of the critical steady-state and transient rheological features of dilute wormlike micelle solutions, particularly shear-thickening and -thinning, non-zero normal stress differences, and stress-overshoot; moreover, this formulation is able to predict the formation of shear-induced structures that give rise to reentrant (i.e., discontinuous) shear-thickening. We further demonstrate excellent agreement between model predictions and experiments for both steady and transient shear and extensional rheology. We then use the reformulated reactive rod model (RRM-R) to analyze the dynamics and behavior of dilute WLM solutions in circular Couette flow, in which a number of instabilities and rheological properties can manifest. We focus on critical conditions for viscoelastic and elastic instability formation, paying close attention to parameter regimes in which the RRM-R predicts a reentrant flow curve (a necessary condition for vorticity banding).

Tuesday 3:45 Meeting Room A-B FE24

Medium amplitude parallel superposition (MAPS) rheology of a wormlike micellar solution

Kyle R. Lennon[1], Gareth H. McKinley[2], and James W. Swan[1]
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We investigate the weakly nonlinear, simple shear rheology of a wormlike micellar solution using a recently developed multi-tone experimental protocol and the framework of medium amplitude parallel superposition (MAPS) rheology. These data-rich experiments probe intrinsic nonlinearities of viscoelastic materials under a broad range of conditions and deformation time-scales. MAPS rheology defines weakly nonlinear material properties, such as the third order complex compliance, that are measured directly by multi-tone experiments, and may be compared to analytical solutions of constitutive models. We compare our data for a CPyCl micellar solution to the predictions of a reptation-reaction constitutive model, which treats micelles as linear polymers that can break apart and recombine in solution. Despite the apparent complexity of this constitutive model, we are able to solve for its MAPS response analytically, and formulate a convex parameter estimation problem from the weakly nonlinear

data. The result of this parameter estimation reveals new insight into how these breakage and recombination processes are affected by shear, and demonstrates the importance of using information-rich data to infer precise estimates of model parameters.

Tuesday 4:10 Meeting Room A-B FE25

Rheology of wormlike micellar gels formed by long-chained zwitterionic surfactants

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Wormlike micellar solutions have found widespread use in industrial applications due to a host of attractive properties. In this paper, we rheologically characterize a commercially used long-chained viscoelastic surfactant (VES). We show that this surfactant forms a wormlike micellar gel at room temperature and a viscoelastic solution at higher temperatures. We probe both states by conducting linear and nonlinear rheological tests and outline key departures from the rheology of more conventional micellar solutions. Shear rheology uncovers evidence of a shear-induced fracture as well as possible shear-banding in these systems. Our work provides a detailed understanding of an important class of wormlike micellar solutions and is likely to inform the design of smart and efficient soft matter.

Tuesday 4:35 Meeting Room A-B FE26

Measuring the structure and rheology of wormlike micelles at high shear rates with capillary rheoSANS

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Our team is developing tools to enable simultaneous rheology and neutron scattering measurements to investigate complex fluids at high strain rates. Our current suite of tools include a prototype slit rheometer for relatively low viscosity or shear thinning fluids (?8 < 5 mPa·s) at shear rates up to 100,000 s-1 and a capillary rheoSANS instrument capable of simultaneously measuring structure and rheology in excess of 106 s-1. In this talk, we will discuss recent work that uses a combination of Couette, capillary and slit rheometry to study structure and rheology in wormlike micelle solutions. Commercially available cationic and/or anionic surfactants are formulated with sodium chloride and/or sodium salicylate in D2O to form extended wormlike micelles. For instance, in the case of CTAB wormlike micelles, the salt/surfactant ratio is varied to tune the quiescent morphology of the micelles. The structure and rheology of these micelles systems are characterized at low shear rates (< 10^3 1/s) with traditional rheoSANS and high shear rates (10^3-10^6 1/s) with capillary rheoSANS to directly correlate rheology and structure. By controlling the quiescent length distribution we plan to examine the extent to which SANS can be used to characterize changes in the length distribution of aligned wormlike micelles with increasing shear rate which is critical to our unravelling the origin of the apparent reduction in alignment at high shear rates observed for some wormlike micelle solutions.

Tuesday 5:00 Meeting Room A-B FE27

Developing a scattering model for semiflexible chains in flow to assess flow-enhanced scission of wormlike micelles

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Understanding changes in microstructural dynamics under nonlinear deformations is critical for designing flow processing of semiflexible chains, such as wormlike micelles, bottlebrush polymers, and DNA. Although flow-small angle neutron scattering (flow-SANS) is suitable for studying how the material deforms in flow, scattering models for semiflexible chains in flow haven't been developed previously due to the challenge of describing the combined effect of the overall chain conformation and the segmental orientation. To address this challenge, we develop a detailed scattering model for semiflexible chains in flow by using connected rods to represent the chains and incorporating an orientation distribution for the segments that is self-consistent with the overall stretch and orientation of the chain. We apply this new modeling framework to study wormlike micelles to deconvolute the contributions to the scattering from changes in micelle orientation, stretching, and interactions from effects due to changes in micelle length in flow. These comparisons are used to provide an outlook for whether the length distribution of wormlike micelles is significantly affected by flow. The development of the scattering model opens up new possibilities for obtaining microstructural information from flow-SANS experiments of semiflexible chains.

Symposium AB
Active and Biological Materials

Organizers: Sujit Datta and Danielle Mai

Tuesday 1:30 Meeting Room C-D AB15

Rheological study of epithelial cell layer by air-liquid interface induced delamination

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The ocular surface is under constant interrogations from the air-liquid interface. However, it remains overlooked how the air-liquid interface can influence cell behaviors. In this study, we demonstrated that the high surface tension at the cell-air interface can induce the delamination of a stratified corneal epithelial cell layer. Bulk moduli of cell layers were extracted by analyzing stresses at the triple line via Neumann's construction, and showed nonlinearity at high strain values. Interfacial tension at cell-air and cell-medium interfaces were obtained via a modified Schultz's method. EDTA treatment showed that the cortical tension of the cytoskeletal components, instead of the adhesive forces at the cell adherens junctions, was the predominant contributor to the viscoelasticity of the epithelial sheets, consistent with previous reports. In addition, we constructed a simple model to demonstrate the balance among cortical tension, focal adhesion, and cell surface tension is necessary to maintain a mechanically stable ocular surface. Overall, we illustrated a method to measure the interfacial properties of corneal epithelium that can be adapted to a wide range of epithelial tissues.

Tuesday 1:55 Meeting Room C-D AB16

A dilatational rheology perspective on acute respiratory distress syndrome

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Acute respiratory distress syndrome (ARDS) is a disease characterized by severe breathing difficulties affecting 200,000 people in the US annually with no known cure and 40% mortality. ARDS begins with trauma to the lung either by disease (including COVID-19 induced pneumonia) or injury. These underlying factors trigger an inflammatory response that leads to increased permeability of alveolar-capillary barriers causing phospholipases and other components of the innate immune system to flood the alveolar spaces. Phospholipases degrade double-chain lipids of lung surfactant into soluble single-chain lysolipids. The resulting increased concentration of surface-active lysolipids in the alveoli leads to changes in the interfacial properties of native lung surfactants. We hypothesize that these phenomena lead to mechanical instabilities in lung inflation through the evolution of interfacial composition and dilatational modulus causing a subsequent alveolar collapse, which is a typical complication of ARDS. We perform simultaneous dilatational modulus measurement and imaging using a Langmuir trough situated under a confocal microscope. The use of Langmuir troughs for dilatational modulus measurements is often complicated by the combined interfacial dilatation and shear deformations resulting from the motion of the trough barriers. However, for lung surfactant monolayers, the dilatational modulus is 2 orders of magnitude greater than the shear modulus, so contributions from shear are negligible. We find that by adding lysolipid to our in vitro lung surfactant monolayers, the dilatational modulus spontaneously decreases by orders of magnitude, and the interfacial morphology also transitions from solid-like to liquid-like, consistent with our hypothesis that the elevated concentration of lysolipid is one of the dominant mechanisms in ARDS progression. The confirmation of this hypothesis is crucial in providing a mechanistic view of ARDS progression which can lead to new therapeutic interventions to treating ARDS.

Symposium IN
Flow-induced Instabilities and Non-Newtonian Fluids

Organizers: Dana Grecov, Irmgard Bischofberger and Antonio Perazzo

Tuesday 3:45 Meeting Room C-D IN6

Transiently linked FENE dumbbells under shear flow

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The effect of the attractive potential of a bead on the breaking and reforming between elements of transiently networked fluids under shear are explored via a mesoscale mathematical model, represented by a stochastic differential equation coupled with associated breaking/reforming dynamics. The macroscale behaviors of these transiently networked, surfactant or polymeric, fluids can include shear thinning, shear thickening, shear banding, and slow, non-exponential, relaxation. The network elements of the model consist of finitely extensible, nonlinear elastic dumbbells. The model is considered under homogeneous imposed shearing flow and the macroscale effects of varying the mesoscale parameters of the model are examined. The computational algorithm to accommodate the model is presented, which ensures that the transient behavior is accurately captured topologically and that a maximum spring length is not exceeded for the case of the finitely extensible spring. The steady-state and transient results are presented with a discussion of the effects of varying the association and dissociation parameters. Further, the results of

the multi-scale model simulations are described, showing desired macroscopic material behavior, such as a nonmonotonic homogeneous flow curve which suggests shear banding in a nonhomogeneous flow.

Tuesday 4:10 Meeting Room C-D IN7

Unification of the rheological physics of yield stress fluids

Krutarth M. Kamani[1], Gavin J. Donley[2], and Simon A. Rogers[1]
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The physics above and below the yield stress is unified by a simple model for viscoplasticity that accounts for the nonlinear rheology of multiple yield stress fluids. The model has a rate-dependent relaxation time, allows for plastic deformation below the yield stress, and indicates that rapid elastic deformation aids yielding. All parameters are obtained from a linear-regime frequency sweep and a steady-shear flow curve. A range of commonly observed rheological behaviors are predicted, including avalanches and viscosity bifurcations, yield strains, the smooth overshoot in the loss modulus and the recently discovered contributions from recoverable and unrecoverable strains in amplitude sweeps.

Tuesday 4:35 Meeting Room C-D IN8

The specific sequence of physical processes that causes the loss modulus overshoot in yield stress fluids

Gavin J. Donley[1], Krutarth M. Kamani[2], Piyush K. Singh[2], Abhishek Shetty[3], and Simon A. Rogers[2]
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We gain a deeper understanding of the yielding transition by performing an experimental decomposition of the rheological response of simple yield stress fluids under oscillatory shearing. By iteratively performing recovery tests throughout the period, combining strain- and stress-controlled rheometry, the transience of the recoverable and unrecoverable strains is distinguished, allowing the solid-like and fluid-like contributions to the material's behavior to be experimentally separated in a time-resolved manner. The decomposed strains allow for solid- and fluid-like contributions to G" to be defined which are both significant across the entire amplitude sweep. We specifically show that the gradual increase in the acquisition of strain unrecoverably at intermediate amplitudes is responsible for the overshoot in the loss modulus, which has been referred to as the Payne effect or a Type III response. We show that this behavior is consistent across different classes of yielding materials (e.g. microgels, glasses, associative polymers, filled polymer solutions), suggesting a universality of our observations. Beyond the explanation of the G" overshoot, the time-resolved nature of the experimental strain decomposition leads directly to a novel, fully-experimental paradigm for the understanding of large amplitude oscillatory shear (LAOS) data. This approach utilizes a novel time-resolved version of the Deborah number, which allows for the relative instantaneous viscoelasticity to be characterized, and for yielded and unyielded responses to be distinguished. We experimentally identify the specific sequence of physical processes that occurs in these materials during LAOS: 1) elastic deformation, 2) rapid, non-instantaneous yielding, and 3) plastic flow. We also show that this sequence of processes is nearly identical to that obtained from the analytical sequence of physical processes framework (SPP), which can therefore adequately capture the non-linear physics of yielding materials via simple measurements.

Tuesday 5:00 Meeting Room C-D IN9

Reynolds "stress" realizability and Cauchy stress objectivity

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Cauchy's stress is an objective (i.e., temporal frame indifferent) dyadic-valued operator inasmuch as molecular-scale momentum fluctuations are caused by spatial gradients of objective thermodynamic scalar-valued potentials. For a second-order, irreducible, compressible, Newtonian fluid, the Cauchy stress and the strain rate are symmetric and objective. The phenomenological coefficients for this model are objective scalar-valued functions of the local thermodynamic state and the eigenvalues of the local strain rate. For some materials, the Cauchy stress is asymmetric and objective. The Reynolds average of the equation-of-change for linear momentum is an exact, albeit unclosed, vector-valued equation for the mean velocity field of a single-phase fluid. The instantaneous equation is Galilean invariant; but not frame-indifferent. The Reynolds "stress" is a dyadic-valued, real, symmetric, non-negative, and non-objective operator for all inertial and non-inertial temporal frames-of-reference. The Cauchy stress is a dyadic-valued, real, symmetric, and objective operator. The Reynolds "stress" and the Cauchy stress are complementary, but they are not similar operators. Turbulent Flows of compressible and in-compressible fluids are encountered ubiquitously in industry. Advances in computational software over the past 30 years and recent theoretical adjustments (see Koppula et al., Physica Scripta, T155, 2013) may provide a means to predict statistical properties of complex fluids in complex geometries. It is noteworthy that URAPS (Universal Realizable Anisotropic PreStress) predicts that the Coriolis acceleration causes an anisotropic re-distribution of the turbulent kinetic energy among the three components of the fluctuating velocity in a rotating homogeneous decay. The presentation will illustrate how the URAPS closure could be applied to simulate turbulent flows of an interpenetrating continua.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Marie-Claude Heuzey, Sara Hashmi and Rahul Pandey

Tuesday 1:30 Ballroom 6 SC20

Shear thickening: A transition from unconstrained to the constrained state

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Concentrated suspensions of rigid neutrally buoyant spheres can exhibit various non-Newtonian features such as shear thickening, normal stress differences, and shear jamming. The viscosity of such suspensions is often found to undergo an abrupt increase making a transition from a low-viscosity to a high-viscosity state, termed as discontinuous shear thickening (DST). We show that this observed behavior can be explained based on a transition from lubricated "unconstrained" rheology, where close interactions between suspended particles take place through a thin liquid film, to a "constrained" rheology, where particles make unlubricated frictional contacts. Here, we consider resistance to all degrees of relative motion between two particles, viz., sliding, rolling, and twisting modes. Interlocking due to roughness and adhesive forces can lead to hindered rolling and twisting motion between particles. We find that the volume fraction to jamming decreases with increasingly more anisotropic microstructure as more constraints are present. A jamming phase diagram and critical coordination number to jamming as a function of various constraints will be presented.

Tuesday 1:55 Ballroom 6 SC21

Unifying disparate non-Newtonian regimes in suspensions: One model to unify them all

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A typical dense non-Brownian particulate suspension exhibits a strong non-Newtonian behavior even if the suspending fluid is Newtonian. Here we present a numerical framework based on discrete particle dynamics and rooted in fundamental physics of microscopic inter-particle interactions like hydrodynamic, attractive/repulsive DLVO and non-DLVO (Derjaguin and Landau, Verwey and Overbeek), the inter-particle contact, and friction to quantitatively predict this non-Newtonian behavior in suspensions. Specifically, a suspension undergoes shear thinning (decreasing viscosity) at low shear rate/stress followed by a Newtonian plateau (constant viscosity) at intermediate shear rate/stress values which transitions to shear thickening (increasing viscosity) beyond a critical shear rate/stress value and finally, a second shear thinning transition is observed at extremely high shear rate/stress values. We unify and quantitatively reproduce all the disparate non-Newtonian regimes and the corresponding transitions with increasing shear rate/stress for the first time. Direct comparison with experimental data from the literature corroborate the validity of the proposed numerical method. Inclusion of traditional hydrodynamic, attractive/repulsive DLVO forces, the inter-particle contact forces and a constant friction reproduce the initial thinning as well as the shear thickening transition consistent with the previous studies. However, to quantitatively capture the intermediate Newtonian plateau and the second shear thinning, an additional non-hydrodynamic interaction of non-DLVO origin and a decreasing coefficient of friction, respectively, are essential; thus, providing the first explanation for the presence of the intermediate Newtonian plateau along with reproducing the second shear thinning in a single framework. We also demonstrate the capabilities of the proposed framework in capturing other non-Newtonian behaviors such as thinning - thickening, thinning - thickening - thinning, normal stress differences along with the effect

Tuesday 2:20 Ballroom 6 SC22

Shear-induced transition from disorder to coexisting ordered states in dense colloidal suspensions

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We report on simulations of a dense suspension of colloidal hard spheres under shear. Similar suspensions at rest have been shown to form a metastable glassy state or a stable crystal/liquid coexistance. We quench the system to an amorphous initial configuration and apply steady shear. At low rates, the system stays disordered over simulation times, but we find that at high rates, for Pe>1, the shear flow induces an ordering transition that drastically decreases the measured viscosity of the suspension. The ordering is analyzed in terms of the layering and the planar structure, and we determine that particles are packed into hexagonal crystal layers (with numerous defects) that slide past each other. By computing different order parameters, we find that the defects correspond to chains of particles in a square-like lattice. The hexagonal packing is more efficient and allows for higher local density, while the secondary lattice emerges in regions of lower local density. By computing the individual particle contributions to the stress tensor, we discover that the largest contributors to the shear stress are primarily located in these lower density regions.

Tuesday 2:45 Ballroom 6 SC23

Modeling the flow of aggregating suspensions using a multiscale tensor approach

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Thixotropy, viscoelasticity, and yield stress result in complex fluid flow behavior in aggregating suspensions. Numerous phenomenological models accurately describe aggregating suspension rheology by employing scalar structure parameters; however, a general model that incorporates the physics of aggregation and breakage remains to be explored. Previous work by Mwasame et al. [1] that uses a model based on population balances that shows good agreement with the shear rheometry experiments. This approach also replaces some empiricism in the structure kinetics approach with a more physically informed modeling. A full tensor description would allow one to go beyond rheometric flows and model fluid flows in arbitrary geometries. A promising framework has been proposed by Stephanou and Georgiou [2], where the authors have derived a non-equilibrium thermodynamics (NET) based constitutive model that uses a conformation tensor to describe the mesoscale structure and thixotropy in thermodynamically consistent fashion.

In this work, we show that a population balance based rheological model can be recast such that the aggregation and breakage kernels are consistent with NET [3] framework. Specifically, we address the breakage kernel, which has been shown to scale as a function of stress for both shear and extensional flows [4]. The resulting tensorial model can potentially describe macroscopic flows in arbitrary three-dimensional geometries. The model predictions for both simple shear and uniaxial extensional flow are compared against the existing models. As non-equilibrium thermodynamics offers a more consistent tensor description, we also explore how the model can capture flow inhomogeneities and effects such as stress-induced migration.

References:
1. Mwasame, Beris, Diemer and Wagner, AIChE J., 2017, 63, 517-531
2. Stephanou and Georgiou, J. Chem. Phys., 2018, 11
3. Beris and Edwards, Thermodynamics of flowing systems, Oxford University Press, 1994
4. Harshe and Lattuada, Langmuir, 2012, 28,283-292

Symposium MC
Micro- and Nanofluidics and Confined Flows

Organizers: Xiaolong Yin and Amanda Marciel

Tuesday 3:45 Ballroom 6 MC6

Capillary flow of chiral liquid crystals

Sepideh Norouzi[1], Mohsen Esmaeili[1], Kyle George[1], Jose A. Martinez-Gonzalez[2], Nader Taheri-Qazvini[1], Rui Zhang[3], and Monirosadat Sadati[1]
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Microfluidic technology provides a platform to study the effect of flow forces on the configurational evolution of anisotropic fluids such as chiral liquid crystals and blue phases. Blue phases (BPs) are high chirality liquid crystals with cubic-crystalline symmetries and submicron lattice parameters capable of reflecting visible light. In BPs, liquid crystal molecules self-organize into double-twisted cylinders (DTCs), which can then assemble into three-dimensional body-centered cubic symmetry (BPI) or a simple-cubic symmetry (BPII). Here, we investigate the effect of flow deformations on the structural topology evolution, chiral relaxation, and phase transitions of two low and high chirality liquid crystals in microfluidic devices. To generate shear flow and extensional deformation, we used a cylindrical capillary and a flow-focused capillary, respectively. Our rheological measurements and flow-induced birefringence results, complemented by computational simulations, illustrate that the coupling of helical organization and shear flow in a circular capillary gives rise to striking rheological behaviors in low chirality liquid crystals associated with director orientation, flow parameters, and channel dimensions. While a high level of shear forces can align the individual chiral liquid crystals, lower flow rates can drive the formation of the DTC structures. The extensional flow in the flow-focused capillary, on the other hand, significantly alters the structural arrangements and decreases the phase transition temperatures; the higher the extensional deformation, the lower the phase transition temperatures. These findings can pave the way to new strategies in designing applications based on liquid crystalline materials such as pressure sensors and tunable filters.

Tuesday 4:10 Ballroom 6 MC7

Rheological analysis of complex fluids at the point-of-need via capillary filling dynamics

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Viscosity analysis at the point-of-need (PON) can be enabled by microfluidic systems that process small sample volumes (microliters) in a portable, easy-to-operate, and low-cost format. Self-driven capillary flow in microchannels that are large enough (~400-800 micrometers in diameter) to be monitored and recorded using a smartphone camera is a convenient realization for PON viscosity analysis. Such capillary filling dynamics span

an important range of shear rates that can be modulated in open/closed configurations of capillary channels and, in principle, leveraged to probe the rheological behavior of the fluid. But a critical drawback emerges from poorly understood capillary dynamics, mainly originating from high imbibition velocities. These conditions produce significant deviations from simple models such as the Lucas-Washburn equation and limit the ability to probe viscosities at moderate to high shear rates. Failure to account for these deviations, including a dynamic contact angle, hinders the applicability of this approach for accurate rheological characterization. Here we introduce advances that enable a precise analysis of non-Newtonian behavior from capillary filling phenomena over a wide range of shear rates. First, we develop an empirical correlation to account for dynamic effects and facilitate probing Newtonian viscosities even when high imbibition velocities are involved. We then compare our model's performance to existent dynamic contact angle models in the literature. This improved modeling is then extended to a power-law fluid, enabling the formulation of an innovative approach whereby the model is locally applied over small changes in shear rate to retrieve a variable power-law exponent n as a function of shear rate. With this framework, video recording of capillary filling using a smartphone and analysis with the proposed approach makes it possible to straightforwardly measure the rheology of complex fluids in PON and resource-limited settings.

Tuesday 4:35 Ballroom 6 MC8

Experimental and theoretical studies of cross-stream migration of non-spherical particles in a quadratic flow of viscoelastic fluid

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Particulate suspension in a viscoelastic fluid is common in industrial applications as well as in the fields of microbiology and microrheology. When in a quadratic flow, particles migrate in lateral direction due to the imbalance of normal stress over the particle surface. A detailed understanding on the migration and rotation behavior of non-spherical particles within such system will be vital to developing precise particle manipulation and separation techniques. In the first part of this work, we develop a theory based on the general second-order fluid model under the limit of weak viscoelasticity (Wi " 1) and provide solutions to the polymer force and torque on a non-spherical particle when subject to an arbitrary flow up to quadratic order. Specifically for spheroidal (prolate and oblate) particles, we further investigate the combined effect of fluid normal stress ratio (a = ?_2/?_1), particle geometry and orientation behavior on the overall particle migration trajectory in a quadratic flow. Particles in general gain faster migration speed with the increasing magnitude of a. In terms of particle geometry, the length the particle spans in the shear gradient direction dominates the particle migration speed. In addition, prolate and oblate particle shows distinct orientation behavior, which leads to difference in overall migration speed towards flow center. In the second part of this work, we experimentally verify the theory in a microfluidic system. A suspension of spherical, prolate and oblate polystyrene (PS) particle in 8% polyvinylpyrrolidone (PVP) solution is flowed in a straight glass capillary channel at the rate of vanishing inertia (Re=O(10^(-3))) and weak viscoelasticity (De=O(10^(-2))). We estimate the average particle migration speed by the particle distribution at various distances from the channel inlet. The results show a good agreement with the theory prediction at the corresponding conditions. We also comment on the observation on the particle orientation behavior in the microfluidic system.

Tuesday 5:00 Ballroom 6 MC9

Controlling alginate gelation dynamics in confined flows

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The formation of polymer gels in flow is a case study in transitions between Newtonian and non-Newtonian flow. Understanding the dynamics of such a system has implications for processes ranging from important biological processes such as venous thrombosis to manufacturing processes such as casein adhesion in continuous cheese making. We investigate alginate gelation dynamics in a microfluidic device, simultaneously measuring flow parameters while imaging gel formation. In mixing a calcium chloride solution with a dilute alginate solution at constant flow rates, we observe cyclical formation of clot-like gel structures which partially occlude the channel. Clot growth is followed by complete shear-ablation at regular intervals. Preliminary results suggest that the formation frequency can vary by more than an order of magnitude with adjustments to control parameters including concentration and flow rate. The pressure required to ablate the gelled clot structure reflects a combination of the clot adhesion strength and its yield stress. We provide independent measurements of solution rheology as well as adhesion measurements using a quartz crystal microbalance. Our results generate a deeper understanding of the relationships between flow conditions, reaction kinetics, and clot rheology and behavior. Developing our knowledge of these processes may help illuminate the related, yet more complex, biological phenomena.

Symposium GG
Arrested Systems: Gels and Glasses

Organizers: Emanuela del Gado and Jyoti Seth

Tuesday 1:30 Ballroom 1 GG15

Hierarchical nature of linear viscoelastic response in colloidal gels

Minaspi Bantawa[1], Bavand Keshavarz[2], Michela Geri[2], Mehdi Bouzid[3], Thibaut Divoux[4], Emanuela Del Gado[1], and Gareth H. McKinley[2]
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Colloidal gels are materials in which a relatively small amount of solid material (colloidal particles or small aggregates) is embedded in a fluid. The solid component is spatially organized into an open, porous network and, in spite of being the minority constituent, is able to provide rigidity and control the mechanical response of the whole material. In many practical applications, these gels are marginally rigid and measuring their response is hard both in simulations and experiments, because they are extremely soft and viscoelastic. We have used large scale simulations with a 3D numerical model and Optimally Windowed Chirp (OWCh) signals to investigate the microscopic origin of the viscoelastic response of soft particulate gels. The main ingredients of the model are short-ranged attractive interactions and bending stiffness for the inter-particle bonds. Using the OWCh protocol we have analyzed the key features of the frequency-dependent dynamic modulus G*(\omega) and their dependence on the gel connectivity and on the preparation protocol. Our analysis indicates that the viscoelastic spectrum of a wide range of gels, with different microstructures, is controlled by an underlying fractal characteristic of the gel network, i.e., its initial rigid backbone, and by the associated hierarchy of time scales. We discuss the microscopic structural and dynamical origin of these hierarchical processes and the emerging scaling behaviors.

Tuesday 1:55 Ballroom 1 GG16

Intersection of percolation, phase separation and glassy behavior sets minimal conditions for gelation of colloidal systems

Brian K. Ryu[1], Scott Fenton[2], Tuan Nguyen[2], Poornima Padmanabhan[3], Matthew E. Helgeson[2], and Roseanna N. Zia[1]
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Thermodynamic phase instability provides a versatile toolkit for developing non-equilibrium structure in atomic and molecular mixtures, where the tendency for kinetic arrest underlies processing strategies for biphasic materials. Repeated annealing and quenching produces materials that combine the properties of individual phases, such as ductility, strength and memory. While such techniques have existed since antiquity, the use of sophisticated thermal processing of colloidal systems is in its infancy. The first step forward is establishing precise locations of arrested states on a phase diagram. Attempts to locate arrested states on equilibrium phase diagrams have met with some success, including identification of glass transition and gel lines which define regions of extremely slowed kinetics. Yet, a mechanistic understanding of how gelation occurs for a particular set of thermodynamic state variables applicable across multiple material classes lags behind. A key element missing in current models is the impact of kinetic rate processes during quenches that arrest phase transition. As a result, predictive connections between particle concentration, interparticle potential and final state are weak. Here we present a method for systematically determining the location of the gelation line on a colloidal phase diagram via modulated quenches in attraction strength using a novel combination of experiments and dynamic simulations. The method is applied to develop gelation lines for an experimental thermoresponsive nanoemulsion system as well as two computational model systems. We identify three distinct regimes on the gelation line, which emerge for all in vitro and in silico systems. We additionally present a detailed investigation of structural and rheological properties at each regime to describe the mechanism of gelation relative to percolation, phase transition, and glass transition. We find that an interplay of these three processes sets the conditions necessary for gelation of colloidal systems.

Tuesday 2:20 Ballroom 1 GG17

Bond forming dynamics of a model colloidal suspension with depletion interaction

Qi Li and Eric M. Furst
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The structure and rheology of colloidal gels are closely related to the attractive interactions between particles and their bonding dynamics. Our current understanding of the colloidal bonding process is based on interaction potential models, such as DLVO, and their assorted energy barriers. These models relate the depth and width of the potential energy wells with activation-type processes that underlie bulk rheological properties, such as the gel viscoelastic moduli and yield stress, and even extend to other rheological behaviors, like shear thickening and thixotropy. Previous experiments measuring the rupture forces between particle pairs revealed the stochastic nature of the bond rupturing process and determined the rupture force distribution with varying the magnitudes of a depletion attraction or depth of a secondary attractive minimum in the potential [1,2]. In this talk, the bond formation process will also be taken into consideration by altering the time scales and forces between colliding particles. A laser tweezer with varying trap stiffness is used to control the trajectory of two colloidal particles, performing approach-retract loading cycles in

different attraction environments controlled by depletant concentrations. The external-force- and attraction-dependent bonding dynamics will be discussed and compared to existing models.

[1] Kathryn A. Whitaker, Eric M. Furst. J. Rheol. 60, 517-529 (2016). [2] James W. Swan, Matthew M. Shindel, Eric M. Furst. Phys. Rev. Lett. 109, 198302 (2012).

Symposium RI
Rheology and Mobility at Interfaces

Organizers: Patrick Anderson and Vivek Narsimhan

Tuesday 3:45 Ballroom 1 RI1

Shear and dilation rheology of complex fluid interfaces

Y. Summer Tein[1], Charles Majkrzak[2], Brian Maranville[2], Jan Vermant[3], Benjamin Thompson[1], and Norman J. Wagner[1]
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Interfacial structure and rheological properties are critical for function in natural and biological systems (e.g. lung surfactants, membranes) as well as many consumer products and industrial processes (e.g., foams, emulsions). As interfaces are often rheologically complex, the goal of this research is to develop instrumentation to accurately measure mechanical properties of complex interfaces that depend on time and deformation-history, e.g., interfaces with viscoelasticity and thixotropy. Mixed flow fields typical of classical Langmuir troughs convolute interfacial dilation with shear, often creating an interface out of equilibrium. Consequently, attempts have been made to deconvolute the interfacial stress by multiple measurement protocols in Langmuir trough experiments[1]. Alternatively, a purely radial deformation is used to determine the instantaneous dilation modulus in a radial trough [2]. However, complex interfaces may be far from equilibrium upon compression with exceptionally long relaxation times. To address these needs, we present a new interfacial trough designed to apply well-defined shear and dilation deformation histories with well-defined interface kinematics. Interfacial kinematics are validated with PIV and meso and nanoscale structure are measured in situ with BAM and neutron reflectivity. The rheological capabilities of this new interfacial trough are demonstrated through experiments on stearic acid at the air-water interface and in the presence of salts in the subphase, leading to an interfacial gel as a complex, shear-history dependent material. Further, the effects of compression and shear annealing of complex interfaces at the air-water interface are demonstrated on microgels, polymers, lipids and biopolymers. The further development of an instrument suitable for use on neutron and x-ray beamlines as well as individual laboratories will be described.

[1] Petkov, Jordan T., et al. Langmuir?16.8 (2000): 3703-3711. [2] Pepicelli, Martina, et al. Soft matter?13.35 (2017): 5977-5990

Tuesday 4:10 Ballroom 1 RI2

Influence of interfacial viscosity on the stability of droplet shapes during sedimentation

Natasha Singh and Vivek Narsimhan
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In this study, we examine how interfacial viscosity affects the stability of droplet shapes during sedimentation. The viscous interface of the droplet is modeled using the Boussinesq-Scriven constitutive relationship, and the interfacial velocity is computed using the boundary-integral method. We observe that below a critical value of the capillary number, Ca_C, the initially perturbed droplet eventually reverts to its spherical shape. Above this Ca_C, the droplet deforms continuously and becomes unstable, resulting in a growing tail at the rear end for initial prolate perturbations and a cavity for initial oblate perturbations. We observe that interfacial shear viscosity stabilizes the droplet, i.e., it increases the Ca_C compared to a clean droplet by inhibiting/delaying the growth of the instability at the droplet's rear end. In contrast, the interfacial dilational viscosity destabilizes the droplet, i.e., it reduces the Ca_C compared to a clean droplet by increasing the rate at which instability grows at the droplet's rear end. Interestingly, both surface shear and dilational viscosity appear to increase the time at which pinch-off occurs compared to a clean droplet, although the mechanisms are distinct. We also examine the combined influence of surface viscosity and surfactant transport on droplet stability by assuming a linear dependence of surface tension on surfactant concentration and an exponential dependence of interfacial viscosities on the surface pressure. We find that pressure-thinning/thickening effects are not very pronounced for dilational viscosities but are significant for the shear viscosity case. Lastly, we provide phase diagrams for the critical capillary number to demonstrate how interfacial viscosity alters the stability for different values of the droplet's viscosity ratio and the initial Taylor deformation parameter.

Tuesday 4:35 Ballroom 1 RI3

High throughput assessment of shear surface viscosity of bilayer membranes

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The shear surface viscosity of lipid bilayer membranes plays an important role in dictating the function of embedded biomolecules. In this study, we devise a high throughput and probe-independent method to measure shear surface viscosity of bilayer membranes based on transient vesicle electrodeformation. We simplify the existing theory from Vlahovska et al. BJ 96, 4789-4803 (2009) with facile design considerations to fit for membrane viscosity as the only fitting parameter in the deformation regime. Our method is probe-free and sensitive enough to allow for robust measurement of membrane viscosity of single-and multi-component lipid vesicles and polymersomes. We find good match of the viscosity values with the existing methods in the literature. Surprisingly, we find that shear surface viscosity depends on the surface charges of the membrane. This has important implications for biomolecular transport of native cell membranes that are intrinsically charged with a transmembrane potential across.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Ballroom 5-6-7 PL3

Electrified droplets: Instabilities, interactions, and rheology

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The interaction of fluids and electric fields is at the heart of natural phenomena such as the disintegration of raindrops in thunderstorms and many practical applications such as electrosprays, ink-jet printing, microfluidics, and crude oil demulsification. Many of these processes involve droplets and there has been a long-standing interest in understanding drop electrohydrodynamics. In this talk I will overview some intriguing phenomena involving viscous drops: symmetry-breaking instabilities in strong fields due to the Quincke rotation effect (droplet pancake-like flipping, formation of a belt of vortices around the drop equator), streaming from the drop equator that creates visually striking ``Saturn-rings" around the drop, non-axisymmetric "kiss-and-run" interactions of a drop pair, and a negative electrorheological effect in emulsions. These complex behaviors arise from nonlinear dynamics in the Stokes flow regime that is yet to be fully understood.

Symposium SM
Polymers Solutions, Melts, and Blends

Organizers: Dimitris Vlassopoulos, Christopher Evans and Poornima Padmanabhan

Wednesday 9:50 Ballroom 5 SM29

Spinnability and centrifugal force spinning of fibers of poly(ethylene oxide) solutions

Jorgo Merchiers[1], Cheryl Slykas[2], Carina Martínez Narváez[2], Naveen Reddy[1], and Vivek Sharma[2]
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Centrifugal force spinning has recently emerged as a highly promising alternative technique for the production of nonwoven, ultrafine fiber mats. Due to its high production rate, it could provide a more technologically relevant fiber spinning technique than electrospinning. In this contribution, we examine the influence of polymer concentration and solvent properties on the centrifugal spinning process and the fiber morphology. We find that increasing the polymer concentration transforms the process from a beaded-fiber regime to a continuous-fiber regime. Furthermore, we find that not only fiber diameter is strongly concentration-dependent, but the choice of solvent and nozzle properties also influence the fiber morphology and mechanical properties. A comprehensive investigation of shear and extensional rheology of the PEO solutions is carried out using torsional rheometry and dripping-onto-substrate (DoS) rheometry respectively to correlate spinnability to the processing conditions as well as to material properties.

Wednesday 10:15 Ballroom 5 SM30

Extensional rheology and pinching dynamics of polysaccharide food thickener

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Foods are multicomponent soft materials that often contain dispersed drops, bubbles, particles, or proteins. Often protein-based foams, emulsions, suspensions, and pastes contain polysaccharides that act as binders, thickeners, gelling agents or rheology modifiers, and influence shelf-life, rheology, processability as well as control over fiber, fat, salt, calorie count, texture, and mouth-feel. Stream-wise velocity gradients associated with extensional flows spontaneously arise during extrusion, calendaring, coating, dispensing, bubble growth or collapse as well as consumption including swallowing and suction via straws. Even though shear rheology response is fairly well characterized and utilized in food industry, elucidating, measuring and harnessing the extensional rheology response have remained longstanding challenges. The characterization challenges include the lack of robust, reliable and affordable methods for measuring extensional rheology response, whereas the product design challenges stem from the difficulties in assessing or predicting the influence of macromolecular properties on macroscopic rheological behavior. In this contribution, we address the characterization challenges for specific case of xanthan gum thickener by using dripping-onto-substrate (DoS) rheometry protocols that we developed that rely on analysis of capillary-driven thinning and break-up of liquid necks created by releasing a finite volume of fluid onto a substrate. The DoS rheometry protocols emulate the heuristic tests of thickening, stickiness or cohesiveness based on dripping a sauce from a ladle or dispensing from a nozzle onto a substrate. We investigate the concentration-dependent variation in shear and extensional rheology of xanthan gum solutions. We show that changing salt concentration can be used for tuning the pinch-off dynamics, extensional rheology response, and processability of solutions of xanthan gum.

Wednesday 10:40 Ballroom 5 SM31

Rheological investigation of magnetically induced disorder/order transition in block copolymer micelles

Grace V. Kresge[1], Karthika Suresh[2], and Michelle A. Calabrese[1]
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[2]University of Illinois Chicago, Chicago, IL 60607, United States

Block copolymers (BCPs) have garnered sustained academic and industrial interest due to unparalleled tunability in material properties and widespread applications. Yet, a central obstacle in the application of these materials is controlling self-assembly over long length scales. Directed assembly via magnetic fields is a promising method for improved block copolymer processing but this method has traditionally relied on using large applied fields (> 6 T) or BCPs with anisotropic constituents such as crystalline blocks. We recently discovered anomalous field-induced phase transitions in industrially-relevant amphiphilic block copolymer micelle solutions (20-30 wt%) using weak magnetic fields ($B = 0.5$ T), which can be used to control their self-assembly and long-range ordering. These solutions exhibit an anomalous transition from a low viscosity fluid (10^{-2} Pa·s) to an ordered soft solid (10^{5} Pa·s) under weak magnetic fields after a critical induction time. Magnetorheological characterization reveals that the critical induction time is independent of frequency and strain amplitude; however, the maximum achievable induced modulus decreases with increasing strain, suggesting that shear acts antagonistically to the field. Magnetic field intensity, magnetization time, temperature, and solvent highly influence the system kinetics, phases formed, and propensity for relaxation. While BCPs magnetized for short times typically exhibit rapid relaxation upon field cessation, BCPs magnetized for long times or at higher temperatures exhibit little relaxation. These induced structures require substantial cooling or high shear rates to destroy the induced structure which is otherwise stable for hours or days, after which the starting material is fully recovered. These unique magneto-rheological studies reveal new processing methods for tuning ordered BCP micelle phases induced via weak magnetic fields.

Wednesday 11:05 Ballroom 5 SM32

Magneto-rheology and field-dependent phase separation of aqueous solutions of nanorods and thermo-responsive polymers

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Polymer-particle suspensions composed of anisotropic constituents have great promise for next-generation smart materials requiring fine structural control. Previous work in elastomers has shown that nanoparticles can be introduced into polymers and precisely directed by external forces such as shear and magnetic fields, though work on the mixture of two or more fields is noticeably lacking. Efforts on the magnetic-field directed assembly of polymer solutions has focused on systems that align and/or crystallize under applied magnetic fields. However, Vshikov recently observed that magnetic fields can also decrease solvent quality in semi-crystalline polymer solutions, motivating the present study. The role of magnetic fields on solvent quality and phase transitions in thermo-responsive polymers-which form amorphous phases upon separation from solvent above a certain lower-critical solution temperature (LCST)-has yet to be explored. Here, we investigate the role of magnetic fields on the rheological behavior and phase separation of aqueous poly(N-isopropyl acrylamide), and the impact of silica nanorod addition on altering these properties. Signatures of the LCST transition are examined two-fold: optical signatures are characterized using an in-house turbidity tester with static magnetic field capabilities and rheological signatures are measured via a magneto-rheological device. When silica nanorods are incorporated at low concentrations, the LCST of aqueous poly(acrylamides) shifts towards higher temperatures; the magnitude of this shift upon nanorod addition is dependent on aspect ratio. Both magnetic field application and silica nanoparticle addition complexly impact phase transitions in these polymer solutions, often opposing one another. Interestingly, changes in LCST behavior are most pronounced in thin samples, suggesting that interfacial effects may influence this behavior. This unique field-induced behavior can be exploited to achieve increasingly complex stimuli-responsive polymeric materials.

Wednesday 11:30 Ballroom 5 SM33

Microscopic dynamics and rheology of vitrimers

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We propose a new model capable of describing the complex bonds dynamic as well as simulating the viscoelastic behavior of a class of associative covalent adaptive networks known as vitrimers. In contrast to conventional thermosets, vitrimers represent a novel class of plastics in which covalent chemical bonds can be efficiently and reliably exchanged between different positions of the polymer network without risking structural damage or permanent loss of material properties. They show creep and stress-cracking resistance at low temperatures and are malleable at high temperatures.

In this study, a combination of coarse-grained molecular dynamics (MD) and Monte Carlo (MC) simulations is employed to predict the microstructure, dynamics, and linear rheology of vitrimers. Using the time-temperature superposition (TTS) principle, the moduli of a vitrimer network are compared with that of a permanently crosslinked one over a wide range of frequencies. Results of the temperature dependence of the horizontal shift factors, which are the normalized relaxation of time, of the vitrimer show an Arrhenius temperature dependence at a temperature above the topology freezing temperature, while at lower temperatures, they follow the Williams-Landel-Ferry's (WLF) equation. On the other hand, the shift factors obtained from the rheology of a permanently crosslinked network obey the WLF equation behavior over the selected range of the temperature. Using the same shift factors, the mean squared displacement data of the network segments are collapsed on universal curves. Furthermore, these two sets of dynamical and rheological quantities are linked to each other via the generalized Stokes-Einstein relationship. Results will also be presented for the temperature dependence of the characteristic time of the intermediate scattering function, and the correlation between this characteristic time and the shift factors used in creating the universal rheological and dynamic curves using TTS will be discussed.

Symposium AB
Active and Biological Materials

Organizers: Sujit Datta and Danielle Mai

Wednesday 10:15 Ballroom 7 AB20

Giant vesicle dynamics in large amplitude oscillatory extension

Charlie Lin[1], Dinesh Kumar[2], Channing Ritcher[2], Shiyan Wang[1], Charles M. Schroeder[2], and Vivek Narsimhan[1]
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While the behavior of fluid vesicles in steady flows have been studied extensively, how time-dependent oscillatory flows impact the shape dynamics of vesicles is not as well understood. In this presentation, we present our results on the nonlinear dynamics of vesicles in large amplitude oscillatory extensional (LAOE) flows from both experiments and boundary integral (BI) simulations. Our results characterize the transient membrane deformations, dynamical regimes, and stress response of vesicles in LAOE in terms of reduced volume (vesicle asphericity), capillary number (Ca, dimensionless flow strength), and Deborah number (De, dimensionless flow frequency). We find that results from single vesicle experiments agree well with BI simulations across a wide range of parameters. We group our results into dynamical regimes based on vesicle deformation characteristics: the pulsating, reorienting, and symmetrical regimes. The distinct dynamics observed in each regime result from a competition between the flow frequency, flow time scale, and membrane deformation timescale. By calculating the particle stresslet, we quantify the nonlinear relationship between average vesicle stress and strain rate. Additionally, we present results on tubular vesicles that undergo shape transformation over several strain cycles. Broadly, this work provides new information regarding the transient dynamics of vesicles in time-dependent flows that directly informs bulk suspension rheology. We will also present some preliminary work on the dynamics of multicomponent vesicles.

Wednesday 10:40 Ballroom 7 AB21

Mechanical characterization of alginate hydrogel beads

Md Mezbah Uddin, Adity Pore, and Siva Vanapalli
Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

Micrometer-scale hydrogel beads are used in a variety of applications ranging from biomaterials to drug delivery to biosensing. The mechanical properties of the microgel beads play an important role in these applications, where for example in biomaterials, the viscoelastic properties of the microgel beads determine cell morphology, stiffness and differentiation. In this study, we investigate the mechanical properties of alginate beads made using microfluidic methods, with a focus on determining the effect of polymer concentration, cross-linking density and bead diameter on the elastic modulus. We determined the elastic modulus of individual alginate beads from the force-displacement curves obtained from compression testing and by fitting this data to the Tatara contact mechanics model. We found that for a given bead size, the modulus increases with polymer and crosslinker concentration. Interestingly, beads with the smallest size (~60 µm) have higher modulus compared to the beads with the larger sizes (>100 µm). The linear elastic regime was also found to be significantly higher for the smallest beads which is indicative of the effect of the size on the stiffness. To explain the effect of bead size on mechanical properties we estimated the network pore size from swelling experiments and found that smaller beads have smaller pores. Our results suggest that the length-scale dependent modulus should be an important consideration for the use of alginate hydrogel beads in biomaterial applications.

Wednesday 11:05 Ballroom 7 AB22

Correlation of dynamic scaffold rheology with molecular release during material degradation

Nan Wu and Kelly M. Schultz
Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

The goal of this work is to establish a quantitative correlation between molecular release and material degradation. We characterize a radical-initiated photopolymerized and a base-initiated Michael addition polymerized hydrogel, which form gels through distinct cross-linking reactions. Both scaffolds are cross-linked with the same degradable peptide, which enables degradation through the same enzymatic degradation reaction. A fluorescently labeled poly(ethylene glycol) is chemically conjugated to the scaffold and is released during enzymatic degradation. Real-time changes in scaffold rheological properties during degradation are measured using bulk rheology. Molecular release is measured by quantifying the fluorescence in the incubation liquid and the hydrogel scaffold. A complicating factor, described in the literature, is that shear may cause increased cross-linking after initiation of degradation resulting in an increase in storage modulus, which would change release profiles. We also test the hypothesis that shear induces additional cross-linking in degrading hydrogel scaffolds. To do this, enzymatic degradation is characterized using bulk rheology as materials undergo continuous or minimal shear and molecular release is measured when the material is incubated with and without shaking. We determine that shear does not change scaffold degradation or release regardless of gelation reaction. Instead, we determine that the type of hydrogel cross-linking reaction greatly affects both material degradation and molecular release. Hydrogel cross-linking by base-initiated Michael addition does undergo further cross-linking at the start of degradation, which results in minimal release. We correlate release with enzymatic degradation for both scaffolds. We determine that material storage modulus is indirectly correlated with release during degradation. These results indicate that rheological characterization is a useful tool to characterize and predict the release of molecules from degrading hydrogels.

Wednesday 11:30 Ballroom 7 AB23

Metal-coordination crosslink dynamics: A bio-inspired toolbox for engineering hydrogel mechanics

Niels Holten-Andersen
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Growing evidence supports a critical role of metal-coordination complex crosslinking in soft biological material properties such as underwater adhesion, extraorganismal self-assembly and autonomous self-healing. Given their exploitation in such desirable material applications in nature, bio-inspired metal-coordinate complex crosslinking likely offers unique possibilities to further advance sustainable polymer materials engineering. Using bio-inspired metal-binding polymers, growing efforts to mimic these material properties have shown promise. Recently we explored how in situ mechanical reinforcement of polymer hydrogels via metal-coordinated crosslink mineralization can potentially be utilized as a simple method for designing mineralized soft composites. Early lessons from these studies will be presented.

Symposium AM
Additive Manufacturing and Composites

Organizers: Liheng Cai and Jay Park

Wednesday 9:50 Meeting Room A-B AM1

Rheology and formulation in material extrusion additive manufacturing of high solids suspensions

Alexandra Marnot and Blair K. Brettmann
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Materials with high particle loadings are important for several applications: in many cases the particles provide the desired functionality and the polymer acts to bind them together into a shape, so maximizing particle content is required. As new processing technologies become more prevalent, such as extrusion-based additive manufacturing, low binder content has introduced challenges, particularly due to the high particle-particle contact areas encountered in highly loaded systems. Understanding how the formulation elements, including particle and binder properties, impact the rheological properties and how those translate to processing will enable rapid formulation design and robust processes. We specifically focus on two elements of the formulation, particle size distribution modality and surface tension of the binder, which are expected to impact both the flow in the nozzle and slumping behavior after printing in material extrusion additive manufacturing. We show that the storage modulus of the suspension decreases as we approach a ratio of large to small particles close to the maximum packing and that this lower suspension rigidity leads to greater slumping and line spreading after printing, despite good flowability in the nozzle. The binder surface tension is expected to affect the cohesion between particles and the viscosity of the suspension as well as impact the ability of the suspension to recover its rigidity after it is subjected to shear forces, an important consideration for maintaining shape fidelity in material extrusion additive manufacturing. We use thixotropy and restructuring rheological studies to understand the impact of the binder surface tension on the suspension recovery and tie this to line width measurements during 3D printing. This work allows us to understand how to link formulation properties to processing through rheology to design high solids suspensions for material extrusion additive manufacturing.

Wednesday 10:15 Meeting Room A-B AM2

Flow-induced stretch, alignment, and relaxation of semi-crystalline polymers in material extrusion additive manufacturing

Jonathan E. Seppala[1], Anthony Kotula[1], Zheliang Wang[2], Ojaswi Agarwal[3], Thao Nguyen[2], and Kevin J. Hemker[2]
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Most soft matter additive manufacturing processes produce parts with asymmetric material properties due to the weak interface between layers. In thermoplastic material extrusion, these anisotropic properties are attributed to rapid cooling and subsequent limited diffusion time across the interface. However, the thermal history and flow-field have an additional effect on semi-crystalline polymers, resulting in changes to the crystal structure due to non-quiescent or flow-induced crystallization. These effects are most dramatic at the interface and can produce varying and asymmetric crystal morphologies in the extrudate. To quantify these effects, we use a combination of in-situ thermography and polarized light imaging to characterize cooling rate and residual stress during printing and ex-situ polarized imaging and micro-beam wide-angle x-ray scattering to characterize the non-equilibrium state of the polymer and final crystalline morphology. From these measurements, we see high extrusion speeds and low extrusion temperatures leave the polymer in a stretched and aligned state, which changes the nucleation density and crystal morphology

at the interface between layers. In contrast, printing at high temperatures provides sufficient mobility for the chains to relax to an equilibrium state before crystallizing or cooling to the glass transition temperature.

Wednesday 10:40 Meeting Room A-B AM3

3D printing of a Diels-Alder covalent adaptable network with microparticle reinforcement

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A limiting factor preventing the more widespread adoption of extrusion-based 3D printed parts is the relatively poor and anisotropic nature of their mechanical properties due to the inherent layer-by-layer, additive approach. Recently, covalent adaptable networks (CANs) have been used to produce nearly isotropic parts thanks to the thermoreversible, covalent bonds that make up the crosslinked network architecture. At temperatures experienced in the heated extrusion barrel, these bonds begin to either rapidly exchange or break into their monomeric form enabling flow and stress relaxation. The formation of covalent bonds across layers gives the thermoset-like network isotropic strength and a lack of void space in printed objects. In order to impart new properties or enhance mechanical properties, particle fillers can be added to a polymer matrix. In this work, spherical glass microparticles are compounded into a CAN matrix utilizing Diels-Alder chemistry for the first time. First unfilled CAN material is characterized and used in 3D printing to establish a baseline. Subsequently, bare microparticles are compounded into the matrix at varying volume fractions. The unique rheology of the microparticle-filled composites is used to evaluate the material for use in 3D printing. Due to the glassy and brittle nature of the materials at room temperature, a pellet-based printer is used in the printing process that avoids issues with typical filament-based printers. In the future, surface functionalization of the particles will enable thermoreversible bonds to form between the filler and matrix, thus facilitating the transfer of stress more effectively.

Wednesday 11:05 Meeting Room A-B AM4

High strength, high toughness parts via dual material fused filament fabrication

Brian Koker[1], Jay H. Park[1], Rebecca Ruckdashel[1], Hikma Abajorga[1], Ryan Dunn[2], Eric Wetzel[2], and David Kazmer[1]
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Previous research in the field of bicomponent thermoplastic 3D printing material showed promise in developing structures with tough, near-isotropic properties; a feat that is unheard of in tradition fused filament fabrication (FFF) systems. The combination of a core with a significantly higher glass transition temperature (Tg) than the sheath allows for parts that can be annealed to increase chain diffusion across layers while maintaining dimensional stability. The use of a thermal draw tower in previous research allowed for rapid prototyping of material and geometric combinations, but lacks viability as a larger scale manufacturing process due to the bottleneck of creating dual material preforms and requiring secondary processing. Using a convention coextrusion technique, with an additive manufacturing driven iteration process, showed promise as a scale-up technique, and was able to produce larger quantities of consistent filament needed for more comprehensive analysis and production. Compared to current state of the art ABS filaments, this filament showed a 5 time increase in z- direction impact toughness, and a 3 time increase in z-direction tensile strength after annealing. The enhanced thermal stability of this material allowed for higher print temperatures which also significantly improved strength. This research continues to demonstrate the groundbreaking improvements to FFF that are possible through dual material filaments as well as the manufacturing feasibility of such a product.

Symposium IN
Flow-induced Instabilities and Non-Newtonian Fluids

Organizers: Dana Grecov, Irmgard Bischofberger and Antonio Perazzo

Wednesday 9:50 Meeting Room C-D IN11

Linear versus branched: Flow of a wormlike micellar fluid past a falling sphere

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We report experiments on flow of linear and branched wormlike micellar solutions past a falling sphere. A combination of particle tracking, particle image velocity and flow-induced birefringence has been used to obtain the velocity of the sphere and the detailed form of flow structure around the falling sphere. Our results indicate three significant differences in flows of branched versus linear micelles. First, while the sphere drag rapidly decreases upon increasing Weissenberg number (Wi) in linear micelles, it shows an apparent local maximum at Wi~3 in branched micelles. Second, despite its high viscoelasticity, the time-averaged flow of branched micelles around the falling sphere exhibits a fore-and-aft symmetry, while a strong negative wake is observed in linear micelles at relatively weaker flows. Third, branched micelles exhibit a stronger flow-induced birefringence than linear micelles in an otherwise identical condition. Our hypothesis is that subject to strong flows around the falling sphere, branched micelles can relax much more efficiently than linear wormlike micelles through sliding of the branched junctions. This additional stress relaxation mechanism may facilitate micellar orientation, produce a marginal sphere drag reduction and a Newtonian-like flow profile around the falling sphere. Finally, unsteady flow is observed in both linear and branched micellar solutions beyond some critical thresholds of the extensional

Weissenberg number. Our results corroborate a recently proposed criterion for onset of instability in flow of wormlike micelles past a falling sphere, thereby, suggesting that micellar branching does not affect the mechanism of flow instability.

Wednesday 10:15 Meeting Room C-D IN12

Effects of micellar entanglement density on kinetics of shear banding flow formation in wormlike micelles

Peter Rassolov[1], Lin Zhou[2], Pamela L. Cook[3], and Hadi Mohammadigoushki[1]
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We investigate the effects of micellar entanglement density on kinetics of shear banding flow formation in a Taylor-Couette flow via a combination of rheo-PTV experiments and simulations using the VCM model. In experiments, three sets of micellar solutions, each with fixed fluid elasticity and zero-shear viscosity and a range of various entanglement densities, are measured and imaged under start-up steady shear. Fluid elasticity is defined as the ratio of Weissenberg to Reynolds number. Our experiments indicate that at the lowest fluid elasticity, the transient shear banding flows are characterized by formation of a transient flow reversal beyond a critical entanglement density, while beyond a second threshold of micellar entanglements, the flow reversal is not observed. Although the former observation is consistent with existing theoretical predictions of the diffusive Rolie-Poly and VCM models, the latter result cannot be explained by existing predictions. Moreover, a similar second critical transition is observed at higher fluid elasticities. Additionally, we observed transient and in some cases, quasi-steady wall slip at both the inner and outer cylinders. Our analysis shows that wall slip does not affect formation of transient flow reversal. On the other hand, the quasi-steady flows are accompanied by flow instabilities and sometimes characterized by formation of multiple bands that prevail for a long time. Finally, we attempt to produce some of these experimental observations using the simulations of the VCM model. Although VCM model successfully predicts some of the experimental observations, more improvements in the theoretical modeling of the wormlike micelles are needed to capture the results of experiments.

Wednesday 10:40 Meeting Room C-D IN13

Flow-induced concentration non-uniformity and shear banding in entangled polymer solutions

Michael C. Burroughs[1], Abhishek Shetty[2], L. Gary Leal[1], and Matthew E. Helgeson[1]
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A foundational assumption of most rheological models is that an initially homogeneous fluid remains compositionally homogeneous when subjected to flow. A notable exception is the phenomenon of flow-enhanced concentration fluctuations in polymer solutions, which has been successfully modeled by the Helfand-Fredrickson mechanism where coupling of polymer viscoelasticity with osmotic stresses can lead to enhanced local fluctuations. However, it is unclear whether these local fluctuations can propagate to induce macroscopic demixing of the fluid, and whether this affects viscoelastic flows of polymer solutions. In this work, we address these questions for highly entangled polymer solutions. To do so, we present new rheo-fluorescence microscopy experiments in which the concentration profile of a labeled species can be directly imaged in situ in a rheometric flow. For polymer solutions that are sufficiently entangled and sufficiently close in temperature to the equilibrium cloud point, we observe steady state shear-induced concentration "bands" in Taylor-Couette flow for a range of imposed Weissenberg numbers. Simultaneous velocimetry measurements reveal that these concentration bands are concomitant with shear banding, whose existence for entangled polymers has been highly controversial and the subject of conflicting experimental reports. Comparison to a recently developed two-fluid model that couples the nonlinear polymer rheology to Helfand-Fredrickson type osmotic stresses shows near quantitative agreement with both the concentration and velocity profiles over a range of solution conditions, and suggests that banding is a result of unstable shear-induced demixing. The results provide a potential new mechanism for shear banding in entangled polymers. More broadly, they call for a re-examination of the basic assumption that homogeneous polymeric fluids remain macroscopically homogeneous in flow, and provide an initial exploration of new flow phenomena that emerge when this assumption is relaxed.

Wednesday 11:05 Meeting Room C-D IN14

The influence of polymer entanglement on air entrainment dynamics under droplet impacts

Ziwen He and Min Y. Pack
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Droplet impact dynamics is essential for achieving optimized drop deposition on surfaces including agrochemical applications, spray coating and cooling processes. Recent studies have revealed that droplets tend to rebound from the surface when the air film survives from the impact and decelerates the approaching droplet as a cushion. While this air cushioning effect has been studied under Newtonian liquid droplets, the air entrainment mechanism underneath polymeric droplets is lacking in the literature. In this study, we demonstrate that for intermediate Weber numbers, We~O(1-10), the spatiotemporal evolution of the air film responds to the viscoelasticity of aqueous polymeric droplets. Herein, a submicron air layer is visualized during droplet impact of aqueous polyethylene oxide and xanthan gum solutions at different polymer concentrations varied between O(10 - 1000) ppm with a total internal reflection microscopy (TIRM) technique. We observe that the slope of the air film induced by impacting droplets with PEO additives is attenuated by polymer concentration beyond the entangled regime yet enhanced before reaching the critical overlap concentration. In contrast, for xanthan gum solutions, we observe that the air film slope is enhanced beyond the entangled regime.

Wednesday 11:30 Meeting Room C-D IN15

Instabilities and turbulence in planar jets of dilute polymer solutions

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Fluid turbulence enhances the mixing of regions with high and low momentum but viscous effects also result in high dissipative energy losses that are notoriously difficult to mitigate. Dilute polymer solutions, typically containing less than 100 parts per million of polymer, are important exceptions; they can fundamentally modify the flow dynamics and reduce the turbulent losses that cause frictional drag. Jets are canonical shear-flow configurations to examine the spatially developing instabilities and turbulence of dilute polymer solutions. In this work, we study high aspect ratio (i.e. 1:10 and 1:20) planar jets using stereo-Schlieren imaging. Synchronous side- and front-view Lagrangian visualizations reveal the dynamical changes in the flow structure arising from the presence of small amounts of polymer. We apply dynamic mode decomposition to identify the dominant unstable, spatially growing modes due to viscoelasticity that are stable for a Newtonian jet. The advective growth of these inertio-elastic modes leads to a turbulent region downstream of the jet. In this region, we map the Schlieren images to a concentration fluctuation profile and perform laser Doppler velocimetry to measure the local velocity fluctuations. We discuss how viscoelasticity produces elongated turbulent structures in the direction of the flow and modifies the power-law spectral decay of local velocity and concentration fluctuations.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Marie-Claude Heuzey, Sara Hashmi and Rahul Pandey

Wednesday 9:50 Ballroom 6 SC24

Spherically confined Brownian suspensions: Influence of locally heterogenous structure on diffusion and rheology

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Spherically confined, hydrodynamically interacting colloids provide a framework for understanding biological cells over length and time scales where interparticle interactions and particle motion play central and nontrivial roles in whole-cell behavior. Under different biological conditions, a cell's overall size, crowding level, and the strength of electrostatic interactions of its constituent molecules can change. Therefore, it is important to understand how each of these changes alters the physics of biological processes that take place inside cells. In this work, we perform dynamic simulations with both Confined Stokesian Dynamics and Confined Brownian Dynamics algorithms. Confinement induces new and disparate length and time scales of colloidal relaxation on a suspension, which results in a heterogeneous microstructure and local crowding. This structure in turn impacts dynamics and rheology both entropically and hydrodynamically. We disentangle the role of entropic and hydrodynamic effects on short- and long-time transport properties of particles under spherical confinement to better understand differences between real life systems under conditions of weak and strong hydrodynamics. Additionally, we find relationships between rheological properties, such as osmotic pressure and viscosity, and the variables volume fraction and particle size within the confinement.

Wednesday 10:15 Ballroom 6 SC25

Effect of confinement, flow rate and particle rigidity on the microstructure of semi-dense and dense suspensions

Barcelos Erika[1], Khani Shaghayegh[1], Oliveira Fellipe[2], Arman Boromand[3], Monica F. Naccache[4], and Joao Maia[1]
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Suspensions have been extensively studied over the past decades and continue to be the focus of many works. A particular application in which suspensions have been increasingly explored is in confined systems. Many works in the literature have addressed confinement in suspensions at different particle rigidities, volume fractions and confinement ratios. However, a systematic study evolving the combined effects of confinement, flow rate and particle rigidity in concentrated suspensions is still lacking. In this work, Core-Modified Dissipative Particle Dynamics is employed to model semi-dense and dense suspensions under confinement. The walls as well as the solvent are represented as traditional DPD particles which interact center-to-center by soft potentials. Colloidal particles, on the other hand, are modelled as Core-Modified particles, having a rigid core and a soft shell and the interactions are driven by a semi-hard potential. Colloidal particles interactions take place by means of a core force, responsible to tune the rigidity, and a lubrication force, representative of the short-range hydrodynamic interactions. In this work, the effect of flow rate, confinement and particle rigidity were systematically studied in semi-dense and dense suspensions in a pressure driven flow. At stronger confinement ratios, lower rigidity and weaker flow strengths the overall particles velocity tends do decrease. Rigid particle suspensions are more viscous and have a slower motion compared to the soft ones. Additionally, rigidity leads to opposite migration effects. Different microstructures and particles arrangement were observed depending on the values of the parameters adopted, with confinement being the most important factor driving particle migration.

Wednesday 10:40 Ballroom 6 SC26

Predicting particle wall penetration in multicomponent systems using Machine Learning

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In computational studies, a key aspect in the design of a reliable system is the creation of a simulation domain able to represent the correct physics of the system of interest. In wall-based DPD methods, establishing the wall interactions is a challenge in multicomponent environments. Since the interactions between wall and the particles are soft, penetration may occur, which is undesirable. Controlling the interactions when multiple parameters are playing a role is a complex task, specially due to the fact that there might be non-linear and collective effects between the variables that are hard to quantify. Machine Learning, ML, is particularly useful when the knowledge about the influence of the input parameters on the response variables is limited and when there is available data to train a model. In this work, Core-Modified Dissipative Particle Dynamics was used to build up the system and a supervised learning approach was employed to make predictions in colloidal suspensions. Five input parameters were fed in the ML model: volume fraction, body force, confinement, wall-solvent repulsion, aij, and particle rigidity. The predicted outputs were solvent and colloid penetration. By using statistical correlations analysis, it could be seen that solvent penetration is strongly negatively correlated with repulsion interactions and moderately positively correlated with volume fraction. In the colloids case, a moderate correlation was observed with aij, rigidity and volume fraction. The model performance yielded pretty satisfactory results, presenting an accuracy of over 90% for both solvent and colloid penetration. The most important features in predicting the outputs were repulsion interaction in solvent penetration and volume fraction in the colloids case. This study showed the potential and of ML techniques to be used in combination to mesoscale methods to perform parametric studies.

Wednesday 11:05 Ballroom 6 SC27

Thixotropic spectra and Ashby-style charts for thixotropy

Samya Sen and Randy H. Ewoldt

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There is no universal model for thixotropy, so comparing thixotropic effects between different fluids is difficult. Specific model fits provide thixotropic timescales, but these alone are insufficient: a long recovery time suggests significant thixotropy, but it may be negligible if the rheological change due to thixotropy is small. We thus introduce a generalized (model-insensitive) framework for comparing thixotropic properties to assess its importance across different systems. The approach is based on thixotropic spectra, a superposition of exponential stress modes distributed over thixotropic timescales, to quantify buildup and breakdown times and mode strengths in response to step-change of shear rate tests. This mathematical framework is tested with several experimental step-shear datasets on colloidal suspensions, including yield-stress fluids such as fumed silica and carbon black. Discrete and continuous spectra obtained from regularized data fits are considered as a function of initial and final shear rates probed, including parameterized continuous spectra and the use of credibility metrics (such as BIC) to assess model credibility based on a balance between goodness of fit and the number of model parameters involved. Common models, such as stretched exponential fits, are a subset of this generalized thixotropic spectra framework. Low-dimensional metrics based on moments of the distribution serve as general thixotropic yardsticks, including average timescales, dispersity of timescales, and amount of thixotropic stress change, all of which are visualized on Ashby-style diagrams. These methods establish a framework to describe thixotropy across a diverse range of microstructures, validated here for aggregating colloidal suspensions but more broadly applicable, supporting scientific studies as well as material selection for engineering design applications.

Wednesday 11:30 Ballroom 6 SC28

Rheology of sheared suspensions of conductive particles in an electric field

Siamak Mirfendereski[1] and Jae Sung Park[2]

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Electrochemical flows have gained growing attention as a promising energy storage system, such as electrochemical flow capacitors. In such a flow, rheological properties of the suspension of conductive particles driven by an external electric field and flow are crucial for the overall performance. To this end, we use a large-scale particle simulation to study the rheology of sheared suspensions of ideally conductive spheres in an electric field. This suspension is primarily controlled by two nonlinear electrokinetics, namely induced-charge electrophoresis and dielectrophoresis, where the former is predominant. In the limit of zero-shear-rate, non-trivial rheology was observed that particle pressure exhibits a non-monotonic variation with concentration, where it becomes negative at concentrated regimes. We then impose an external simple shear flow via Lees-Edwards boundary conditions for which a gradient direction is set to align with the electric field direction. The relative importance of the hydrodynamic stress due to an external shear rate with respect to the electric stress is captured by the Mason number. In this talk, we focus on dilute and semi-dilute suspensions. At small Mason numbers, the electric stress still dominates, and the apparent viscosity exhibits a significant fluctuation as the induced-charge electrophoresis leads to chaotic dynamics. At higher shear rates, this fluctuation diminishes. The particle normal stresses normalized by characteristic electrical stress remain almost constant at small Mason numbers but start to decrease, showing a transition at a specific Mason number. The first and second normal stress differences are positive and negative at small Mason numbers, respectively. Interestingly, around the transitional Mason number, the former starts to decrease, while the latter starts to increase. This transition will be

manifested by a change in the local microstructure. Lastly, we will briefly discuss the effect of high concentrations on the rheology and microstructure of the system.

Symposium GG
Arrested Systems: Gels and Glasses

Organizers: Emanuela del Gado and Jyoti Seth

Wednesday 9:50 Ballroom 1 GG19

Dynamics of polymer gels near surfaces

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Polymer gels are crosslinked polymer networks swollen in a solvent. Due to their unique structure, these soft materials are useful for many applications, including therapeutic materials, absorbent materials, and adhesives. Many of these technologies rely on the thermodynamic and swollen nature of polymer gels, which can be controlled locally. However, only bulk material property characterization techniques are available that do not rely on a probe, which limits material engineering and discovery. We have shown that local, directionally-resolved polymer gel characterization is possible with benchtop techniques such as 2D dynamic small-angle light scattering (DSALS) and differential dynamic microscopy (DDM), which image the gel network dynamics directly without the use of a probe. Using DSALS, gel network dynamics are resolved in any arbitrary direction, particularly parallel or perpendicular to any deformation imposed on the gel. With DDM, we have resolved surface dynamics, which impact material properties such as adhesion. We find that dynamics of fluorescently-labeled poly(vinyl alcohol) and hyaluronic acid are ~ 50 times slower than in the bulk and interpret this effect in terms of polymer adsorption. The slow dynamics persist over a few microns into the material. These techniques could be implemented on many systems to investigate the polymer network motion locally.

Wednesday 10:15 Ballroom 1 GG20

Under pressure: Hydrogel swelling in a granular medium

Jean-François Louf and Sujit S. Datta
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Hydrogels hold promise in agriculture as reservoirs of water in dry soil, potentially alleviating the burden of irrigation. However, confinement in soil can markedly reduce the ability of hydrogels to absorb water and swell, limiting their widespread adoption. Unfortunately, the underlying reason remains unknown. By directly visualizing the swelling of hydrogels confined in three-dimensional granular media, we demonstrate that the extent of hydrogel swelling is determined by the competition between the force exerted by the hydrogel due to osmotic swelling and the confining force transmitted by the surrounding grains. Furthermore, the medium can itself be restructured by hydrogel swelling, as set by the balance between the osmotic swelling force, the confining force, and intergrain friction. Together, our results provide quantitative principles to predict how hydrogels behave in confinement, potentially improving their use in agriculture as well as informing other applications such as oil recovery, construction, mechanobiology, and filtration.

Wednesday 10:40 Ballroom 1 GG21

Modeling temperature-dependent rheological aging in bentonite suspensions

Joshua David John Rathinaraj[1], Kyle R. Lennon[2], Miguel Gonzalez[3], Ashok Santra[3], James W. Swan[2], and Gareth H. McKinley[1]
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Clay slurries are both ubiquitous and essential in the drilling industry, most commonly as drilling fluids. Due to its natural abundance, bentonite clay is often the de facto choice for these materials. Understanding and predicting the mechanical response of these fluids is critical for safe and efficient drilling operations, to avoid undesired effects such as back-flow which may cause significant economic and environmental harm. However, the rheological modeling of bentonite clay suspensions is complicated by the fact that microscopic arrangements of particle aggregates lead to a continual evolution of the viscoelastic properties with time. Ergodic relations fundamental to linear viscoelastic theory, such as the Boltzmann superposition principle, do not hold in this scenario of 'rheological aging'. In this work, we present an approach for modeling the linear viscoelastic response of aging bentonite suspensions across a range of temperatures, which is based on a transformation from laboratory time to an effective 'material time' in which the typical relations of non-aging linear viscoelastic theory hold. In particular, we model bentonite suspensions as fractional Maxwell gels which respond in material time, in parallel with a Newtonian viscous mode which responds in laboratory time. This approach is supported by experimental stress relaxation and exponential chirp data, which are used to develop fits of the model parameters.

Wednesday 11:05 Ballroom 1 GG22

Local mechanism governing the global reinforcement of filler-hydrogel composites

Ippolyti Dellatolas[1], Minaspi Bantawa[2], Brian Damerau[2], Thibaut Divoux[3], Emanuela Del Gado[2], and Irmgard Bischofberger[1]
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The reinforcement of hydrogels by the addition of filler particles usually requires a filler content of ~50%. Here, we probe the linear viscoelastic properties of soft hydrogels containing filler nanoparticles and reveal that significant reinforcement can be achieved at unexpectedly low volume fractions of fillers when the fillers and the polymer are attractive. At ~10% volume fraction of fillers we report a tenfold increase in the modulus of the composite material, independent of polymer concentration, polymer type and filler size. We show that this robust reinforcement can be rationalized with an effective medium theory that holds for attractive filler-gel systems. Using 3D numerical simulations, we probe the microscopic structure and dynamics of the reinforced gels to provide a microscopic origin of the reinforcement. We show that the attractive interaction between the fillers and the gel induces an increase in the local gel density around the fillers, which in turn constrains the gel displacements and couples the stresses throughout the system. These local changes in the gel structure around the fillers lead to a global reinforcement of the filler-gel composite.

Wednesday 11:30 Ballroom 1 GG23

New insights into the rheological aging of a model thermoreversible colloidal gel with short-range interactions

Khushboo Suman and Norman J. Wagner
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In this work, we investigate the aging behavior in a well-studied model system of adhesive hard spheres (AHS) quenched above and below the spinodal. The AHS system is comprised of octadecyl-coated Ludox TM-50 silica nanoparticles. On cooling, the AHS particles suspended in tetradecane exhibit a thermoreversible gel transition from a fluid-like (sol) state to a soft-solid state. The decrease in the temperature drives the crystallization of the surface brush layer, which results in the development of short-range attraction between the particles in contact. While the literature suggests evidence of shear-reversible aging and overaging behavior for gels quenched only slightly below the gel temperature, Rheo-SANS studies (Min Kim et al., Journal of Rheology, 2014, 58(5)) on this system suggest that deeper quenches may lead to gel densification under shear. We investigated the effects of deeper quenching on this system in our work. The aging behavior in the model AHS system is monitored by small amplitude oscillatory shear rheology measurements conducted while rapidly quenching from 40°C to a temperature below the critical gel temperature. Interestingly, for deeper quenches, a unique and new phenomenon is reported - namely after an initial rise in the modulus, a sudden and reproducible drop in the modulus at a time period of 300 - 600 s is observed, followed by a plateau in the modulus value. After this drop of nearly an order of magnitude in modulus, the AHS gel remains in the softened state over the experimental timescale. Our rheological characterization at different volume fractions shows intriguing effects of the extent of quenching to different states relative to the underlying phase behavior on aging behavior of colloidal gels. Through this research, we aim to establish a relationship between the mechanical aging and various quench protocols in these gels.

Symposium OP
Online Program

Organizers: Anne M. Grillet and Marie-Claude Heuzey

Wednesday 9:50 Virtual OP3

Online discussion: Session 3

Anne M. Grillet[1] and Marie-Claude Heuzey[2]
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Online discussions will be broken up into two topics each day. Each group will start with a full-length (20 minute) virtual keynote presentation then authors of flash presentations will be allowed 10 minutes to provide a quick (3 minute) overviews of their key findings followed by questions and discussion with the audience.

Wednesday:
- Nature-based soft matter
- Foams, emulsions and interfaces

Lists of each discussion group, keynote and list of flash presentation authors as well as zoom links will be provided by October 1st.

Wednesday Afternoon

Symposium SM
Polymers Solutions, Melts, and Blends

Organizers: Dimitris Vlassopoulos, Christopher Evans and Poornima Padmanabhan

Wednesday 1:30 Ballroom 5 SM34

Unentangled vitrimer melts: Generalized Rouse theory illuminates interplay of cross-link exchange and backbone relaxations on linear viscoelasticity

Ralm G. Ricarte[1] and Sachin Shanbhag[2]

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Vitrimers are covalently cross-linked polymers that flow at elevated temperatures. Their cross-links engage in associative exchange reactions that preserve network connectivity but permit topology fluctuations, rendering the networks to be both insoluble and processable. Here, we use a generalized inhomogeneous Rouse model (IHR) to elucidate structure-viscoelasticity relationships for unentangled vitrimer melts with cross-link densities well beyond the gel point. This model accounts for interactions between relaxation modes of regular monomers and those that are "sticky" (i.e., cross-links). We employ the IHR to investigate the effect of structure and temperature on the zero-shear viscosity (η_0) and characteristic relaxation time (τ_η). Polydimethylsiloxane vitrimer (which has a flexible backbone) has an Arrhenius temperature dependence for η_0, while polystyrene and poly(methyl methacrylate) vitrimers (which have rigid backbones) are only Arrhenius at high temperatures. During stress relaxation, the short time dynamics represent monomer friction, while the long time dynamics describe a combination of network strand relaxation and cross-link exchange. The different temperature dependences of the two processes causes time-temperature superposition to fail. The effective rheological activation energy is estimated a priori from the cross-link exchange activation energy and the backbone Williams-Landel-Ferry parameters. Based on these findings, we discuss the utility of the IHR for understanding vitrimer rheology, and best practices for characterizing η_0 and τ_η.

Wednesday 1:55 Ballroom 5 SM35

Determination of the number-average molecular weight of polyelectrolytes

Aijie Han[1], Shravan Uppala[2], Benjamin J. Dixon[1], Louis A. Madsen[2], and Ralph H. Colby[1]

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We have developed four methods using the chain dynamics in the semidilute unentangled regime to determine the number-average molecular weight (Mn) of polyelectrolytes based on the scaling model. Our team is collaborating to measure the correlation length (?) using X-ray scattering, the specific viscosity (?sp) and relaxation time (t) using rheometry, and the diffusion coefficient (D) using NMR diffusometry. Our methods show that combining the measured properties of polyelectrolyte solutions yields the number density of chains in solution which directly determines Mn. In this work, five nearly monodisperse cesium polystyrene sulfonate (CsPSS) solutions without salt are studied in water, anhydrous ethylene glycol (EG) and anhydrous glycerol to test each method. The molecular weights are also confirmed by means of static light scattering and intrinsic viscosity measurements in 0.1 M NaCl aqueous solutions. We found that all four methods work generally well for the highest molecular weight (N = 9150 chemical repeat units). For lower molecular weights, the method using ?sp is found to systematically underestimate Mn compared with the manufacturer's reported value, while the method using D overestimates Mn. Both methods require prefactors which depend on degree of polymerization (N). This observation likely underlines the importance of non-uniform stretching along the chain of polyelectrolytes which disappears in the long chain limit. Additionally, using EG and glycerol as solvents slows down the relaxation dynamics significantly and enables us to obtain t for lower molecular weight CsPSS from the shear rate dependence of viscosity. The relaxation times of CsPSS in three different solvents can be reduced to a common curve in the semidilute unentangled regime using the scaling model. We found that the method using the combination of relaxation time and correlation length has similar N dependence of prefactors as the method using ?sp, and using the terminal modulus is the only method that does not require prefactors.

Wednesday 2:20 Ballroom 5 SM36

Influence of small ions on composition and viscoelasticity of polyelectrolyte complexes

Samanvaya Srivastava, Vaqar Syed, Divya Iyer, and Advait Holkar

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The addition of salt speeds up chain relaxation dynamics in polyelectrolyte complexes (PECs). Time-salt superposition (TSS) approaches to describe the linear viscoelastic response of PECs are well-established. However, TSS is carried out at fixed initial polymer concentrations, and varying the initial polymer concentration results in distinct TSS master curves. In the first part of this presentation, we will show that accounting for the small ions that accompany the oppositely charged polyelectrolyte chains enables the assimilation of these distinct TSS master curves into a single universal master curve. This approach, which we christen as time-ionic strength superposition (TISS), enables a unified description of the PEC viscoelastic response in terms of the solution ionic strength that accounts for both the accompanying counterions and the added ions and underlines the dynamic similarities between PECs and semi-dilute polymer solutions. The sticky electrostatic associations among the oppositely charged chains, however, contribute additional relaxation modes in the PECs. We will demonstrate that the timescales of these additional relaxation modes are described quantitatively by a modified sticky Rouse model that accounts for the influence of solution ionic strength on the electrostatic screening and chain friction.

In the second part of this presentation, we will discuss the non-trivial effects of the cationic valency of the added salt on the composition and rheology of the PECs. A stronger screening of electrostatic interactions is observed with increasing cation valency, leading to higher concentrations of polyelectrolytes in the supernatant phase and lower concentrations in the complex phase. In addition, electrostatic bridging of the polyanion chains by the multivalent cation alters the chain relaxation process in PECs by competing with the electrostatic interactions between the oppositely charged chains, resulting in non-monotonic variations of PEC moduli with increasing ionic strength of the solution.

Wednesday 2:45 Ballroom 5 SM37

Polyelectrolytes dynamics and rheology, in a pinch

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Biological macromolecules like proteins, DNA, polysaccharides, and many industrial polymers, are classified together as polyelectrolytes. In solution, the repeat units in their backbone are decorated with dissociated, charge-bearing ionic groups, surrounded by a cloud of counter-ions. Even though a large number of polyelectrolytes are processed or used as rheology modifiers in paints, pharmaceuticals, fertilizers, pesticides, and cosmetics, the shear and extensional rheology response of the charged macromolecular solutions is not as well understood as for their uncharged counterparts, and motivate this study. We characterize the pinching dynamics as well as shear and extensional rheology of solutions of three model polyelectrolytes poly(sodium 4-styrene sulfonate) (NaPSS), poly(acrylic acid) (PAA), and sodium carboxymethylcellulose (NaCMC) as a function of solvent and salt concentration. We show that dripping-onto-substrate (DoS) rheometry protocols that involve visualization and analysis of pinching of a columnar neck formed between a nozzle and a sessile drop can be used for measuring extensional viscosity and extensional relaxation time of aqueous polyelectrolyte solutions. We identify universalities in the shear and extensional rheology response of salt-added unentangled semi-dilute solutions and examine the influence of solvent properties on polyelectrolyte dynamics. Unlike shear relaxation time that decreases with an increase in polymer concentration in the unentangled, semidilute salt-free solutions, the measured extensional relaxation time always shows an increase with polymer concentration for the unentangled systems. We elucidate the influence of both electrostatic and hydrodynamic interactions and stretching of macromolecules on stickiness, printability, jettability, and overall processability.

Wednesday 3:45 Ballroom 5 SM38

Dynamic signatures of gelation in associative polymer solutions

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Solutions of associative polymers form reversible gels at moderately low concentration by physical cross-linking of sticky groups distributed along the chain backbones. While at least three different static signatures of gelation, such as the percolation transition, the maxima in the free-chain concentration and the occurrence of bimodality in the cluster-size distribution have been identified in these systems [1], the relationship between these static measures and the dynamic response of associative polymer solutions close to the gel point remains unresolved. The formation of intricate topologies leads to the existence of complex relaxation behaviour. In this work, multi-chain Brownian dynamics simulations with hydrodynamic interactions incorporated, have been carried out to examine the dynamic and linear viscoelastic behaviour of multi-sticker associative polymer solutions at finite concentrations and the various static and dynamic gelation signatures have been studied. Equilibrium and shear flow simulations have been performed to compute the zero-shear rate viscosity and storage and loss moduli. It is found that the zero-shear rate viscosity and a variety of different characteristic relaxation times exhibit a cross-over in their scaling behaviour with monomer concentration close to the location of the maxima in free chain concentration. The influence of the time scales associated with the binding and unbinding of stickers on the overall relaxation behaviour has also been explored. Finally, simulation results are compared with the predictions of the sticky Rouse model proposed by Rubinstein and Semenov [2,3], in the relevant regimes, and excellent agreement is observed.

[1] A. Santra, B. Duenweg, and J. R. Prakash, J. Rheol., 65, 549-581, 2021.
[2] M. Rubinstein, A. N. Semenov, Macromolecules, 31, 1386-1397, 1998.
[3] M. Rubinstein, A. N. Semenov, Macromolecules, 34, 1058-1068, 2001.

Wednesday 4:10 Ballroom 5 SM39

Understanding solvation of cellulose in ionic liquids by time dissolution evolution (TiDE) rheometry

Crystal E. Owens[1], Pablo Sanchez[2], Jianyi Du[1], A. John Hart[1], and Gareth H. McKinley[1]
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Cotton-based textiles are produced, used, and scrapped at unprecedented rates. However, due to strong interchain hydrogen-bonding interactions, the main ingredient of cotton - cellulose - does not dissolve in common solvents. While this promotes durability, it hinders recyclability, and over

80% of all cotton-based goods end up in landfills. As a possible remedy, ionic liquids have been shown to disrupt hydrogen bonds and progressively solvate cellulose so that liquid solutions can be processed and, ideally, re-spun into new cotton threads to form new textiles.

In this work, we monitor the dissolution of cotton-based textiles in 1-ethyl-3-methyl-imidazolium acetate (EMIMOAc) from chopped fiber to homogeneous dispersion using small amplitude oscillatory shear (SAOS) rheometry. We seek a quantitative description through a method of reduced variables analogous to time-temperature superposition. However, dispersions of rigid H-bonded cellulose fibers in ionic liquid are not "solvo-rheologically simple," hence standard shifting is invalid. Instead, we outline a new method of Time Dissolution Evolution (TiDE) to understand and predict this cellulose rheology over a wide range of weight concentrations (0.5 = c = 12%). The time-evolving SAOS measurements are well-described using systematic regression to the Baumgaertel-Schausberger-Winter (BSW) relaxation spectrum to extract the evolution of the underlying material relaxation times. This results not only in kinetic information but also in observability of the majority of the material relaxation spectrum. The kinetic data can further be compared with polarized microscopy of the same dissolutions, and to prior published data for low-concentration solutions. This approach is particularly valuable for otherwise hard-to-access high-concentration and "gel-like" regimes that are required for economical cellulose regeneration. The resulting solvent-specific information is useful to guide processing of cellulose into new synthetic fibers, and to inform limits to recycling.

Wednesday 4:35 Ballroom 5 SM40

Associating polymer features of native cellulose in ionic liquid solutions

Daniele Parisi, Joshua Bostwick, Nyalaliska W. Utomo, Ravisara Wattana, Behzad Nazari, and Ralph H. Colby
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Cellulose is the most abundant bio-based polymer natural resource on Earth today. Certain ionic liquids (IL) have been discovered to be the best solvents to dissolve cellulose at the molecular level. Despite the promising role that natural polymers may undertake in the near future in replacing synthetic polymers, still many challenges exist. In the past few years, we demonstrated that cellulose in ionic liquid solutions are very sensitive to humidity, with significant increase of the elastic properties with increasing water content. It has been also observed that cellulose chains adsorb at the solution/gas interface, yielding a total rheological response which is the sum of bulk and interfacial contributions, studied using a double wall ring interfacial measurement and a cone partitioned plate bulk solution measurement. Here we address the associating polymer features exhibited by native cellulose in solutions with varying IL, in both linear and nonlinear viscoelastic regimes. We observed three aspects attributed to associations between cellulose chains: i) For a given cellulose sample, the viscoelasticity is very different in the three ionic liquids we study. ii) The concentration (c) dependence of the terminal time (t) is much stronger (t ~ c^7) than that of neutral polymers in good solvent (t ~ c^4). iii) The shear stress growth coefficient in steady-shear flow overcomes the complex viscosity, violating the empirical Cox-Merz relationship. We attribute the unusual positive divergence to chain-chain associations promoted by the shear flow, occurring when chains are significantly stretched in the flow direction. The effect of various IL on the association properties was investigated as well.

Wednesday 5:00 Ballroom 5 SM41

Retaining structural color in a diblock bottlebrush copolymer solution

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Building upon previously established structure-property-property relations between the self-assembled microstructure of a diblock bottlebrush polymer solution, its color, and the applied shear conditions, two avenues for retaining the induced structure over longer periods of time are explored. In-situ UV curing was carried out on a functionalized polylactic acid-b-polystyrene bottlebrush copolymer and dispersed in toluene at 5 °C forming a solution with a concentration of 175 mg/ml. Photo initiator and a thiol were added to the solution to promote crosslinking between functionalized polymers when exposed to UV radiation. The dynamics of this curing process were characterized with both traditional techniques and the SPP framework. The timeframe for forming a percolated network was found to be on the order of a couple of seconds when exposed to UV intensities between 300 and 950 mW/cm^2. As an alternative to UV curing, a diblock bottlebrush solution with a concentration of 350 mg/ml was explored. This solution was found to exhibit yield-like behavior. Using oscillatory recovery rheology, the moduli were decomposed into recoverable and unrecoverable components. By defining a time resolved Deborah number, we can identify when the material begins to exhibit more solid-like and more liquid-like behavior. Structural characterization will be carried out to identify the structural changes that correspond to the liquid to solid transition. The two approaches we present can be used to potentially retain the structures induced through shear.

Symposium AB
Active and Biological Materials

Organizers: Sujit Datta and Danielle Mai

Wednesday 1:30 Ballroom 7 AB24

Polymer nanoparticle hydrogels: Physical hydrogels with extreme extensibility

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Supramolecular hydrogels are appealing for biological applications such as drug delivery, 3D printing bio-inks, cell therapies and bioadhesives. Polymer nanoparticle (PNP) hydrogels are one class of injectable yield stress fluids that been shown to be effective in biomedical translational studies requiring non-invasive injections, biocompatibility and slow degradation. These hydrogels are composed of core-shell polymeric nanoparticles and dodecyl-modified cellulose polymers. The dodecyl-modified polymers interact with the nanoparticles yielding a robust network with shear-thinning and self-healing properties. These completely physically crosslinked materials exhibit functional yield stress values and gel-like properties across a wide range of frequencies. Herein, we use several techniques, including shear rheology, extensional rheology, fluorescence-recovery-after-photobleaching, and microrheology to elucidate the structure and dynamics of these hydrogels. We then modify the outer shell of the nanoparticles with different polymer coronas, including polyethylene-glycol and various acrylamide polymers, and observe great changes in mechanical properties of the resulting PNP hydrogels, suggesting variations in supramolecular PNP interactions. Notably, different nanoparticle formulations in PNP hydrogels exhibit different strain rate dependence in extensional testing. Nanoparticles with an outer corona of poly(N-isopropylacrylamide) in the PNP hydrogel exhibit extensional properties past 2000% Hencky strain. We find that the physical on and off rates of the dynamic interactions can be non-dimensionalized to elucidate mechanism behind extreme extensibility. These extensional physical hydrogels show great promise in applications requiring bioadhesion and provide insight in designing and understanding new hydrogel materials.

Wednesday 1:55 Ballroom 7 AB25

Non-affine deformation of semiflexible polymer networks

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Biopolymer networks formed by semiflexible polymers exhibit different non-affine deformation from flexible polymer networks. Most of the theoretical studies of this non-affine deformation have focused on numerical simulation, while an analytical understanding of the deformation is lacking. Here, we present an analytical framework for the non-affine deformation of semiflexible polymer networks. We find a universal relation between the macroscopic deformation of the entire network and the microscopic deformation of the individual polymers. Together with an effective-medium theory we are able to predict both the linear and non-linear non-affine moduli. Our prediction on 3D crosslinked networks agree favorably with previous numerical simulations.

Wednesday 2:20 Ballroom 7 AB26

Mechanical response of phantom tissues to compressive loading

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Mechanical forces are critical to development and healthy tissue maintenance. How tissues and biopolymer networks respond to shear deformations has been well studied, but their response to uniaxial compression is less understood. An emerging in vitro model system for studying tissue rheology are fibrin networks embedded with inert particle inclusions (beads). These phantom tissues, hydrogels containing a crosslinked fibrous polymer network with volume-excluding beads, mimic the structure of the cell-loaded extracellular matrix. They also exhibit mechanical behavior associated with real tissues, such as an apparent stiffening response under uniaxial compression. An aspect of these phantom tissues not well characterized is their poroelastic nature. Compressive stress on a hydrogel creates a complex deformation response from the viscoelasticity of the polymer network and the fluid flow through the network pores. As we show with a custom compression device that allows for real-time imaging of the network microstructure, the presence of beads also alters the poroelastic behavior of these hydrogels. This altered poroelasticity can be detected with bulk rheological compression tests, where signatures in the normal force relaxation indicate an altered compressive state for the networks with beads. These combined results indicate a predominate role of network compaction and fluid flow in modeling phantom tissue compression response, qualities that may be important for understanding how mechanical stimuli mediate biological functions.

Wednesday 2:45 Ballroom 7 AB27

Strain-induced critical slowing of stress relaxation in elastic networks

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Many biological materials contain embedded fibrous networks that stiffen significantly in response to applied strain, a phenomenon that provides living tissues with enhanced mechanical resilience and enables long-range force transmission by cells. Prior work has shown that strain-induced stiffening in mechanically under-constrained elastic networks corresponds to the traversal of a "critical point" in strain, at which the energy-minimizing network configuration becomes marginally stable. Near this transition, various quantities measured via quasistatic deformation exhibit power law scaling with respect to the reduced strain. However, the dynamic behavior of systems near this transition has not yet been characterized. Here, we model the small-amplitude oscillatory shear and stress relaxation of under-constrained, fluid-immersed elastic networks subjected to applied extensional pre-strain (e.g. swelling and simple shear). We show that the rheology of these networks is controlled by a pre-strain-controlled correlation length and corresponding characteristic relaxation time that both diverge at a connectivity-controlled critical point, giving rise to weak power law scaling of the complex modulus with frequency and diverging strain fluctuations.

Symposium AR
Applied Rheology and Rheology Methods

Organizers: Mubashir Ansari, Ruel Mckenzie and Jörg Läuger

Wednesday 3:45 Ballroom 7 AR29

Connecting structural thixotropic models with non-equilibrium thermodynamic principles for human blood

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Recent work modeling the rheological behavior of human blood indicates that blood has all of the hallmark features of a complex material, including shear-thinning, viscoelastic behavior, a yield stress and thixotropy. This complex rheological behavior emerges as a consequence of a complex microstructure to which key components are the deformable red blood cells that at the high concentrations present and facilitated by fibrinogen tend also to aggregate forming mostly linear (but connected into loose networks) rouleaux structures. A key component to most blood flow models has been the presence of one or more structural parameters to characterize the dynamics of those rouleaux structures (present at lower shear rates) while, more recently, additional viscoelastic modeling components have been proposed to address viscoelastic effects due to the individual red blood cell deformation, at higher shear rates. Following that path, successive recent improvements in the family of phenomenological structural thixotropic models have begun to asymptotically approach their respective limits with respect to accuracy for steady state and transient shear flows. Their application remains limited to unidirectional shear flows. A new family of full tensorial models has recently emerged using a thermodynamically consistent framework. Those models have as yet though to be tested against the detailed transient data employed in our earlier work. Finally, a parallel multiscale modeling effort has attempted to better connect the structural dynamics to more physical models of the rouleaux aggregation process using a population balance approach. We perform that comparison here as well as between the predictions of those models and the most recent enhanced thixotropic modified Horner-Armstrong-Wagner-Beris (mHAWB) and several versions of a new proposed Non-Equilibrium Thermodynamics modified Horner-Armstrong-Jariwala-Wagner-Beris (mHAJWB). Following the formalism of Beris & Edwards. The (NET) mHAJWB model is a fully tensorial model.

Wednesday 4:10 Ballroom 7 AR30

Method to compute time-for-flight in a viscoelastic material by linear network model

Nilesh V. Salvi[1] and Jinglu Tan[2]

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A representation of wave propagation in viscoelastic materials with a finite-order linear network model is provided to facilitate their analysis with linear systems techniques. Linear network models, used commonly to describe viscoelastic behavior, fail to sufficiently account for the time of flight or phase velocity of a propagating wave through a viscoelastic material. In this representation the time-of-flight can be computed as a function of model order and the excitation frequency. The model accounts for lumped density, elasticity and viscosity with mass-spring-damper composites, as is commonly done in characterizing viscoelastic materials by the Maxwell, Kelvin-Voigt, and other linear network models. A phase correction, found necessary to match a finite order model with measurements, is computed in terms of model parameters. The need for such a correction in linear network models and an optimization algorithm to derive it for a one-dimensional homogenous material is discussed.

Wednesday 4:35 Ballroom 7 AR31

Determination of the most probable molecular weight distribution function for given dynamic moduli and other linear viscoelastic data using the maximum entropy method

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Flow curve inversion to determine the underlying molecular weight distribution has been a mainstay of analytic rheology for over 30 years. We introduce two new developments to the flow curve inversion problem. First, we introduce the polydisperse Mead-Larson-Doi (MLD) mixing rule for viscosity. Second, and more significantly we invoke the maximum entropy method for determining the most probable molecular weight distribution function consistent with all known rheological data and constraints specifically, consistency with a set of dynamic moduli data, the zero-shear viscosity and steady state recoverable compliance. Both the MLD and Bersted-Malkin viscosity mixing models have been inverted successfully to quantitatively yield the MWD underlying the flow curve for a variety of model MWDs. The Bersted-Malkin model performs better in general than the MLD viscosity mixing model inversions. The inversion is particularly sensitive to the high molecular weight tail of the molecular weight distribution. The enhanced sensitivity at the high end of the MWD comes at the expense of sensitivity to the low end. The maximum entropy method is shown to be a powerful method for inverting flow curves and defeating the ill-posed nature of such processes.

Wednesday 5:00 Ballroom 7 AR32

Validation of the three component model using a newly formulated yield stress model fluid and analytical solution for laminar pipe flow

Marco Caggioni, Emilio Tozzi, Julie B. Hipp, and William H. Hartt
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We designed a model yield stress fluid composed by 2 ingredients - Propylene glycol and Carbopol. It's also suitable for detailed rheology measurement over a large temperature range for having a reduced tendency to sample evaporation. Unlike with water-Carbopol fluids, the proposed fluid does not require a neutralization step for its preparation, and it does not display wall slip, thus minimizing measurement artifacts. The temperature-dependent flow curves were measured using standard cone and plate geometry over 6 decades of the shear rate. The measurements were fitted using the recently proposed three component (TC) model[1] and the more commonly used Herschel-Bulkley (HB) model for yield stress fluids. We compared the two models in terms of a) closeness of fit to the data, b) insights into the microstructural processes. The TCM model showed substantial advantages over HB on both items. We also present an analytical solution of the TC model in laminar pipe flow to predict flow rate and pressure drop.

[1] Caggioni M, Trappe V, Spicer PT. Variations of the Herschel-Bulkley exponent reflecting contributions of the viscous continuous phase to the shear rate-dependent stress of soft glassy materials. Journal of Rheology. 2020 Mar 5;64(2):413-22.

Wednesday 5:25 Ballroom 7 AR33

Spiral mold flow processability characterization of polyethylene

Mubashir Q. Ansari[1], Kurt A. Koppi[1], Daniel Ramirez[2], Eric Marchbanks[1], John Kohn[1], David Kababik[2], and Ryan Schneider[2]
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Processability is a key performance property metric when developing thermoplastic formulations for various applications. In the injection molding process, processability is not only associated with the flow behavior of thermoplastic formulations but also the solidification process in the mold. In-mold part solidification depends on various factors such as part geometry, tool design (including cooling channel design), and thermal properties of both the mold components and the thermoplastic formulation. Simulation packages are widely used as an aid for part and mold design. Common design factors include the prediction of flow balancing and short shots as well as quantifying pressure requirements to fill the mold cavity. Input data such as viscosity curves (typically measured via capillary rheometry) and thermal properties (specific heat and thermal conductivity) are required to solve coupled equations of motion and heat transfer associated with injection molding models. Rheological properties of the formulations can be tested under various rheological protocols to predict how a formulation will perform for various applications. However, these rheological protocols are carried out under ideal scenarios (e.g., controlled shear rates, temperature ramp rates, ideal geometries, etc.) that may not be practical in real world processes. Therefore, it is important to understand how accurately simulation results compare with injection molding experimental data. In this study, spiral mold flow experiments were performed on two high density polyethylene (HDPE) materials: high and low viscosity formulations. The resulting flow length measurements were compared to simulation-predicted flow lengths. Molding conditions (injection pressure, barrel temperature, and injection speed) were varied to identify which conditions were more impactful on flow length and to confirm whether simulation packages could detect the sensitivity of those processing conditions.

Symposium AM
Additive Manufacturing and Composites

Organizers: Liheng Cai and Jay Park

Wednesday 1:30 Meeting Room A-B AM6

Multi-material fused filament fabrication via core-shell die design

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Additive manufacturing (AM), commonly referred to as 3D printing, promises avenues of rapid prototyping with enormous customization and cost savings in the development of new designs. Fused filament fabrication (FFF), also known as material extrusion (ME), is one of the emerging AM technologies that creates three dimensional objects by adding a melted polymer in a layer-by-layer manner based on computer-aided design (CAD) models. However, a key limitation for practical applications of FFF parts is the weak interlayer strength (aka, bond strength) due poor surface contact and limited molecular inter-diffusion at the interface between neighboring tracks. The use of composite core-shell filaments in FFF has shown a promising approach for increasing the extensibility and impact strength of printed objects as demonstrated by the work of Peng et al. [1]. In light of their findings, an annular coextrusion featuring a core and shell configuration has been design to fit directly into a desktop FFF machine. This new method advances the capability of FFF to extrude two different polymer melts simultaneously, using commercially available filaments, offering the advantage of producing composite filaments in a single step, which would otherwise necessitate multi-step operations. In this study polyethylene terephthalate glycol (PETG) and acrylonitrile butadiene styrene (ABS) will be used as the shell and core polymers, respectively. 3D printing results as well as mechanical testing of the printed objects will be discussed. In addition, rheological and thermal analyses are conducted to predict the development of healing over time, which is an important measure to quantify the interlayer welding quality, by using a non-isothermal healing model developed Yang and Pitchumani.

References: 1. Peng, F., Jiang, H., Woods, A., Joo, P., Amis, E. J., Zacharia, N. S., & Vogt, B. D. (2019). 3D Printing with Core-Shell Filaments Containing High or Low Density Polyethylene Shells. ACS Applied Polymer Materials, 1(2), 275-285. https

Wednesday 1:55 Meeting Room A-B AM7

Suppression of filament defects in embedded 3D printing

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Embedded 3D printing is an emerging additive manufacturing technique wherein a submerged nozzle extrudes fluid inks into a support bath. Because the support bath holds the print in place before curing, inks can have lower viscosities than conventional direct ink writing inks and do not need to be yield stress fluids. As a result, the technique is amenable to a wide range of materials and is particularly useful for bioprinting. However, embedded 3D printing is vulnerable to defects including Plateau-Rayleigh instabilities, surface roughness, and positioning accuracies. This talk summarizes the key fluid properties which can be leveraged to suppress defects. Often, the support baths are yield stress fluids, the inks are non-Newtonian, and the surface tension between the two is close to zero. However, rheology and surface tension can both be leveraged to control defects. Using experiments, we identify how the viscosity ratio and surface tension between the ink and support influence defect formation in single filaments. Using computational fluid dynamics simulations, we isolate yielded behavior from unyielded behavior of Herschel-Bulkley fluids, identifying that the local viscosity ratio near the nozzle controls the shape of printed filaments. Critically, material systems with low, non-zero surface tensions and moderately viscous supports can suppress surface roughness, Plateau-Rayleigh instabilities, and positioning inaccuracies.

Wednesday 2:20 Meeting Room A-B AM8

Can the power law model predict behavior of colloidal dispersions for 3D printing applications?

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Colloidal dispersions have great potential to be used as a material for 3D printing as they have tunable mechanical, electrical, optical and rheological properties that make them useful in applications ranging from medicine to the semiconductor industry. However, tuning a colloidal dispersion into a printable ink is not a well standardized process, leading to significant delays in formulation of inks and reliance on user experience. In particular, controlling and predicting flow rate is extremely important to the utility of these inks in extrusion-based 3D printing. In this work, we attempt to see if prediction from simple power law models can be used to model extrusion flow rate of colloidal dispersions.

Silica nanoparticles of several diameters are dispersed in Polyethylene Glycol (PEG) at varying volume fractions to create model colloidal dispersions. Using measured rheological data, power law models are fitted in the shear thinning regime and used to make theoretical predictions of flow rate for pressure driven extrusion and pressure assisted auger geometries are made. These results are then compared to experimental measurements made using a model 3D printing extrusion head with and without an auger. Although a phenomenological model, power law modeling accurately predicts flow rates in low to moderate volume fraction fluids for all particle sizes in both geometries. However, even in regimes where power law models effectively fit viscosity, they fail to predict flow rates in most conditions for high volume fraction dispersions because of increased jamming caused by flow in restricted geometries. These results provide some encouragement that 3D printing can be benefited by simple non-physics based models rather than material/system specific modeling to improve outcomes in some conditions.

Wednesday 2:45 Meeting Room A-B AM9

Methods of microencapsulation of responsive microparticle suspensions

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Particle containing composite microcapsules have become increasingly prevalent and are widely employed for applications including pharmaceutical, personal care, nanocomposite self-healing barrier films and coatings industries. Most commonly, small particles are held at the interface or physically arrested in a solid core. Microencapsulation through polymerization at the interface of emulsion droplets has been successful in creating capsules of fluids that can be then incorporated in other media. However, due to surface energy and Pickering stabilization, it is difficult to encapsulate suspensions of diffusive or spatially responsive particles. We present two approaches to encapsulating spatially manipulatable Janus microparticles (JPs), over a broad particle size range (1-50 microns in diameter), within the core of polyurea microcapsules, avoiding substantial Pickering stabilization. Firstly, to make JPs on a sufficient scale, Automated Langmuir Blodgett deposition, where particle monolayers are fabricated on roll-to-roll substrates at meter per minute rates, is used (overcoming the typical rate-limiting step for functionalization). Subsequent particle monolayers are then functionalized through physical vapor deposition (PVD). The first encapsulation approach uses emulsified yield-stress suspensions (JPs in yield stress fluid). This yield stress material is tuned to match the physical properties of the encapsulated microparticles to hinder particle diffusivity, whilst also not permanently fixing particle positions. Particles are actively released through either a temperature change or by manipulation through external forces. A second approach looks at the use of density matching between binary solvents and microparticles to achieve a similar effect without the need for an external activating force. Both methods prove viable over a range of particle sizes and could be applicable to a number of composite microcapsule applications.

This work is supported by the Applied Physics Lab at Johns Hopkins University.

Wednesday 3:45 Meeting Room A-B AM10

3D-printing of chiral inks within jammed microgels

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Aqueous suspensions of cellulose nanocrystals (CNC) can form the chiral nematic structure below 7 wt.% of CNC. Chiral CNC suspensions exhibit the characteristic flow behavior of lyotropic chiral liquid crystals: shear-thinning at low shear rates, where the chiral domains start to flow (regime I); a plateau viscosity profile at medium shear rates, where chiral domains are broken (regime II), and a shear-thinning regime at high shear rates, where individual particles start to align (regime III). The low viscosity of the pure aqueous chiral CNC suspensions, however, makes using these materials as ink for 3D printing and direct ink writing challenging. The viscoelastic properties of the chiral inks can be improved by incorporating synthetic monomers, e.g., acrylamide (AAm)), which polymerize upon exposure to UV light. The monomer type and concentration are defined based on the compatibility with the chiral structure in the initial ink and printed filament, which is evaluated based on the flow characteristics and optical features. Once the chiral structure is recovered, photopolymerization of the monomers will lock the chiral arrangement and form a chiral gel. Although incorporating synthetic monomers can significantly increase the viscosity of the chiral suspension, it is not sufficient for self-sustained printing. We exploit the jammed microgels approach to provide support to low viscosity inks. The rheological properties of the microgel play a critical role in supporting printed structures. By tunning the concentration and pH, the rheological properties of the support bath are adjusted to ensure higher applied hydrostatic stress at the end of the nozzle than the yielding stress of the supporting bath. This engineered approach can pay the way to manufacture 3D-printed complex architectures with programmable nanoscale ordered structures for advanced mechanical and photonic applications.

Wednesday 4:10 Meeting Room A-B AM11

Robust networks of interfacial localized graphene in cocontinuous polymer blends

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Conductive polymer composites enjoy specialized applications such as electrostatic discharge protection. In this work, we create interfacially localized graphene nanoplatelets (GNPs) in a cocontinuous polymer blend of polylactide (PLA) and poly(ethylene-*co*-vinyl acetate) (EVA). Based on wetting coefficient analysis, GNPs are found to favor localization in the EVA phase. A two-step compounding sequence is designed such that a PLA/GNP masterbatch is first prepared via solution blending, and then melt compounded with the EVA. In the second step, GNPs transfer from the PLA phase to the EVA phase but become kinetically trapped at the interface, as confirmed by TEM imaging. Using this approach, we create electrically conductive composites (~10^{-6} S/cm) at the low GNP concentration of 0.5 wt%. We systematically study the shear and extensional rheology of the ternary composite system and found that the cocontinuous polymer blend with interfacial GNPs exhibits higher shear and extensional viscosities compared to samples with GNPs localized entirely within the EVA phase. Rheology, in-situ dielectric measurements, and TEM imaging after nonlinear deformations all show that the interfacial GNP network undergoes structure recovery and largely remains at the PLA/EVA interface. Moreover, high conductivity is maintained during 2 to 10 min. melt compounding. These results suggest that these robust networks will preserve their bulk electrical conductivity during subsequent melt processes.

Wednesday 4:35 Meeting Room A-B AM12

Rheological optimization of high solids loading for additive manufacturing

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In the past few years, interest has increased in using routes for additive manufacturing to obtain structures from fluids that are considered high-solids loaded. To realize these manufacturing routes, the rheology at various flow conditions remains critical. In this work, we report on protocols and pre-requisite rheology that is necessary to use direct write for fabrication from fluids where solids loading is in excess of 85 wt%. The role of surface modification and the morphology of inclusions will be detailed.

Wednesday 5:00 Meeting Room A-B AM13

Viscosity and storage modulus recovery of direct ink write polymer inks

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The shear rate of polymer inks moving through direct ink write nozzles can vary over orders of magnitude. Most inks are designed to be shear thinning so that they easily flow through the nozzle and then behave with a much higher viscosity after exiting the nozzle. While measurements of the rate of viscosity or storage modulus recovery (i.e. how fast an ink behaves with a higher viscosity or higher storage modulus) are often made to determine if an ink is "printable" or not, there is very little insight into the physical mechanism behind the structure development within the ink that leads to the higher viscosity or modulus. Here we show that the rate of viscosity recovery of fumed silica loaded poly-diphenyl-co-dimethyl-siloxane (PDPDMS) inks varies with the amount of thixotropic additive (Bluesil Thixo Add 22646, BTA) added to the ink. Below ~1 wt% BTA, the viscosity and modulus of the inks with 20% fumed silica increases with increasing BTA loading. Above this threshold, the viscosity and modulus decreases. The same holds for the rate of viscosity and modulus recovery. We interpret these results in the context of the hydrogen bonding structure that forms within the ink and relate them to kinetic bonding properties. Finally, we demonstrate that the amount of BTA in the ink also affects the space filling nature of the printed material. This suggests that the same polymer ink can have its flow properties optimized not just for flow through the nozzle but also for final print tolerances.

Wednesday 5:25 Meeting Room A-B AM14

Inorganic micro-particle transfer from liquid carrier system by dipping

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Coating or depositing nano-materials (d<30 nm) on a substrate (i.e., flat plate, cylinder, convex surface) by dipping into homogeneous density-matching solutions are commonly investigated for various applications, including surface passivation, surface functionalization, selective activation of surface energy. Controlled delivery of inorganic microparticles by the dipping process can open up 3D near-net-shape production techniques through sintering, robocasting or additive manufacturing, and material joining. However, micro-scale inorganic particles (d>1 µm) have reduced surface area and higher density, making them negatively buoyant in dip-coating mixtures and challenging for high yield solid transfer through entrainment due to the density mismatch. In this work, the physical phenomenon of the dip-coating process with negatively buoyant, non-Brownian micro-particles from density mismatching mixture is investigated on the cylindrical substrate. Liquid carrier system (LCS) solution is prepared by the combination of a binder polymer and an evaporating solvent. Inorganic micro-particles are dispersed with the assistance of a magnetic stirrer to maintain the suspension characteristics of the mixture. The effect of solid loading and the binder volume fraction on solid transfer has been reported. Two coating regime is observed (i) heterogeneous coating where particles clusters are formed at a low capillary number and (ii) effective viscous regime, where full coverage can be observed on the cylindrical substrate. In our experiment, we have not observed 'zero' particle entrainment even at the low capillary number of the mixture, which can be attributed hydrodynamic flow of the particles due to the stirring of the mixture. Different metrics of the transferred particle are also compared with the analytical expression of density matching suspension.

Symposium IN
Flow-induced Instabilities and Non-Newtonian Fluids

Organizers: Dana Grecov, Irmgard Bischofberger and Antonio Perazzo

Wednesday 1:30 Meeting Room C-D IN16

Route to elastoinertial turbulence via Tollmien-Schlichting instability

Ashwin Shekar[1], Ryan M. McMullen[2], Beverley J. McKeon[2], and Michael D. Graham[1]
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Recent studies of channel and pipe flows of dilute polymer solutions at Reynolds numbers Re~1000-10000 have revealed a viscoelasticity-driven chaotic flow state denoted elastoinertial turbulence (EIT). Computations indicate that EIT displays tilted multilayered sheets of polymer stretch with weak spanwise-oriented flow structures - a sharp contrast to the 3D quasistreamwise vortex structures that make up inertia-driven Newtonian

turbulence. The present work aims to elucidate the origin of the EIT state and its distinct structure. Direct simulations of two-dimensional channel flow of a FENE-P fluid have revealed the existence of a family of flows that is nonlinearly self-sustained by viscoelasticity with structure closely related to the classical Tollmien-Schlichting (TS) wave. Here, we describe the evolution of this branch in parameter space and its connections to the Newtonian TS instability and to elastoinertial turbulence (EIT). At Reynolds number Re=3000, there is a solution branch with TS-wave structure but which is not connected to the Newtonian solution branch. At fixed Weissenberg number, Wi, and increasing Reynolds number from 3000-10000, this attractor goes from displaying a striation of weak polymer stretch localized at the critical layer of the TS mode to an extended sheet of very large polymer stretch. We show that this transition is directly tied to the strength of the TS critical layer fluctuations and can be attributed to a coil-stretch transition when the local Weissenberg number at the hyperbolic stagnation point of the Kelvin cat's eye structure of the TS wave exceeds 1/2. At Re=10000, unlike 3000, the Newtonian TS attractor evolves continuously into the EIT state as Wi is increased from zero to about 13. We describe how the structure of the flow and stress fields changes, highlighting in particular a ``sheet-shedding" process by which the individual sheets associated with the critical layer structure break up to form the layered multisheet structure characteristic of EIT.

Wednesday 1:55 Meeting Room C-D IN17

Axisymmetric numerical simulations of viscoelastic jets

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Droplet formation in a non-Newtonian fluid is central to numerous industrial applications such as spray-drying, atomisation and paint application. The flows associated with spray formation involve large interfacial deformations and complex spatio-temporal dynamics. The aim of the present work is to establish a robust numerical basis for systematic examination of viscoelastic fluid sprays. To achieve this, we begin with two-dimensional axisymmetric simulations of an impulsively-started jet exiting a nozzle and entering a stagnant gas phase. We use an adaptively-refined volume-of-fluid technique to capture the interface and the log-conformation transformation for stable and accurate solution of the viscoelastic constitutive equation. We simulate, for the first time, the entire jetting and breakup process of a viscoelastic fluid, including the flow through the nozzle which results in an initial radial stress distribution that is shown to affect the subsequent breakup dynamics. We validate the numerical simulations against the predictions of linear stability analysis. Subsequently, we explore the effect of shearing flow inside the nozzle on the thinning dynamics of the viscoelastic jet via analysis of the spatio-temporal evolution of the polymeric stresses. We also examine the role of the finite extensibility of the polymeric chains on the breakup process and demonstrate the capacity of the numerical formulation to resolve the elasto-capillary regime as a function of mesh resolution and the finite extensibility of the fluid. Finally, we investigate systematically the dependence of the rate of filament thinning on the axial momentum of the jet and the fluid relaxation time; this permits efficient exploration of the material parameter space, capturing the competing effects of elastic, viscous, and inertial forces on the ejected droplet size distribution.

Wednesday 2:20 Meeting Room C-D IN18

Torsional fracture of viscoelastic liquid bridges

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Short liquid bridges are stable under the action of surface tension. In applications like electronic packaging, food engineering, and additive manufacturing, this poses challenges to the clean and fast dispensing of viscoelastic fluids. Here, we investigate how viscoelastic liquid bridges can be destabilized by torsion. By combining high-speed imaging and numerical simulation, we show that concave surfaces of liquid bridges can localize shear, in turn localizing normal stresses and making the surface more concave. Such positive feedback creates an indent, which propagates toward the center and leads to breakup of the liquid bridge. The indent formation mechanism closely resembles edge fracture, an often undesired viscoelastic flow instability characterized by the sudden indentation of the fluid's free surface when the fluid is subjected to shear. By applying torsion, even short, capillary stable liquid bridges can be broken in the order of 1 s. This may lead to the development of dispensing protocols that reduce substrate contamination by the satellite droplets and long capillary tails formed by capillary retraction, which is the current mainstream industrial method for destabilizing viscoelastic liquid bridges.

Wednesday 2:45 Meeting Room C-D IN19

Secondary or adverse effects in the use of polymer additives for turbulent drag reduction

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The effect of adding small amounts of long-chain polymers on turbulent shear flows has long been studied and noted in the literature; the global effect of which is a reduction in the mean shear at the wall. The dynamics of these flows are also completely altered from those observed in the Newtonian case. These include the presence of extended low-drag periods and streamwise-invariant structures, which lead to the global reduction in mean wall shear stress. However, little attention has been given to secondary effects in these flows, specifically significant "bursts" that are observed in various flow variables (e.g., wall shear stress). Therefore, in this study, we define and characterize secondary effects observed in direct numerical simulations of plane Poiseuille (channel) flow of a dilute polymer solution at friction Reynolds numbers up to 180. While the level of drag reduction increases with Weissenberg number, it is observed that both the frequency and magnitude of significant bursting events increase, which is indicative of secondary effects or seemingly adverse effects. The magnitude of very strong bursts or so-called extreme events was even observed to surpass the mean Newtonian value in some cases. Lastly, the dependence of Reynolds number on the altered turbulent dynamics and additional secondary effects of polymer solutions are explored and discussed further.

Wednesday 3:45 Meeting Room C-D IN20

Reverse transition routes from inertial to elasticity-dominated turbulence in viscoelastic Taylor-Couette flow

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A high-order transition route from inertial to elasticity-dominated turbulence (EDT) in Taylor-Couette (TC) flows of polymeric solutions has been discovered via direct numerical simulations. This novel two-step transition route is realized by enhancing the extensional viscosity and hoop stresses of the polymeric solution via increasing the maximum chain extension at a fixed polymer concentration. Specifically, in the first step inertial turbulence is stabilized to a laminar flow much alike the modulated wavy vortex flow. The second step destabilizes this laminar flow state to EDT, i.e., a spatially smooth and temporally random flow with a -3.5 scaling law of the energy spectrum reminiscent of elastic turbulence. The flow states involved are distinctly different than those observed in the reverse transition route from inertial turbulence via a relaminarization of the flow to elasto-inertial turbulence in parallel shear flows, underscoring the importance of polymer-induced hoop stresses in realizing EDT in the TC geometry that are absent in parallel shear flows.

Wednesday 4:10 Meeting Room C-D IN21

Interfacial flows and instabilities of elastic fluids

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Constant viscosity, but finite elasticity make Boger fluids an ideal choice for investigation of the role and influence of elasticity on interfacial flows and instabilities. In this contribution, we examine the pinching dynamics and extensional rheology response of model Boger fluids using dripping-onto-substrate (DoS) rheometry protocols, showing measurable viscoelastic effects even though elastic properties like modulus and first normal difference are either below the resolution limit of torsional rheometers or source of elastic instabilities. We thereafter show how elasticity influences fingering instability by visualizing flows within Hele-Shaw cell, and discuss the connections with other free surface flows and instabilities where viscoelasticity can influence pattern formation and evolution.

Wednesday 4:35 Meeting Room C-D IN22

Influence of polymer diffusivity in nanoconfinement on the onset of viscous fingering

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The onset of nanoscale viscous fingers within nanoporous media is a function of polymer concentration and molecular weight and the media permeability. Comparing the onset of these fingers to prior literature, it suggests the polymer effective viscosity and diffusivity must vary greatly in nanoconfinement as compared to in bulk solutions. Aiming to understand how confinement influences polymer dynamics, this work uses Fluorescent Recovery After Photobleaching (FRAP) via laser scanning confocal microscopy to measure the mobility of fluorescent poly(vinyl alcohol) (PVA) in both bulk solutions and in colloidal crystals. PVA used in this study has an average molecular weight of 67,000 Da and the colloidal crystal is fabricated from 1 micron silica microspheres. Diffusivity of PVA in both cases is extracted by fitting a model to the fluorescent intensity recovery in the bleached region. In the bulk, fluorescence recovery matches the model well. In the colloidal crystal, the model describes the initial fluorescence recovery, suggesting the effective diffusivity is two orders of magnitude lower than in the bulk solution, but overestimates the long-time polymer fluorescence. This deviation from the predicted longer recovery times within the colloidal crystal suggests either a partitioning of polymer by molecular weight or more complex interactions of polymer chains in confinement. Molecular dynamics simulations using coarse-grained models for polymer chains and explicit solvent in bulk (i.e., no confinement effects) and in nanoporous colloidal crystal describe the primary influence of nanoconfinement on the polymer chain conformations and diffusion. It is theorized that a combination of pore size and molecular crowding, which is a function of polymer concentration and molecular weight, slows the polymer dynamics considerably. This effective decrease in polymer diffusivity and increase in effective viscosity results in the conditions that support continuous fingering in these films.

Wednesday 5:00 Meeting Room C-D IN23

Elastic turbulence generates anomalous flow resistance in porous media

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Polymer solutions are often injected in porous media for applications such as oil recovery and groundwater remediation. In many cases, the macroscopic flow resistance abruptly increases above a threshold flow rate in a porous medium, but not in bulk solution. The reason why has been a puzzle for over half a century. Here, by directly visualizing the flow in a transparent 3D porous medium, we demonstrate that this anomalous

increase is due to the onset of an elastic instability in which the flow exhibits strong spatio-temporal fluctuations reminiscent of inertial turbulence, despite the vanishingly small Reynolds number. We find that the transition to unstable flow in each pore is continuous, arising due to the increased persistence of discrete bursts of instability above an onset flow rate; however, this onset value varies from pore to pore. Thus, unstable flow is spatially heterogeneous across the different pores of the medium, with unstable and laminar regions coexisting. Guided by these findings, we quantitatively establish that the energy dissipated by unstable pore-scale fluctuations generates the anomalous increase in flow resistance through the entire medium. Thus, by linking the onset of unstable flow at the pore scale to transport at the macroscale, our work provides generally-applicable guidelines for predicting and controlling polymer solution flows.

Wednesday 5:25 Meeting Room C-D IN24

Transient dynamics of viscoelastic turbulent flows subject to a sudden injection of polymer additives

Alexia Martinez Ibarra and Jae Sung Park
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Injecting small amounts of long-chain polymers into a viscous fluid can lead to beneficial changes in the flow phenomena, such as reduced operating pressure or consumption costs. In particular, numerous studies have been performed to investigate the overall effects of polymers on a turbulent flow, where substantial reduction of friction drag is achieved by polymer solutions when comparing to Newtonian fluids. However, there are fewer studies on transient behavior in polymer solutions when polymers are injected into a turbulent flow. For this study, we perform direct numerical simulations of viscoelastic turbulent flows to investigate the overall and transient effects of injecting different polymer concentrations on a turbulent flow. A wide range of polymer concentrations is considered from dilute to semi-concentrated regimes at friction Reynolds numbers of 85 and 113. Preliminary results show that the drag reduction percentage almost behaves linearly with polymer concentration for both Reynolds numbers studied. It is observed that turbulent flows tend to laminarize when subjected to higher polymer concentrations. During the transition from turbulent to laminar, the decay of turbulence is anisotropic along the different directions. The wall-normal and spanwise velocities decay faster than the streamwise velocity, which is in agreement with the results shown for Newtonian fluids. We also observe that the wall-normal velocity has the fastest decay. The anisotropic decay of turbulence becomes more prominent as the polymer concentration is increased. Lastly, transient flow responses to a sudden injection of polymers are presented. Initial flow instabilities are observed, and its magnitudes increase monotonically with polymer concentration. Interestingly, the transient and post-transient dynamics seem to strongly depend on flow characteristics at the polymer injection sites. This dependence will be further discussed.

Symposium RI
Rheology and Mobility at Interfaces

Organizers: Patrick Anderson and Vivek Narsimhan

Wednesday 1:30 Ballroom 6 RI6

Nonlinear interfacial rheology and adsorption behavior of clinical lung surfactant

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Diminished lung compliance, restriction of lung volume, and hypoxemia are symptoms common to both neonatal respiratory distress syndrome (RDS) in premature infants and adult RDS. The mechanisms through which ARDS arises and develop the severe disease are unclear. However, as the immune system responds to infection, phospholipase A2 (PLA2) flows out into the alveolar fluids and catalyzes the hydrolysis of double-chain phospholipids in bacterial, fungal, and viral membranes into single-chain lysolipids and fatty acids. This study used clinical lung surfactants like Survanta and introduced lysolipid to the system to mimic the aforementioned scenario. We examined the adsorption of the Survanta monolayer diluted at different temperatures. Repetitive behavior demonstrates the breaking of aggregates plays an important role in how it adsorbs. Response to dilatational deformation of Survanta monolayer was also studied both in linear viscoelastic (LVE) and non-linear (NLVE) regimes. An order of magnitude drop of LVE modulus exhibited the stripping of good lung surfactant as lysolipid was introduced to the system. We have seen similar behavior on the trough as well. As our tidal volume of lung changes from 4-8 mL/kg of body weight, it is apparent that large-amplitude (>5%) oscillatory dilation (LAOD) measurement is necessary. Nonlinear LAOD behavior is represented in the Lissajous plot where yielding and recovery were obvious.

Wednesday 1:55 Ballroom 6 RI7

Interfacial tensions and film drainage times with surfactant stabilized emulsions: Towards improved liquid-liquid separation

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The interfacial properties of surfactant stabilized liquid-liquid systems inform liquid separations and treatment strategies, such as coalescence. Liquid-liquid separation becomes harder in the presence of surfactants that make droplets more stable. Therefore, the effective removal of the dispersed phase droplets requires understanding of the effect of surfactant presence in these emulsions on their dynamics and stability. In this presentation, we highlight this effect using measurements performed across a range of droplet size, surfactant concentration, and viscosity ratios.

The first factor studied here is the interfacial tension (IFT), as well as the characteristic timescale required for the IFT to reach equilibrium. Dynamic IFT measurements are performed here at two length scales: a millimeter scale using pendant drop experiments and a microscale using microfluidic tensiometry, with systems of light and heavy mineral oil containing varied concentrations of SPAN80 surfactant. It is found that the IFT decays faster in the case of micro-scale droplets due to a shift from diffusion-limit to adsorption-limited surfactant transport mechanism. In addition, as expected, the equilibrium IFT decreases with increasing SPAN80 concentration, and the decay rate of the dynamic IFT is higher at greater surfactant concentrations. It was also found that the equilibrium IFT increases with increasing viscosity ratio of the outer to the inner phase, and that the rate of IFT decay is lower at a greater viscosity ratio. The surfactant diffusivity and interfacial adsorption and desorption rates are extracted by fitting a surfactant diffusion and equation of state equations to the dynamic IFT measurements. The second factor studied here is the time for the thin film to drain between two coalescing droplets. Similar to dynamic IFT, the film drainage time is closely tied to the stability of the droplet, with faster film drainage events indicative of less stable emulsions. This relation is shown in this work by presenting the film d

Wednesday 2:20 Ballroom 6 RI8

Coronavirus rotational diffusivity

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Just 11 weeks after the confirmation of first infection, one team had already discovered and published [D. Wrapp et al., "Cryo-EM structure of the 2019-nCoV spike in the prefusion conformation," Science 367(6483), 1260-1263 (2020)] in exquisite detail about the new coronavirus, along with how it differs from previous viruses. We call the virus particle causing the COVID-19 disease SARS-CoV-2, a spherical capsid covered with spikes termed peplomers. Since the virus is not motile, it relies on its own random thermal motion, specifically the rotational component of this thermal motion, to align its peplomers with targets. The governing transport property for the virus to attack successfully is thus the rotational diffusivity. Too little rotational diffusivity and too few alignments are produced to properly infect. Too much, and the alignment intervals will be too short to properly infect, and the peplomer is wasted. In this paper, we calculate the rotational diffusivity along with the complex viscosity of four classes of virus particles of ascending geometric complexity: tobacco mosaic, gemini, adeno, and corona. The gemini and adeno viruses share icosahedral bead arrangements, and for the corona virus, we use polyhedral solutions to the Thomson problem to arrange its peplomers. We employ general rigid bead-rod theory to calculate complex viscosities and rotational diffusivities, from first principles, of the virus suspensions. We find that our ab initio calculations agree with the observed complex viscosity of the tobacco mosaic virus suspension. From our analysis of the gemini virus suspension, we learn that the fine detail of the virus structure governs its rotational diffusivity. We find the characteristic time for the adenovirus from general rigid bead-rod theory. Finally, from our analysis of the coronavirus suspension, we learn that its rotational diffusivity descends monotonically with its number of peplomers.

Wednesday 2:45 Ballroom 6 RI9

Artificial tap water and interfacial rheology of tea varieties

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Tap water is known to contain ions including calcium, magnesium, sodium, sulfate, and chloride [1]. While water composition has been shown to be important to the flavanol content of brewed tea [2], most everyday tea drinkers use their local tap water. For tea brewed in tap water, an interfacial phenomenon can be observed. The surface film that forms is brittle and mildly iridescent, it cracks like ice floes when disturbed. Ion content of the water influences the mass of tea film generated such that deionized water forms no collectable film [3]. This ion content, as well as pH, has been shown to have an effect on theaflavin extraction from tea leaves [4]. Additions of common tea add-ins, such as lemon, milk, or sugar effect the physical thickness of the tea film but physical thickness does not correlate directly with the film rheological properties [3]. The interfacial film rheological properties are assessed using interfacial rheometry. All films formed in artificial tap water (ATW) exhibit yielding point behavior in interfacial oscillatory shear. Green and black tea are produced from the same plant, Camellia sinensis (L.), and form visible films, while rooibos tea forms no film, visibly or rheologically. Green tea films are less brittle than black tea films. Interfacial moduli of green tea are less affected by ions than black tea. When the effect of milk components is studied, β-caseins extend the yielding interfacial shear strain by two orders of magnitude; β-lactoglobulins extend this same metric by only 0.4 %. Addition of salt in ion rich ATW brews reduced interfacial viscous and elastic moduli equally by 0.8 Pa m. Conditions forming the weakest film may be useful in producing dried tea mixtures to reduce film appearance in regions with ion-heavy tap water.

[1] C.E. Boyd, Hydrobiologia 80 (1981) 91
[2] M. Spiro, P.L.L. Lam, Food Chem. 54 (1995) 393
[3] C.E. Giacomin, P. Fischer, Phys. Fluids. Submitted (2021)
[4] W.E. Price, M. Spiro, J. Sci. Food Agric. 24 (1987) 51

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Marie-Claude Heuzey, Sara Hashmi and Rahul Pandey

Wednesday 3:45 Ballroom 6 SC29

Shear-induced grain boundary dynamics in magnetically actuated colloidal crystals

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Polycrystalline materials, such as metals and ceramics, contain interfacial defects between their crystalline grains. These grain boundaries (GBs) play a pivotal role in determining bulk material properties, in part, because they are dynamic and can move to accommodate stresses in the material, such as shear stress. Despite many efforts however, much of the shear-coupled GB dynamics are not well understood. Here, we show a tunable system of superparamagnetic particles under a time-varying magnetic field creates two-dimensional crystalline sheets that contain inherent shear at particle-free voids. We describe the mechanism of shear in this system and showcase its effect on the polycrystalline bulk. Using the local bond orientational order parameter (?6), GBs in the system are identified and monitored with time. We observe reorganization of ordered grains and disordered grain boundaries under a constant magnetic field strength. We find new low angle grain boundaries form in the system. Furthermore, we apply classical material science theory to these shear-induced low angle grain boundaries and find good agreement, thereby directly connecting our soft colloidal system to hard-condensed matter.

Wednesday 4:10 Ballroom 6 SC30

Periodic deformation of semiflexible colloidal filaments in eccentric time-varying magnetic fields

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Chains of linked superparamagnetic particles actuated by external time-varying magnetic fields exhibit diverse dynamics that depend on the field parameters and the filament length. Their motion serves for the microscopic manipulation of fluids and as model systems of active filaments. These dynamics can be described by the competition among viscous, magnetic, and elastic forces during chain actuation. Current literature has focused mostly on studying the dynamics under symmetric (circular) time-varying fields, which have a constant strength. The colloidal chains initially coil or fold under these conditions, but eventually collapse into smaller structures that can only rotate like rigid bodies. Therefore, these fields restrict the possible configurations that the filaments can acquire. Here, we explore novel nonlinear filament dynamics by applying asymmetric (eccentric) time-varying magnetic fields, which are characterized by a time-dependent strength. When actuated with eccentric fields, the chains bend and stretch periodically, showcasing four distinct stages of motion characterized by different morphologies during a single period of the magnetic field. These stages are described in terms of the instantaneous Mason number, the phase lag angle between the chain and the field, and the bending energy. The extent of deformation during the bending stage is affected by the chain length, the field frequency, and the field ellipticity.

Wednesday 4:35 Ballroom 6 SC31

Dynamics of interacting paramagnetic particles with finite magnetic relaxation time in rotating fields

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We study the effect of a finite magnetic relaxation time in the dynamics of suspended interacting paramagnetic particles in rotating magnetic fields. The hydrodynamic interactions between the particles are taken into account under the Stokesian Dynamics perspective. At low field frequencies relative to the magnetic relaxation of the particles, the dipole-dipole interactions between the particles lead to the ordinary formation of rotating linear and 2D clusters structures widely reported in the literature. However, by increasing the field frequency for its period to be at the same order as the magnetic relaxation time, we predict a relative demagnetization of the particle and an emergence of a phase lag angle with respect to the external field. The relative demagnetization can cause the cluster structures to dissolve due to the weakening of the dipole-dipole attractions, while the phase lag angle induces magnetic torques on the individual particles. Our numerical simulations suggest this later effect to be responsible for clusters rotating dynamics at high-frequency fields.

Wednesday 5:00 Ballroom 6 SC32

The dynamics in and rheology of dilute suspensions of semi-flexible, 2-D colloids

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In this talk, I will discuss simulations of semi-flexible, 2D colloids -- sheets -- in simple shear flow. I will show how sheets deform and flip in this flow field in ways that are well described by Jeffery orbits of very thin oblate spheroids when the sheets are stiff and thermal forces are weak. I will discuss a transition to a a regime of chaotic motion for the sheets when the strength of the flow grows much large. In the chaotic regime, the sheets become crumpled into objects that are more isotropic, and so they more much like spheres through the flow field. Thermal forces have the effect of causing the sheets to flip more often in flow. Because the sheets are two dimensional, they tend to find a stable state in which they become

flat in the flow-vorticity plane. Thermal forces perturb this state. We show that the time between thermal events that perturb the sheet from this flat state is well described by the same theories used to explain polymer flipping in solution. Finally, we identify the bounding ellipsoid for the sheets throughout their trajectories in the simple shear flow and use this bounding ellipsoid to estimate the hydrodynamic stresses born by the sheet and from that the viscosity of a dilute solution of sheets in a simple shear flow as a function of shear rate, bending rigidity, and strength of thermal forces.

Wednesday 5:25 Ballroom 6 SC33

Phase behavior and effective aspect ratio of polydisperse carbon nanotube solutions

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Carbon nanotubes (CNTs) are well known for their remarkable material properties, being attractive building blocks for producing multifunctional materials like fibers and thin films. The performance of these CNT materials is a strong function of CNT aspect ratio, which directly impacts the phase behavior of CNTs in solution. Most works to date focused on producing and characterizing CNT materials made from solutions with a single CNT species. Previous work demonstrated that CNTs usually follow a log-normal length distribution that is narrowly disperse in comparison to standard polymeric samples. In addition, the phase behavior of CNTs is well described by CNT aspect ratio, such that the isotropic-to-nematic phase transition behaves accordingly to Onsager's classical theory for rigid rods. Highly polydisperse samples in which long and short CNTs coexist in solution might be a feasible alternative to produce high-performance CNT materials at lower cost and higher efficiency. Nevertheless, the phase behavior of strongly length-polydisperse CNT solutions as well as a measure of their effective aspect ratio have not been addressed in the literature and are not yet fully understood. In this work, we present an experimental study of highly polydisperse CNT solutions. We use two different CNT batches with distinct aspect ratios and prepare dilute solutions in chlorosulfonic acid at different proportions of each batch. We use transmission electron microscopy, cross-polarized optical microscopy, and extensional rheometry to characterize the phase behavior and viscosity-averaged effective aspect ratio of these bimodal CNT solutions. The results show how the fraction of long-to-short tubes in solution affect the isotropic-to-nematic phase transition and the solution effective aspect ratio as determined by capillary thinning extensional viscosity measurements. These predictions are key to better understand and optimize the properties of macroscopic CNT materials made from polydisperse solutions at high concentrations.

Symposium GG
Arrested Systems: Gels and Glasses

Organizers: Emanuela del Gado and Jyoti Seth

Wednesday 1:30 Ballroom 1 GG24

Cellulose nanocrystals for gelation and percolation-induced reinforcement of a photocurable poly(vinyl alcohol) derivative

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Nanomaterials are regularly added to crosslinkable polymers to enhance mechanical properties; however, important effects related to gelation behavior and crosslinking kinetics are often overlooked. In this study, we combine cellulose nanocrystals (CNCs) with a photoactive poly(vinyl alcohol) derivative, PVA-SbQ, to form photocrosslinked nanocomposite hydrogels. We investigate the rheology of PVA-SbQ with and without CNCs to decipher the role of each component in final property development and identify a critical CNC concentration (1.5 wt%) above which several changes in rheological behavior are observed. Neat PVA-SbQ solutions exhibit Newtonian flow behavior across all concentrations, while CNC dispersions are shear-thinning <6 wt% and gel at high concentrations. Combining semi-dilute entangled PVA-SbQ (6 wt%) with >1.5 wt% CNCs forms a percolated microstructure. *In situ* photocrosslinking experiments reveal how CNCs affect both the gelation kinetics and storage modulus (G') of the resulting hydrogels. The modulus crossover time increases after addition of up to 1.5 wt% CNCs, while no modulus crossover is observed >1.5 wt% CNCs. A sharp increase in G' is observed >1.5 wt% CNCs for fully-crosslinked networks due to favorable PVA-SbQ/CNC interactions. A percolation model is fitted to the G' data to confirm that mechanical percolation is maintained after photocrosslinking. A ~120% increase in G' for 2.5 wt% CNCs (relative to neat PVA-SbQ) confirms that CNCs provide a reinforcing effect through the percolated microstructure formed from PVA-SbQ/CNC interactions. The results are testament to the ability of CNCs to significantly alter the storage moduli of crosslinked polymer gels at low loading fractions through percolation-induced reinforcement.

Wednesday 1:55 Ballroom 1 GG25

Investigation of the yielding transition in concentrated colloidal systems via rheo-XPCS

Gavin J. Donley[1], JD Park[2], Matthew A. Wade[3], Suresh Narayanan[4], Robert L. Leheny[5], James L. Harden[6], and Simon A. Rogers[3]
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We probe the microstructural yielding dynamics of a concentrated colloidal system by performing creep/recovery tests with simultaneous collection of scattering data via X-ray Photon Correlation Spectroscopy (XPCS). This combination of rheology and scattering allows for time-resolved observations of the microstructural dynamics as yielding occurs, which can be linked back to the applied rheological deformation to form structure-property relations. To more accurately track the non-equilibrium processes which occur under yielding, we utilize two-time correlation functions, which provide additional time-resolved information that is inaccessible via more typical one-time correlations. Under sufficiently small applied creep stresses, examination of the correlation in the flow direction reveals that the scattering response recorrelates with its pre-deformed state, indicating nearly-complete microstructural recovery, and the dynamics of the system under these conditions slows considerably. Conversely, larger creep stresses increase the speed of the dynamics under both applied creep and recovery. The data show a strong connection between the microstructural dynamics and the acquisition of unrecoverable strain. By comparing this relationship to that predicted from homogeneous, affine shearing, we find that the yielding transition in concentrated colloidal systems is highly heterogenous on the microstructural level.

Wednesday 2:20 Ballroom 1 GG26

Transient yielding of soft particle glasses

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Yield stress fluids (YSFs) are materials that respond elastically to small deformations but deform irreversibly and flow when subjected to a large external shear. The way that YSFs switches from solid to liquid behavior is characterized by a complex transient rheological response. Understanding transient yielding is vital in process operations since startup flow regimes are often associated with stress overshoots that generate important pressure perturbations. It is also crucial from a fundamental perspective because it contains the evolution of the structure of the material from its initial state and reveals the microscopic mechanisms associated with yielding and flow. Here we address this question for the case of soft particle glasses made of soft colloids jammed well above close-packing.

First we show that the capacity of soft particle glasses to store residual stresses when they are sheared makes their transient response dependent of the mechanical history. We identify and rationalize two phenomena: memory effects where the material "remembers" the direction of preshear thereby suppressing reversibility, and aging where the stress overshoot becomes sharper with time. We propose specific experimental protocols to erase the effect of the mechanical history.

In a second part, we show that the transient response of concentrated suspensions of soft microgels and dense emulsions depends on several microscopic parameters such as the microstructure of the particles, the existence of attractive interactions, and the degree of packing. In spite of their apparent diversity the results obtained for many different materials can be rationalized and collapsed onto universal variations when the shear rate and the stress are scaled by the appropriate characteristic time and stress. We will compare these results to existing predictions from theory and simulations

Wednesday 2:45 Ballroom 1 GG27

Accelerated yielding of binary colloidal gels

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When sheared at a stress that is large enough to induce plastic deformation yet small enough to prevent immediate fluidization, a colloidal gel creeps at gradually decreasing shear rates for a prolonged period of time, until it eventually yields and flows - a phenomenon known as delayed yielding. Using two types of polystyrene-poly(N-isopropylacrylamide) core-shell particles in water, we show that when the different types of particles are mixed, the resultant binary gel yields faster than the homogeneous gels composed of either type of particles. This accelerated yielding of the binary gel results from its lower critical strain at which the fluidization occurs. To investigate the mechanism for the distinct yielding timescales, we study the stress response of the gels in shear start-up and large amplitude oscillatory shear and find that the yielding of the binary gel is preceded by competing effects of strain-hardening and strain-softening, which lead to more brittle fracture.

Thursday Morning

Symposium MP
Metzner Presentation

Metzner Award Presentation

Thursday 8:30 Ballroom 5-6-7 MP1

Dynamics of physically and chemically reversible polymers

Quan Chen
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Introduction of dynamically associative interactions in polymers modifies their dynamics, which has been extensively utilized in molecular design of novel materials including self-healing, stimuli-responsive, and shape-memory materials. Different dynamic features stem from differences in the lifetime, density, and position of the associative sites of the chains. This presentation summarizes recent advances in our understanding of dynamics of both physically and chemically reversible networks in those materials. A particular focus is placed on assumptions and predictions of the molecular-level theories that include the reversible gelation, the sticky-Rouse, and the sticky-reptation theories. Dynamic features not expected from these theories will then be highlighted for the state-of-the-art materials, including the physically reversible networks like the ionomers and the chemically reversible networks like the vitrimers. Finally, some new pathways for future theoretical development will be discussed.

Pre-Recorded Flash Presentaton

Symposium VP
Pre-recorded Flash Presentations (virtual)

Organizers: Cari Dutcher, Patrick Underhill, Anne M. Grillet and Marie-Claude Heuzey

Asynchronous Any Time Virtual VP1

Re-entrant melting in interpenetrating and interconnected grafted nano cylinders from amphiphilic star block copolymers

Esmaeel Moghimi[1], Iurii Chubak[2], Luca Cipelletti[3], Kell Mortensen[4], Christos Likos[2], and Dimitris Vlassopoulos[1]
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A powerful combination of rheological, small angle X-ray and dynamic light scattering experiments along with computer simulations are utilized to examine the self-organization of a new class of tunable soft patchy colloidal particles of the star family, whose arms are diblock copolymers. These stars were synthesized by K. Ntetsikas and N. Hadjichristidis (KAUST). By tuning the solvent quality and block sequence a variety of intriguing opportunities to control the structure and dynamics of such soft colloids emerges, the most notable being the transition from high temperature disordered liquid to a low-temperature solid crystalline structure. The proposed state diagram with the re-entrant transition where an ordered/solid state can be formed both on heating and cooling shows the richness of the structural and rheological (linear and nonlinear) behavior of this kind of patchy particles. The main difference from respective ordered micelles when the solvophobic block is the inner one, is the organization into bridged grafted cylinders and interpenetrated grafted cylinders, respectively.

Asynchronous Any Time Virtual VP2

Microscopic dynamics and shear rheology of unentangled polymer nanocomposite melts: Simulation and theoretical description

Emmanuel N. Skountzos[1], Katerina S. Karadima[2], Vlasis G. Mavrantzas[3], and Vlasis G. Mavrantzas[4]
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Motivated by experimental data[1] for the important role of terminal groups in the microscopic dynamics of poly(ethylene glycol) (PEG) / silica nanocomposites, we use detailed molecular dynamics (MD) simulations with a reliable, well-validated atomistic model to obtain direct predictions of the structural and (particularly) dynamic properties of such melts with PEG chains terminated either with hydroxyl (-OH) or with methoxy (-CH_3) groups. It is found that the two types of PEG chains (PEG-OH and PEG-CH_3) adsorb differently on the surface of the silica nanoparticle. Hydroxyl-terminated PEG chains prefer to adsorb only by their ends thus forming brush-like structures, whereas methoxy-terminated ones prefer to adsorb along their entire contour resulting in a much denser adsorbed layer.

Simulation predictions[2] for the dynamic structure factor $S(Q,t)/S(Q,0)$ reveals excellent agreement with the experimental data[1] for the same system under the same temperature and pressure conditions. A Rouse model that distinguishes between tails, trains, and loops offers a remarkable description of microscopic dynamics,[2] by borrowing information from the simulations only about the relative population of these species.

In a second step, well-relaxed configurations from the equilibrium simulations are subjected to non-equilibrium simulations under shear flow in order to obtain the viscosity and first and second normal stress coefficients of the two types of PEG / silica nanocomposite melts. Results from these simulations will be discussed in detail and compared to available experimental data.

References
1. T. Glomann, G.J. Schneider, J. Allgaier, A. Radulescu, W. Lohstroh, B. Farago, D. Richter, *Phys. Rev. Lett.*, **110**, 178001 (2013).
2. E.N. Skountzos, D.G. Tsalikis, P.S. Stephanou, V.G. Mavrantzas, *Macromolecules*, **54**, 4470 (2021).

Asynchronous Any Time Virtual VP3

Mechanical degradation of polyacrylamide solutions in nanoparticle suspensions

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Polymer solutions may be used to optimize soil remediation and oil recovery applications. However, polymer molecules breakup as they flow through porous media, leading to a decrease in the solution viscosity and its effectiveness on displacing a high viscosity oil phase. In this work, we analyze the effect of mechanical degradation of different polymer solutions commonly used in enhanced oil recovery processes. We evaluate the changes on both the shear and extensional viscosity of the solutions associated with the flow as a function of the flow rate solution composition.

As expected, the mechanical degradation was stronger at high flow rates and high molecular weight solutions. We also studied the effect of adding nanoparticles to the polymer solution formulation on the rheological properties of the solutions before and after the mechanical degradation. The results show that, at the concentrations used, the addition of nanoparticles had negligible effect on the shear and extensional viscosity of the fresh solutions, but had significant effect on the mechanical degradation associated with the flow.

Asynchronous Any Time Virtual VP4

Nonmonotonic variation of terminal relaxation in star-linear blends

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According to recent experiments by Hall et al. [*Macromolecules* **52**, 7831 (2019)] the terminal relaxation time τ_b of star-linear blends varies nonmonotonically with the weight fraction of the star polymer in the blend w_s, when the linear polymer is more viscous than the star; i.e. the ratio or linear and star viscosities $r_\eta = \eta_l/\eta_s > 1$. Simulations were performed using a fast slip link model on a large number of star-linear blends where the average number of entanglements per star arm was varied between 8-25, and the viscosity ratio r_η was varied between 0.1-1000. Results agree with experiments: nonmonotonic variation of τ_b with w_s is observed only when $r_\eta > 1$, due to partial suppression of constraint release on the star polymers in the blend. These simulations suggest an upper-bound for r_η beyond which the nonmonotonic variation of τ_b with w_s is expected to subside. This prediction is directly confirmed in ecoSLM simulations with $r_\eta \approx 100\text{-}1000$. Thus, we find that $r_\eta > 1$ is a necessary, but not sufficient, condition for nonmonotonic variation of terminal relaxation of a star-linear blend with composition.

Asynchronous Any Time Virtual VP5

Can short, unentangled polymers be effective (self)compatibilizers in polymer blends?

Avanish Bharati, Ruth Cardinaels, and Paula Moldenaers
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Polymer blending offers an efficient strategy to develop materials with optimal properties superior to those of the components. By varying the polymers, the blend composition and processing routes, blends with a wide range of morphologies can be generated for tuning the final properties. Paradoxically, the inherent immiscibility of most polymers mandates their compatibilization to refine and stabilize the biphasic morphology. The classical strategy to improve the blends compatibility is the incorporation of premade block polymers. More recently, compatibilzation by nanoparticles has proven to be a successful alternative route. Here we describe a novel compatibilization strategy by employing novel compatibilizers, in particular short unentangled poly(styrene) (PS) polymers, in phase separating poly[(methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (PMSAN/PMMA) blends or immiscible PS/PMMA blends. The compatibilization effectiveness of the PS polymers is assessed by in-situ characterization of the matrix-droplet morphology as a function of coalescence time using a flow-induced coalescence protocol. Below the entanglement molecular weight (Me), there is good compatibilization, discerned from both the decrease in the interfacial tension and the increase in the extent of coalescence suppression of the PMMA droplets in 85/15 PMSAN/PMMA and PS/PMMA blends. However, compatibilization significantly decreases if the molecular weight (Mw) of the PS polymers is increased above Me. The compatibilization effects are independent of the functionalization of the PS terminal groups and also hold when the compatibilizer has exactly the same chemical composition as one of the blend components, thus demonstrating the occurrence of self-compatibilization.

Asynchronous Any Time Virtual VP6

Use of tailored blend morphologies to obtain electrically conductive composites

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In this work, co-continuous blends of two immiscible polymers, polypropylene (PP) and polystyrene (PS) containing multiwall carbon nanotubes (MWCNTs) and PP/MWCNTs composites with different amount of MWCNTs were prepared by melt mixing and characterized rheologically, morphologically, and electrically. Small amplitude oscillatory shear (SAOS) tests were used to access MWCNTs' state of dispersion. The rheological characterization was also fitted to the model based on the estimation that complex modulus of the co-continuous blends is a sum of components contribution and interface contribution (YZZ model) [1] to evaluate the change of morphology undergone by the different samples when subjected to steady shear. The morphology and electrical properties prior and after shear were observed by scanning electron microscopy (SEM) and broadband dielectric spectroscopy, respectively. The results obtained from both SAOS and SEM observations indicated that upon the addition of MWCNTs, the characteristic domain size of co-continuous PP/PS/MWCNTs decreases drastically, indicating that MWCNTs refined the morphology. Furthermore, it was possible to quantify the morphology of the blends using the model based on YZZ [1]. Using this model, it was shown that MWCNTs could stabilize the morphology of a co-continuous blend once added at a certain concentration.

1. Yu, W.; Zhou, W.; Zhou, C. Linear viscoelasticity of polymer blends with co-continuous morphology. Polymer 2010, 51, 2091-2098.

Asynchronous Any Time Virtual VP7

Investigation of compatibilization of PE/PP blend by graphene

S M Nourin Sultana[1], Emna Helal[2], Giovanna Gutierrez[2], Nima Moghimian[2], Eric David[1], and Nicole Demarquette[1]
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This work addresses the possibility of using graphene (G) as a compatibilizer for Polypropylene (PP)/ Polyethylene (PE) blends. Graphene, with concentrations ranging from 0.1 to 2 wt% was added to - 90/10 PE/PP blend. The morphology of the blends was analyzed by scanning electron microscopy (SEM). The blends without and with graphene were subjected to small amplitude oscillatory shear (SAOS) in order to evaluate the interfacial tension between the components of the blends using Palierne's model and the relaxation times inferred from the SAOS data. The blends were also subjected to shear-induced coalescence tests which consist of a sequence of steady shear and SAOS. Steady shear was applied at a shear rate of 0.05 s-1 for a duration varying from 3 to 50 min. The analysis of the SAOS data in those sequences together with the values of interfacial tension found enabled the study of the evolution of morphology during steady shear. The results indicated that the diameter of the dispersed droplet within the blend decreased when graphene was added to the blend. Graphene was also shown to reduce the value of interfacial tension between the polymers forming the blends. Upon addition of 1wt% of graphene the interfacial tension reduced from 1.20 mN/m to 0.82 mN/m. The results of shear-induced coalescence also indicated that the presence of graphene prevented some coalescence. All these results indicate that graphene could be a potential compatibilizer for PP/PE blends. Since PE and PP cover a major portion of plastic waste, compatibilization of PE/PP blends by addition of graphene would be interesting to valorize PE/PP mixtures from plastic waste for further application.

Asynchronous Any Time Virtual VP8

Die shape optimization for extrudate swell using feedback control

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Extrusion is a widely used process to create products with a fixed cross-sectional profile. Many applications require cross-sections of complex shapes, where the dies contain sharp corners. Common requirement on the extrudate is dimensional precision. The dimensions of the extrudate are highly influenced by extrudate swelling. The swelling process involves complex dynamics influenced by many parameters, such as viscoelasticity and temperature. Therefore, the optimized shape of a die, to obtain an extrudate with desired dimensions and shape, is now often obtained through trial-and-error.

We developed a transient 3D finite element model, to predict extrudate swelling for extrudates containing sharp edges. This model describes the corner lines of the domain separately to obtain the positions of these lines in the two swell directions. A 2D height function is used to describe the free surfaces of the extrudate, using the positions obtained from solving the material lines to expand the domain of the height function [1].

A novel approach to solve the inverse problem of three-dimensional die design for extrudate swell is developed, using a real-time active feedback control scheme. In this talk we show the validity of this method by showing optimization results for 2D axisymmetric extrusion flows of a viscoelastic fluid for different Weissenberg numbers. Finally, we show that this method is able to obtain the desired extrudate shape in 3D for extrudates of a viscoelastic fluid for different Weissenberg numbers and different amounts of shear-thinning.

[1] M.M.A. Spanjaards, M.A. Hulsen, P.D. Anderson. Journal of Non-Newtonian Fluid Mechanics, 270:79-95, 2019

Asynchronous Any Time Virtual VP9

Capillary extrusion of entangled polymer melts at high stress

Shiwang Cheng, Zipeng Xu, and Ruikun Sun
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Capillary extrusion has been frequently applied to study the flow behavior of highly entangled polymer melts, where the stick-slip and gross melt fracture typically emerge when the applied stress is approaching the plateau modulus, Gpl, of the polymer. In this contribution, we show that the stick-slip and the gross melt fracture can be strongly suppressed or eliminated with properly chosen entangled polymer melts and testing temperatures. In addition to the terminal flow (the region I) and the shear thinning (the region II), two new flow regions (regions III and IV) have been observed at the wall stress, sw, higher than the plateau modulus of the polymer, Gpl. Region III violates the empirical Cox-Merz rule with a significantly weaker shear thinning than region II, and region IV exhibits unexpected shear thickening. Moreover, the crossover shear rates between the regions II and III, ?dot(II,III), and between the regions III and IV, ?dot(III,IV), scale with the number of entanglement per chain, Z=Mw/Me, as ?dot(II,III)/?dot(III,IV)~Z1.4 and ?dot(III,IV)/?dot~Z2.2. The observed scaling highlight the influence of the delayed chain retraction for the high-stress flow of entangled polymers.

Asynchronous Any Time Virtual VP10

Sculpting hydrogels using additive advective processing

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Polymer hydrogels find broad application as advanced functional materials due to their biocompatibility, stimuli responsiveness and affordability. In these materials, crosslinking density reports critical properties such as elasticity, permeability and swelling propensity. Patterning this design parameter across the volume polymerized is an attractive means by which to engineer hydrogel performance. Here, we report a novel processing scheme that uses custom millifluidic devices as 3D printheads to direct the organization of crosslinking density across a single gel. Inspired by techniques used to structure polymeric melts, we design serpentine devices that force disparate streams through splitting, rotation and recombination elements. These elements multiply the incoming macromer concentration field across the cross-sectional area while preserving its relative spacing and orientation. Successful operation of these 'advective assemblers' requires that the advective path trace the contour of curvilinear channels with minimal distortion. Viscoplastic materials are ideally suited for this task: yielding is localized in high-shear regions near the wall, while unyielded, layered streams flow as a stable plug. To prepare a viscoplastic hydrogel ink, we blend poly(ethylene glycol) diacrylate with poly(acrylic acid) microgels. The arrested structure of the microgel suspension dominates ink rheology, allowing flow stability to be tuned independently of macromer concentration. This formulation enables extrusion of hydrogel filaments with laminated concentration distributions, which are subsequently arranged via the 3D printing path and secured via photopolymerization. The sculpted gradients cause the hierarchical gels to swell differentially in water, giving rise to predictable shape changes that persist over tens of centimeters. The unique structures achieved, and the geometrically dictated additive manufacturing principles used to achieve them, provide a new means to engineer hydrogels for various applications.

Asynchronous Any Time Virtual VP11

Extrudate instabilities in fused filament fabrication additive manufacturing

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Extrusion defects and instabilities present in polymer processing have been researched in industry for decades. With the advent of the fused filament fabrication (FFF) additive manufacturing technique, small-scale extruders have become the common polymer processing tool of desktop 3D printers. Despite producing flow rates that are orders of magnitude smaller than industry extrusion lines, these compact extruders are still capable of producing pressure drops up to 5000 psi. High pressures producing small flow rates, when coupled with the filament feedstock typical of FFF extruders as well as a generally unoptimized extruder design, present new exercises in mitigating heat transfer limitations and processing instabilities. Sharkskin, melt fracture, die lines, and die swell are all observed in extrudate from a desktop FFF extruder, their impact on the additive manufacturing process is discussed, and methods of abating these phenomena are investigated.

Asynchronous Any Time Virtual VP12

Molecular view on mechanical reinforcement in polymer nanocomposites: New insights from small-angle neutron scattering

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The microscopic origin of mechanical enhancement in polymer nanocomposite (PNC) melts is investigated through the combination of rheology and small-angle neutron scattering. It is shown that in the absence of an extensive particle network, the molecular deformation of polymer chains dominates the stress response on intermediate time scales. Quantitative analyses of small-angle neutron scattering spectra, however, reveal no enhanced structural anisotropy in the PNCs, compared with the pristine polymers under the same deformation conditions. These results demonstrate that the mechanical reinforcement of PNCs is not due to molecular overstraining, but instead a redistribution of strain field in the polymer matrix, akin to the classical picture of hydrodynamic effect of nanoparticles.

Asynchronous Any Time Virtual VP13

Reprocessable, soft, 3D printable elastomers

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3D printing elastomers enables the fabrication of many technologically important structures and devices such as tissue scaffolds, sensors, actuators, and soft robots. However, conventional 3D printable elastomers are intrinsically stiff; moreover, the process of printing often requires external mechanical support and/or post-treatment. Here, we exploit the self-assembly of a responsive linear-bottlebrush-linear triblock copolymer to create stimuli-reversible, extremely soft, and stretchable elastomers and demonstrate their applicability as inks for in situ direct-write printing 3D structures without the aid of external mechanical support or post-treatment. By developing a procedure for controlled synthesis of such architecturally designed block copolymers, we create elastomers with extensibility up to 600% and Young's moduli down to ~100 Pa, 1,000,000 times softer than plastics and more than 100 times softer than all existing 3D printable elastomers. Moreover, the elastomers are thermostable and remain to be solid up to 180 °C, yet they are 100% solvent-reprocessable. Their extreme softness, stretchability, thermostability, and solvent-reprocessability bode well for future applications.

Asynchronous Any Time Virtual VP14

Probing in-cage particle dynamics in hard sphere glasses with high frequency rheometry

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The cage idea has been widely utilized in colloidal suspensions as a central microscopic concept to describe a number of phenomena related with glassy dynamics. Here we probe the evolution of cage formation and shear elasticity with increasing volume fraction in hard sphere suspensions approaching and well inside the glass regime. Emphasis is given in the short-time dynamics utilizing linear viscoelastic (LVE) measurements by means of conventional rotational rheometers and a home-made high frequency (HF) piezo-rheometer to probe the dynamic response in a very broad range of volume fractions up to the very dense regime in proximity to RCP. We focus on the LVE spectra and on times shorter than those corresponding to the G' plateau, where confinement is maximized. In these short times the caging effect is not evident as the particles cannot fully

explore their cage. This results to the virtual solid to liquid transition at elevated frequencies marked by the HF moduli crossover. On the other hand, caging becomes tighter as volume fraction increases and the in-cage rattling becomes more localized. This shifts the HF crossover to higher frequencies (shorter times). Therefore the study of the dependence of the HF crossover properties (frequency and moduli) on volume fraction provides direct insights of the particle in-cage motion, and allows direct comparison with current theoretical models. We find that the above characteristic HF crossover properties exhibit a two regime nearly exponential dependence on volume fraction. This finding is experimentally robust, and consistent with predictions of the microscopic nonlinear Langevin Equation dynamical theory with highly accurate structural input.

Asynchronous Any Time Virtual VP15

Thixotropy, non-monotonic stress relaxation, and the second law of thermodynamics

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There has been a debate in the literature on whether thixotropic constitutive relations (structural kinetic models) that show enhancement in elastic modulus as a function of time under quiescent conditions violate the second law of thermodynamics. Interestingly there has been a recent experimental observation wherein stress has been observed to undergo non-monotonic change as a function of time under the application of constant strain. In this talk, we shall discuss under what conditions a thixotropic constitutive equation may violate the second law. We shall also carry out the second law analysis of the non-monotonic stress relaxation under constant strain conditions.

Asynchronous Any Time Virtual VP16

Cellulose nano-crystalline (CNC) hydrogels as yield stress fluids (YSFs): Effect of temperature, ultrasonication and concentration

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Cellulose nanocrystals (CNCs) are biodegradable, non-toxic and abundant nanoparticles with a great potential for wide range of industrial applications due to their optical, electrical, tribological, rheological, and several other intriguing properties [1-3]. Under high CNC concentrations, their aqueous suspensions form gels with the characteristics of yield stress fluids. The yield stress is a rheological property used to identify the suitability of semi-solid materials for a wide range of cases such as food industry, 3D printing and pharmaceutical applications [4]. The increasing number of applications developed for using CNC hydrogels, necessitates understanding its yielding behavior. Parameters such as temperature, ultrasonic treatment and particle concentration are important factors while developing CNC hydrogels [5]. The objective of this study is to evaluate the effect of temperature, sonication energy and concentration on yield stress of CNC hydrogels. Using rheometry and different chemical characterization methods, we developed a paradigm predicting the effect of aforementioned parameters on yield stress of CNC gels.

References: 1. Beck, S., Bouchard, J., Berry, R.: Dispersibility in water of dried nanocrystalline cellulose. Biomacromolecules. 13, 1486-1494 (2012) 2. Shariatzadeh, M., Grecov, D.: Tribological properties of Cellulose Nanocrystals aqueous suspensions as water-based lubricants. under Revis. Cellul. (2018) 3. Zakani, B., Grecov, D.: Yield stress analysis of cellulose nanocrystalline gels. Cellulose. (2020). https://doi.org/10.1007/s10570-020-03429-7 4. Grishkewich, N., Mohammed, N., Tang, J., Tam, K.C.: Recent advances in the application of cellulose nanocrystals, (2017) 5. Xu, Y., Atrens, A., Stokes, J.R.: A review of nanocrystalline cellulose suspensions: Rheology, liquid crystal ordering and colloidal phase behaviour, (2020)

Asynchronous Any Time Virtual VP17

Elastic storage during flow of yield stress materials

Manon Marchand[1], Marco Caggioni[2], and Véronique Trappe[1]
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In a recent paper Caggioni et. al. [1] introduced a model to describe the shear rate dependent stress of yield stress fluids as a combination of elastic loading, plastic dissipation and viscous dissipation. This "three-component model" successfully describes data sets previously interpreted in terms of the Herschel-Bulkley [2] model, albeit maintaining physically meaningful fit parameters. Among others, it suggests that the shear rate dependent stress is characterized by two characteristic shear rates, the first denoting the onset to plastic dissipation and the second the onset to viscous dissipation.

In this contribution, we systematically probe the elastic strain recovered after applying a constant shear rate to dispersions of Carbopol microgels in propylene glycol. The recovered strain gives insight on the elastic energy stored at different shear rates, allowing us to identify the suggested transitions to respectively the plastic dissipation and viscous dissipation regimes.

These results corroborate the relevance of the three-component model, which we believe to be an interesting approach to further progress in the understanding of the flow behavior of yield stress fluids.

[1] Caggioni M., Trappe V., Spicer P.T., J. Rheol. 2020, 64:413
[2] Herschel, W.H., Bulkley, R. Kolloid-Zeitschrift 1926, 39, 291-300

Asynchronous Any Time Virtual VP18

Linear viscoelasticity of associating star polymer networks

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We present an analysis of the linear viscoelastic behaviour of associating star polymers using a multi-chain Brownian dynamics simulation algorithm that incorporates hydrodynamic interactions. By attaching functional groups that can reversibly bond at the end of each arm of a four-arm star polymer it is possible to create almost ideal viscoelastic gels. Experimental work by Parada & Zhao [1] has demonstrated that such a system can behave as a simple Maxwell material over a range of pH and temperatures. They propose a microscopic network theory model to explain this behaviour which our simulations can observe directly. Critical to the model is the concentration of elastically-active arms, which determines the instantaneous shear modulus. We analyse microscopic trajectories from Brownian dynamics simulations to independently measure the concentration of elastically-active arms and the resulting shear modulus. The model of Parada & Zhao also shows a dependence of the material's relaxation time on the dissociation rate of the stars. Our algorithm allows us to set the well depth in the associative interactions and measure the bond dissociation rate independently from the relaxation time. Through these observations we validate the model of Parada & Zhao and determine the range of system parameters such as concentration and molecular weight over which the model holds. The linear viscoelastic storage and loss moduli of these networks of stars are also computed dynamically as functions of association strength and concentration and compared with results from experiment.

[1] G. A. Parada, X. Zhao, Soft Matter, 14, 5186-5196 (2018).

Asynchronous Any Time Virtual VP19

Simulation of rhamnolipids

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Rhamnolipids (RLs) are biosurfactants produced by bactria Pseudomonas aeruginosa. They are low cost in production and less toxic compared to synthetic surfactants. Due to their high biodegradability their impact on Environment is less. RLs are reported to be useful in oil water separation , food processing and Antifungal activities. P. aeruginosa strain produces two forms of rhamnolipds known as monorhamnolipid (mRL), consisting of one rhamnose molecule and two -hydroxydecanoic acid molecules, and dirhamnolipid (dRL), where two rhamnose molecules are lined to two molecules of -hydroxydecanoic acid. Indorder to design the dosage of RLs on a commercial scale a molecular level undarstanding of conformations made by them at different temperatures, concentrations and mediums is to be understood. Also interfacial behaviour of RLs need to be computed to study adsorption characteristics. Both monoRL and diRL exhibit Langmuir-like adsorption isotherms at the air-water interface, with saturated area/molecule values of about 60 and 75 A ^{2} respectively. In monoRL/diRL mixtures, there is a strong partitioning of monoRL to the surface and diRL competes less favorably because of the steric or packing constraints of the larger diRL dirhamnose headgroup. Due to larger system size requirement and time scales involved in the process, coarse grained simulations are employed. This study is on both bulk and interface simulations of air-water and decane-water system with monoRLs, diRLs, mixture of mono and di RLs. The formation of different conformations like spherical, cylindrical or lamellar structures are obtained using our simulations at diffrent temperatures The results of this work can be used to optimize a large scale usage of RLs. The dRLs has therapeutic actions and experimental studies shows that they can cause cell wall lysis by specifically targeting lipid bilayers based on membrane tension. This can be made use in cancer treatment. Our coarse grained simulation can give a theoretical input to cytokinesis.

Asynchronous Any Time Virtual VP20

Uses of large amplitude oscillatory shear in food products

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Although large-amplitude oscillatory shear (LAOS) has been used on polymers and other engineering materials for decades, this rheological technique is relatively new to food products. Explorations of LAOS in food products to date have shown some promise in connecting food LAOS behaviors to food microstructural features, such as the development of the gluten network in bread doughs and the breakdown of food foams. LAOS behaviors have also been related to food processing behaviors (e.g. the effect of mixing on dough) and sensory attributes (e.g. fracturability, first-bite firmness), but much more work remains to be done to understand if and how food LAOS behaviors can be used to indicate sensory attributes. However, the use of LAOS in foods has multiple challenges, including a lack of a standard analysis method, a lack of a database that encompasses the wide variety of food products, and the general lack of advanced rheological knowledge in food science arenas. Overall, LAOS may be a useful tool for food rheologists, but significant work is required to understand how food LAOS behaviors are generated from microstructural features, and how these behaviors relate to food texture.

Asynchronous Any Time Virtual VP21

An application of lubrication theory for the flow of liquid crystals in a slider bearing

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Liquid Crystals (LCs) are anisotropic viscoelastic materials; the combination of fluid-like flow with crystal-like anisotropy makes its phases interesting as modifiers of interfacial behavior when applied as lubricants. The ability of liquid crystalline materials to form ordered boundary layers with good load-carrying capacity, and to lower the friction coefficients, wear rates and contact temperatures of sliding surfaces, thus contributing to increase the components service life and save energy has been widely demonstrated. The objective of this research is to study the lubrication with nematic LCs through modeling and numerical simulations. Using a second-order tensor to denote evolution of the structure of LC materials, the Landau-de Gennes theory (LdG) could be used to model the flow of LCs. In this study, lubrication theory is applied to a fixed-incline slider bearing to simplify the complex governing partial differential equations in the LdG theory. The coupled system of modified Navier-Stokes equations with stress tensors modelling the viscoelasticity and anisotropy of LCs and the partial differential equations in the LdG theory was solved numerically in COMSOL Multiphysics. The simplified LdG equations due to lubrication approximation coupled with the Navier-Stokes equations were solved numerically in COMSOL Multiphysics as well. It was found that in very thin gaps, the pressure distribution from the simplified LdG model is consistent with that from the full LdG model. In addition, the load carrying capacity and coefficient of friction (COF) were calculated for both the simplified and the full LdG models at various gap sizes. Moreover, a hypothetical Newtonian fluid was chosen for comparison. It was found that the slider bearing with LCs as lubricants have better lubrication performance than the one using a Newtonian fluid as lubricant.

Asynchronous Any Time Virtual VP22

The impact of multiple fluids on the purely-elastic instabilities that arise in a microfluidic flow focusing device

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Microfluidic flow focusing devices operate by having two opposing lateral streams that shape a third central inlet stream, producing a strong extensional flow near the centre of the geometry. Purely elastic flow instabilities have been observed in past research in this type of device (Oliveira et al. 2009, Oliveira et al. 2011), with three distinct flow regimes that depend on both the Weissenberg number (Wi) and the inlet velocity ratios (VR). At low Wi, the flow remains steady and symmetric about the geometry centreline. As the Wi is increased beyond a critical value, while maintaining a low VR, the flow transitions directly to a time-dependent flow. For moderate to high VR, two transitions were found when Wi was increased: a first transition to steady asymmetric flow and a second at higher Wi to time-dependent flow. These instabilities have been shown to arise in the absence of inertia due to high streamline curvature and large normal stress differences in accordance with the Pakdel-McKinley criterion (McKinley et al. 1996). To date, work has been limited to single-fluid flows however, here we experimentally demonstrate the impact when different fluid streams are involved i.e., introducing a Newtonian fluid alongside a dilute viscoelastic fluid. 3D microfluidic flow focusing channels produced by soft-lithography along with fluorescence microscopy for flow visualisation were used to investigate two additional fluid configurations: one where the central fluid stream is Newtonian (N) and the fluid in the lateral streams is viscoelastic (VE), and vice versa. The observed flow instabilities were of a similar nature to that of the single-fluid case. Interestingly our findings show no significant change in the critical Wi for the transition to steady asymmetric flow for the various configurations, but placing the Newtonian fluid in the lateral streams delayed the transition to time dependent flow, suggesting that these elastic instabilities cannot be solely related to the extensional flow.

Asynchronous Any Time Virtual VP23

Characterizing the linear viscoelastic behavior of bimodal polyethylene using their continuous relaxation spectra

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The relaxation mechanisms occurring within a polymer melt are observed by characterizing its mechanical properties in the linear viscoelastic region. The relaxation spectrum helps reveal linear viscoelastic behaviors that otherwise would not be observed by a direct plot of experimental data such as the creep compliance. In this research, molten bimodal polyethylene with improved end-use properties have been characterized in the linear viscoelastic region. Small amplitude oscillatory shear and creep experiments were combined; with the dynamic data providing useful information on the relaxation process at shorter time scale while the creep data provided information at longer time scale. This method has helped us access very long relaxation time that were otherwise inaccessible by using only dynamic data. Our results allow us to evaluate models relation LVE and MWD in the case of bimodal MWD.

Asynchronous Any Time Virtual VP24

Molecular origin of rheological and mechanical properties of well-defined polystyrene POM-POM model systems

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The correlation of molecular and rheological/mechanical properties is one of the key challenges of polymer science. A series of Polystyrene (PS) based model systems with a well-defined POM-POM topology is synthesized by a newly proposed combination of anionic polymerization technique and grafting-onto method to correlate molecular and rheological and mechanical properties. The influence of the three main topological parameters, (I) the distance between the two stars / POMs, $M_{W,BB}$, (II) the number of side chains per POM, n_{Sc}, and (III) their molecular weight, $M_{W,Sc}$, is investigated. Shear and extensional rheological data of these POM-POMs were investigated in the framework of zero shear viscosity ($?_0$) and strain hardening factor (SHF) and correlated with the molecular structure. Experiments revealed that especially $M_{W,Sc}$ has drastic influences of the rheology as well as mechanics, e.g. stretches for high $M_{W,Sc}$ the rubbery regime for a similar backbone up to 8 decades, and drastically increases the zero shear viscosity by over a factor of 500 compared to the sidechain. For high $M_{W,Sc}$, in the terminal regime, G' and G'' are parallel with a constant slope of around 0.6. In extensional rheology, for POM-POM PS with $M_{W,Sc}$ around one entanglement molecular weight, 1 M_e, the highest strain hardening with SHF above 100 could be observed. Moreover, for high $M_{W,Sc}$ the POM-POM topology highly improved the fatigue lifetime of polymers of up to a factor of 5, compared with the linear sidechain with similar molecular weight. The results are compared with model PS combs and stars, as well as with rheological models, such as the MFS and the POM-POM model.

Asynchronous Any Time Virtual VP25

The role of hydrodynamics in flowing semidilute solutions of ring/linear polymer blends

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It is important to understand the dynamics of semidilute polymer solutions at a molecular level, because out-of-equilibrium polymer conformations that arise due to strong processing flows can impact both rheology and eventual material properties in a variety of applications. Despite this practical importance, it remains a challenge to predict how concentration, flow, hydrodynamic interactions (HI) and architecture all govern the dynamics of semidilute polymer solutions. This is particularly true in simulation, where it is computationally expensive to include long-range HI effects that are necessary to accurately model the dynamics of polymer solutions, both in and out-of-equilibrium. We developed an iterative conformational-averaging (CA) method for performing these calculations, circumventing computational bottlenecks to enable the large-scale simulation of polymer solutions in flow. CA calculations demonstrate the importance of HI in semidilute solutions, revealing the effect of 'local hydrodynamics' that enhance conformational fluctuations in planar elongational flows. We demonstrate these effects in the context of ring/linear blends, where there is a competition between topological 'hooking' and chain length effects that showcase the complicated role of polymer architecture in conformational dynamics during both startup and steady-state flows.

Asynchronous Any Time Virtual VP26

Rheology of semiflexible polymers in shear flow via Brownian dynamics and quasi-two-parameter theory

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Even in dilute solutions, quantitatively predicting the shear rheology of semiflexible polymers using parameter-free methods is to date not possible for arbitrary chemical structures and sufficiently large molecular weights. For example, even for a model polymer such as DNA in excess salt, it is not possible to accurately predict the shear-thinning exponent for a particular molecular weight [1].Part of this difficulty arises due to the nature of the coarse-grained bead-spring or bead-rod approximations used to model the polymer molecule, which often give different predictions depending on the details of spring force laws, how hydrodynamic interactions or excluded volume effects are introduced, and whether bending or torsional potentials are used [2,3]. Here we propose a coarse-graining scheme which is consistent with the quasi-two-parameter theory for treating excluded volume effects in dilute solutions of semiflexible polymers [4]. We use a spring force law which can mimic both a traditional FENE spring as well as a rigid rod [5,6], along with a bending potential to account for semiflexiblity. This scheme allows for consistent modelling of a variety of polymer types and molecular weights, shedding light on how this variety affects rheology in shear flow.

[1] S. Pan, D. A. Nguyen, B. Dunweg, P. Sunthar, T. Sridhar, J. Ravi Prakash, J. Rheol. 62 (2018) 845-867
[2] I. S. Dalal, C. Hsieh, A. Albaugh, R. G. Larson, AIChE Journal 60 (2014) 1400-1412.
[3] A. Saadat, B. Khomami, J. Chem. Phys 145 (2016) 204902.
[4] H. Yamakawa, Helical wormlike chains in polymer solutions, 2nd ed., Heidelberg Springer,2016.
[5] I. Pincus, A. Rodger, J. R. Prakash, J. Non-Newtonian Fluid Mech. 285 (2020) 104395.
[6] C. Hsieh, S. Jain, R. G. Larson, J. Chem. Phys 124 (2006) 044911

Asynchronous Any Time Virtual VP27

A two-species model for the rheology of associative polymer solutions from nonequilibrium thermodynamics

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At sufficiently large concentrations, the reversible association of associative polymers in solution leads to the formation of micelles that above a critical concentration percolate to form a reversible network. Developing transport equations to describe the viscoelasticity of reversibly-crosslinked networks has attracted the interest of researchers already since the 1940s, with several important rheological models having been proposed over the years, mostly on the basis of separate contributions from bridges and (temporary) dangling chains.1, 2 In the present work,3 we report an alternative derivation of such two-species models for associative polymers guided by principles of nonequilibrium thermodynamics. For a direct comparison with existing models, we make use of the same state variables as in previous works (number density and average conformation of bridges and dangling chains). Creation of bridging chains from dangling ones or detachment of bridges to form dangling chains is dealt with through a set of attachment/detachment reactions.4 Flow effects on these rates in our model arise naturally, thus completely avoiding the need to invoke specific expressions based on theoretical arguments or intuition. We find that, although the final set of evolution equations are similar to those of earlier models based on network kinetic theory, nonequilibrium thermodynamics sets specific constraints on the form of the attachment/detachment rates, which in some cases deviate significantly from previously reported ones. We also carry out a detailed analysis demonstrating the capability of the new model to describe various sets of rheological data for solutions of associative polymers.

References: 1. F. Tanaka and S.F. Edwards, Macromolecules 25, 1516 (1992). 2. A. Tripathi, K.C. Tam, and G.H. McKinley, Macromolecules 39, 1981 (2006). 3. P.S. Stephanou, I.Ch. Tsimouri, and V.G. Mavrantzas, J. Rheology 64, 1003-1016 (2020). 4. N. Germann, L.P. Cook, and A.N. Beris, J. Non-Newton. Fluid Mech. 196, 51 (2013).

Asynchronous Any Time Virtual VP28

Charge screening effects on the rheology of polymerized ionic liquid solutions in the semidilute unentangled regime

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Polymerized ionic liquids (PILs) are a new class of polyelectrolytes with ionic liquid (IL) structures on their repeating units. The viscoelastic properties of PILs in IL solutions can be affected by the charge screening of PIL chains by IL ions. However, the effect of IL charge screening on the viscoelasticity of PIL solutions has not been well understood yet, especially at high IL concentrations where the classical Debye-Hückel (DH) theory becomes inapplicable. In this work, we aim to understand the effect of the ionic correlation on the rheology of PIL in IL solutions in the semidilute unentangled (SU) polymer regime. We conduct detailed rheological characterization of an imidazolium-based PIL (PC4-TFSI) in a mixture of salt-free solvent (DMF) and an IL (Bmim-TFSI) possessing a similar ionic structure to that of the PIL repeating unit. The specific viscosity (η_{sp}) of PC4-TFSI solutions is measured at varying IL concentrations (c_{IL}) while keeping the polymer concentration fixed. We find that: i) η_{sp} remains as a constant at low c_{IL}; (ii) η_{sp} decreases with increasing c_{IL} at an intermediate c_{IL}, in good agreement with the behavior of ordinary polyelectrolytes attributed to the DH screening at low salt concentrations; (iii) η_{sp} increases at $c_{IL}>1$ M. We have captured the observed trend of η_{sp} versus c_{IL} by proposing and validating a new charge screening model which accounts for the modified screening length and complete charge screening at high IL concentrations. Our model suggests that extended PIL chains initially shrink due to the conventional charge screening effect at low IL concentrations, but revert to expanded configuration at higher IL concentrations due to strong ionic correlations.

Asynchronous Any Time Virtual VP30

Melt rupture and wall slip of metallocene-catalyzed bimodal molecular weight distribution polyethylene under simple shear

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Apparent slip occurs in the flow of linear polyethylene melts over a high surface energy wall changing both the velocity profile and the stress. The slip behavior of bimodal molecular weight distribution (MWD) resins has found to be different from that of unimodal resins and is not yet fully understood. There is a systemic change in MWD of the four resins that are used in this study which make it possible to study the effect of short and long chains on the slip behaviour. The no-slip behavior was measured using a stress-controlled rotational rheometer by conducting small amplitude oscillatory shear (SAOS) tests at 190 °C in the frequency range of 0.01-500 rad/s and assuming the Cox-Merz relationship. A sliding plate rheometer (SPR) was used to study the slip behaviour of bimodal polyethylene resins in simple shear. The SPR tests were conducted at 190 °C and various nominal shear rates to measure the shear stress in the presence of slip. The results show that slip occurs over a broad range of stress. The amount of short chains strongly affects the slip behaviour of these materials. The higher the short chain content, the lower is the stress at which slip is observed in our experiments. The presence of short chains affects the slip behaviour at all stresses within the transition region before strong slip is fully developed. In the stress region where strong slip is fully developed, the slip behaviour is independent of MWD. During

the slip experiments it became obvious that melt rupture was also occurring and therefore we visually studied this aspect of the flow behavior using a glass plate as the stationary plate. The time to rupture at various stresses was also determined from the transient stress curves. The visual studies show that all materials undergo melt rupture after slipping. The amount of short chains also significantly affects the stress at which melt rupture happens in the experiments.

Asynchronous Any Time Virtual VP31

Unravelling the transient network topology of hydrophobically associating multiblock copolymers and their resulting elasticity and relaxation times

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Hydrophobically associating block copolymers are interesting materials for the design of physical hydrogels, and are often studied to gain fundamental understanding of transient polymer networks. In this contribution, linear rheology and small-angle X-ray scattering (SAXS) are combined to unravel the concentration dependent elasticity and relaxation dynamics of these networks. Whereas most studies use telechelic triblock copolymers as model systems, our study focuses on alternating multiblock copolymers having hydrophobic blocks distributed along the chain, thereby complicating their network behavior. Our experimental rheological data are compared to the predictions of a generalized transient network model, which we developed by adapting Annable's mechano-statistical model for telechelic triblock copolymers [1,2] to more general multiblock copolymers, based on a combinatorics approach. The spatial distribution of hydrophobic nodes as inferred from SAXS, is used as input for our transient network model to improve its descriptive strength. The evolution of the high-frequency plateau modulus and hence the elasticity with concentration hints towards a change in network topology upon increasing concentration. The structure evolves from loop-dominated with limited elasticity at low concentrations to bridge-dominated and highly elastic at higher concentrations. The concentration dependence of the relaxation times, on the other hand, reveals the importance of superstructures such as superbridges and superloops, on the sticky Rouse-like relaxation dynamics of the network. A thorough understanding of the network topology and its effect on the rheological properties of the network, should pave the way for the development of transient networks with designed elasticity and relaxation spectra.

[1] T. Annable et al., Journal of Rheology, 1993, 37, 695
[2] T. Annable et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1996, 112, 97

Asynchronous Any Time Virtual VP32

Photopolymerization of methacrylate: From conversion via rheology to mechanical properties

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Stereolithography is an additive manufacturing process in which products are built layer-by-layer from a photo-curable liquid. Typically, the mechanical properties of the 3D-printed product are affected by material heterogeneity along the sample thickness. To study the effect of process conditions on the material properties without sample heterogeneity, single layers of a UV-curable polymer are characterized [1]. Whereas our earlier work showed that the resin formulation significantly affects the network formation [2], our present work focusses on the effects of processing conditions. First, the evolution of monomer conversion with irradiation time is studied by means of FTIR spectroscopy. A model is developed based on the reaction kinetics of photopolymerization that describes the experimental data and predicts the effects of initiator concentration and light intensity on monomer conversion with reasonable accuracy [3]. This model is then used to analyze the effects of pulsed irradiation on the curing kinetics, a phenomenon which is highly relevant when 3D printing multiple layers. The network development during photopolymerization, under various conditions of light intensity, pulse duration and dark time is monitored via oscillatory rheology with in-situ UV illumination. Pulsed irradiation clearly affects the curing kinetics while the final network modulus is rather insensitive to the dark time. Finally, the relations between UV illumination and ultimate network characteristics such as glass transition temperature Tg and yield stress are investigated. Although Tg is uniquely related to conversion, independent of light intensity and curing time, such a relation is not present for the yield stress. Moreover, the yield stress is not uniquely related to the distance to Tg. This indicates that the generated polymeric network microstructure depends on the processing conditions.

[1] Anastasio et al. Polymer 2018 [2] Anastasio et al. J. Appl. Polym. Sci. 2020 [3] Anastasio et al. Macromolecules 2019

Asynchronous Any Time Virtual VP33

Understanding the morphology and self-stratification in multiphase polymer colloidal films

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Latexes (polymer colloids) are frequently used in household paints and varnishes, pressure-sensitive adhesives, textile and carpet backings, paper coatings, inks and gloves etc. While the structure and morphology evolution of a homogenous latex film is well understood, polymer nanocomposite films made from, for example, mixture of latexes or multiphase latexes are still a topic of intensive research. In this work, we study composite latexes to optimize them for self-stratified films, which provide strong adhesion with the substrate and water repellency (or any other desired property) at the air-film interface simultaneously. We tested two multiphase latexes, both comprising of a weakly entangled acrylic component and a strongly entangled acrylic-silicone copolymer, but having different particle morphologies: blend-like mixture of two latexes, and core-shell morphology with acrylic-silicone cores. A confident assessment of the morphology of composite films and the underlying mechanisms required complementary data from different techniques at various stages of drying: Cryo-TEM, rheology, microscopy, SIMS, SAXS and XPS etc. We observe that the morphology of a multiphase latex film is kinetically controlled, and at room temperature (~ Tg +14°C) the large Mw acrylic-silicone cores are embedded in the lower Mw acrylic matrix for both latexes. However, drying at elevated temperatures (~Tg +60°C) results in very distinct morphologies for the two systems. While the core-shell system remains unchanged with heat ageing, the blend-like system results in coalescence of acrylic-silicone domains within the acrylic matrix although an ideal self-stratification with two distinct layers is not observed. Future directions include studying multiphase latexes with both phases comprising of unentangled polymers, and with larger surface energy difference between them. Our work provides a robust toolbox and strategies for studying complex latexes, and fundamental insights into the development of new smart coating formulations.

Asynchronous Any Time Virtual VP34

Protocol-agnostic material functions and more accurate flow diagnostics based on recoverable strain measurements

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Recent studies have shown that rheological material functions that can be linked to structural measures are defined in terms of the recoverable and unrecoverable strains [for example, Lee et al., Phys. Rev. Lett. 122, 248003 (2019)]. In this study, we explore the consequences of applying these ideas to transient nonlinear rheological tests, using new material functions including an elastic modulus and a flow viscosity defined in terms of the recoverable strain and the rate of acquisition of unrecoverable strain, respectively. These material functions, based on recoverable and unrecoverable strains (rather than total strain), are defined in the same way independent of the test protocol and provide the viscoelastic properties of a material in a clear and succinct way without requiring a priori knowledge of the constitutive model. At short times, we observe that for a self-assembled wormlike micellar solution, the new material functions exhibit a constant (plateau) modulus and a constant (zero-shear) viscosity independent of the applied shear rate, even under conditions that eventually lead to nonlinear responses. This observation quantitatively corroborates the intuitive picture of material deformation that when the material is close to equilibrium, it responds according to its linear viscoelastic material properties for both linear and nonlinear deformations. The fundamental, universal, and unifying nature of these new transient measures are showing promise in explaining a range of phenomena, including the Payne effect for filled polymers and yield stress materials [Donley et al., PNAS, 202003869 (2020)], as well as suggesting new improved dimensionless groups for more accurate flow diagnosis [Singh et al, J. Rheol. 65, 129 (2021)]. This work lays the foundation for measuring material functions that are directly related to the material structure and are agnostic of the testing protocol.

Asynchronous Any Time Virtual VP35

On simultaneous fitting of nonlinear and linear rheology data: Preventing a false sense of certainty

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Model parameter estimates and their uncertainties change depending on the fitting method used, yet proper uncertainty quantification is critical when fitting constitutive models for either inferring molecular information or for flow predictions. Here we study and compare sequential (two-step) versus simultaneous (all at once) fitting methods with linear and weakly-nonlinear rheological data. Using an example of a combined dataset on small-amplitude oscillatory shear (SAOS) and medium-amplitude oscillatory shear (MAOS) for a linear entangled polymer melt (cis-1,4-polyisoprene), we demonstrate with a multi-mode Giesekus model how the fit parameter uncertainties are significantly under-estimated with the sequential fit because of the neglect of model parameter correlations. These results are somewhat surprising given the combination of linear and weakly nonlinear data because one might expect linear data to dominate and result in minimal differences between sequential and simultaneous

fitting. The multi-mode model admits low-dimensional average measures in terms of moments of the spectra, and here we derive meaningful average measures of the mobility parameter spectrum of the Giesekus model. These average metrics can show similar uncertainty estimates for sequential and simultaneous fitting with this particular dataset, which we quantify. Our results reveal the importance of using simultaneous fitting for material property inference, even with weakly-nonlinear data.

Asynchronous Any Time Virtual VP36

Impact of various environmental chemical conditions on the rheological behaviour of a system of mixed clay gels using response surface methodology

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Many chemical parameters have to be taken into account when formulating a product as they can impact its rheological behaviour. The rheological properties of a product will depend on several factors: the nature of the active ingredient, the type of surfactant used, the pH of the solution, and so on. Processing conditions such as temperature can also play a role. Taking all this into account adequate thickeners need to be found to form a gel with the right properties. However, industrially it is more convenient to use the same thickeners for different final products through adjusting their concentration, such that the final rheological properties of the product meet the consumer's expectations. Hence, predicting some properties of the product according to its chemical environment can be very useful in product design.

In this work, we study the effect of surfactant addition, ionic strength and pH on the rheological properties of a clay gel made of a laponite-bentonite clay mixture. We focus on different rheological properties of the gel at rest such as the storage modulus (G'), the critical stress (σ_c) and flowing properties such as the yield stress (σ_{ys}) and the flow index (n) given by the Herschel Bulkley model. We use response surface methodology in order to quantify the impact of each term on the characteristics of the network. We utilise a mixture design with one process factor where Tween 20, $MgCl_2$ and water were the mixture components and the pH was the process factor. We fit our data with a full cubic Scheffé model and use an "I-optimal" design to generate the experimental matrix. Such models allow us to predict the different responses to some extent, to quantify or determine the effect of each parameter and of their interactions on the gel.

Asynchronous Any Time Virtual VP37

Relating photovoltaic module stresses to encapsulant thermomechanics

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Photovoltaic module durability and lifetime are often determined by relationships between packaging designs and exposure to stresses in the environment such as wind loads and temperature. Module housings often include a cover glass, polymer encapsulant layer, solar cells, and a filled polymer backsheet layer that combine elements of dissimilar thermal expansion coefficients and polymer aging, stress relaxation, water swelling, and crystallinity. This work summarizes an experimental and computational effort to develop a multi-scale understanding of the mechanical stresses in PV modules that lead to degradation and damage.

Here, we characterize the viscoelasticity of two common encapsulants, poly(ethylene-vinyl acetate) (EVA) and polyolefin elastomer (POE), and their thermomechanical behavior dry and as exposed to water. Crosslinking extents during manufacturing were tracked through differential scanning calorimetry, and encapsulant complex moduli were studied using dynamic mechanical analysis and rheometry. The resultant constitutive models are utilized in a finite element model to predict stress states and likely failure points in typical PV modules as exposed to thermal and humidity cycles. To validate computational predictions, full-scale PV modules were instrumented with strain gauges and subjected to mechanical loads that approximate snow weight or wind pressures. The measured deflections matched well with model predictions, and confirmed a measurable viscoelastic relaxation effect on the cells. The resulting computational model is expected to be invaluable for producing modules with reduced packaging costs and improved field robustness.

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Asynchronous Any Time Virtual VP38

Extensional rheology and pinching dynamics of associative polysaccharide solutions

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Coating formulations often exhibit complex rheological behavior due to the contributions and interactions of dissolved polymers, pigments, and particles. Understanding the response extensional flows of such non-Newtonian fluids is critical to the performance of coatings, in spraying, jetting and rolling applications, where streamwise velocity gradients spontaneously arise in pinching necks. Associative polysaccharides are widely used as rheology modifiers in industrial aqueous-based formulations. In this talk, we contrast the shear and extensional rheology response of hydrophobically-modified hydroxyethyl cellulose (hmHEC, Mw = 300 kg/mol) as a sticky polymer with the bare chain of a higher molecular weight HEC (Mw = 720 kg/mol) via Dripping-onto-Substrate (DoS) rheometry protocols. We show that sticker associations enhance zero shear viscosity and relaxation time (elasticity), and both quantities display stronger concentration-dependent variation for sticky polymers. Striking differences are observed in neck shapes, radius evolution profiles, and extensional viscosity plotted as a function of strain as well as strain rate. We present a comprehensive analysis of changes in pinching dynamics, concentration-dependent variation in steady, terminal viscosity as well as filament lifespan as a function of concentration for the sticky polymer and describe the influence of multiple stickers on the macromolecular strain, relaxation, and dynamics of associative polysaccharides.

Asynchronous Any Time Virtual VP39

Calculation method for the relaxation time spectra of viscoelastic fluids using dynamic moduli

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The influence of different error functions (standard deviation, normalized standard deviation, and chi-square) as objective functions in the calculation of the relaxation time spectrum is studied, as well as the influence of different minimization procedures available in MATLAB (fmincon, fminimax, and patternsearch). Dynamic moduli were used to calculate the spectrum, which implies a well-known ill-posed problem, solved by simultaneously minimizing the regularized error function and a restriction function. The proposed regularization is based on the Tikhonov regularization, with a second differential of the spectrum as the operator, and with an optimal regularization parameter, generated using a modified L Curve. The method was validated by calculating three spectra: two taken from the literature and one simulated, with results in agreement with the expectations. A new way of comparing the different procedures used is proposed, which involves the calculation of the mean between the resulting spectra, and its subsequent use as initial point in the different minimizations studied until some convergence is achieved. Finally, the results show that the best objective function studied is the normalized standard deviation and that the best minimization procedure in most cases is the fmincon.

Asynchronous Any Time Virtual VP40

The rheology of methane and carbon dioxide hydrates at extreme high pressures

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Gas hydrates have been an active research topic due to their occurrence in the oil and gas industry. As a result, much of the body of knowledge focuses on water-in-oil emulsion gas hydrate systems. Recently, however, technologies that take advantage of gas hydrate properties have sparked new research motivation. Most of these technologies require flow systems and do not involve oil-based systems. Based on these facts, the need for the characterization and elucidation of the shear rheology of gas hydrate systems from pure water systems is apparent. This study explores pure water hydrate systems of methane (CH4) and carbon dioxide (CO2) at pressures between 0 and 30 MPag. The viscosity of the system was measured at a constant shear rate and at temperatures between 0 and 10?. The effect of temperature on the viscosity of CH4 hydrate systems was one order of magnitude larger than the pressure effect on viscosity in most of the pressure range. The pressure effect on the viscosity of CO2 hydrate systems was up to one order of magnitude larger than that of the CH4 hydrate system, likely as there was more gas present in solution due to CO2's higher solubility in water. The time to reach maximum viscosity in CH4 hydrate systems was found to decrease by at least a factor of two as pressure increased from 10 to 15 MPag. Several systems with high driving forces for hydrate formation did not form gas hydrates within the 24-hour timeframe. These driving forces were up to 4.1 MPag and 2.07 MPag for the CH4 and CO2 systems, respectively. The key system limitations to the formation of hydrates were categorized as either arising from kinetic, diffusion, and/or heat effects. The presented data and analysis are a significant contribution to the currently sparse characterization of high pressure-low temperature shear rheology of these energy materials, which is crucial to the design and development of new technologies that make use of gas hydrate properties.

Asynchronous Any Time Virtual VP41

Interplay of inertia and stress diffusion in shear flows of viscoelastic fluids

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Steady-state shear banding is an instability of shear flows attributed to the inherent non-monotonic constitutive curve of the fluid. The flow curve obtained experimentally shows a unique stress selection from a region that excludes the non-monotonic region in the constitutive curve. This degeneracy has been solved using a stress or strain rate diffusion coefficient in the constitutive equations. In this work, we analyse the effect of inertia on unique stress selection in the presence of stress diffusion coefficient using the Johnson-Segalman and Giesekus models. We study step-up and step-down shear flows with the shear rate in the monotonic and non-monotonic regions of the flow curve in order to relate unique stress selection to the presence of inertia.

Asynchronous Any Time Virtual VP42

Effect of MW, concentration and anionicity on the linear and non-linear viscoelastic properties of high performance EOR polymers

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Abstract: Several efforts were made in recent time to synthesize stable polymers for high temperature, high salinity polymer enhanced oil recovery (EOR) applications. One such polymers that were reported to have high stability is the ter polymers synthesized using the combination of acrylamide (AM), acrylamide tertiary butyl sulfonic acid (ATBS) and n-vinyl pyrrolidone (NVP). Rheology plays a crucial role in polymer EOR, and several recent studies have highlighted that the significant role that polymer non-linear viscoelasticity has on oil recovery applications. However, most of the bulk shear rheometry studies targeted to quantify the polymer's viscoelasticity were conducted in the linear viscoelastic regime (LVE). In this work, an attempt is made to study and compare the effect of molecular weight, concentration and anionicity on the linear and non-linear viscoelastic properties of the high performance EOR polymer. Initially, LVE regime is determined for all the samples at harsh conditions and the subsequent amplitude sweep test are conducted at both LVE and non-LVE region to determine the oscillatory relaxation time. Among the three variables, an increase in molecular weight appears to reduce the relaxation time significantly when conducted in non-linear viscoelastic regime. The key conclusion from this paper is that when characterizing the polymer for EOR applications, both linear and non-linear viscoelastic properties should be considered.

Asynchronous Any Time Virtual VP43

The effect of rheological properties on pyroelectrodynamic jets

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Abstract A liquid can be induced to emit thin fluid jets when it is subject to a sufficiently strong electric field [1]. Such behavior has both fundamental and practical implications, from raindrops in thunderclouds to pendant drops in electrospray mass spectrometry or microdroplets in inkjet printing technology [2]. The frequency of the jets and the meniscus shape during jetting are affected significantly by the rheological properties of the fluid [3]. However, their effect is not yet fully understood in literature. Herein, we use the pyroelectric effect of a polar dielectric crystal as source of a high intensity electric field, and we study the effect of fluid viscosity on the jetting phenomenon. The use of the pyro-electrodynamics has some advantages in comparison to standard electrodynamics. In particular, the experimental setup can be extremely simplified, being electrode-less and nozzle-less, and, moreover, the amount of material needed in this configuration is very small (in the order of micrograms or nanolitres). In the current work we investigated the effect of the fluid viscosity on the pyro-electrodynamic jetting using a custom-made rheological setup. The results of an extensive experimental campaign show that the number of jets per unit time is a function of fluid viscosity, ceteris paribus. These findings allow us to use our compact setup to measure the viscosity using only micrograms of material and, rapidly, by means of a calibration curve.

References [1] Collins, R. T., Jones, J. J., Harris, M. T., & Basaran, O. A. (2008). Electrohydrodynamic tip streaming and emission of charged drops from liquid cones. Nature Physics, 4(2), 149-154. [2] Gennari, O., Battista, L., Silva, B., Grilli, S., Miccio, L., Vespini, V., Coppola, S., Orlando, P., Aprin, L., Slangen, P. and Ferraro, P., (2015). Investigation on cone jetting regimes of liquid droplets subjected to pyroelectric fields induced by laser blasts. Applied Physics Letters, 106(5), p.054103. [3] Ferraro, P., Coppola, S., Grilli, S., Paturzo, M., & V

Asynchronous Any Time Virtual VP44

Koopman with control for constitutive law identification

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Determining the constitutive law experimentally typically involves subjecting the material to a prescribed deformation and measuring the force required to achieve it. The decision on which constitutive law to fit to the resulting data is then based on the rheologist's knowledge about the fluid in relation to the catalogue of standard models appearing in the literature. In this talk, we present an alternative approach based on the application of Koopman operator theory and Dynamic Mode Decomposition (DMD) in the context of control to extract material parameters that arise in stress-evolution equations of viscoelastic fluids directly from data. We will present results from various tests of the framework that highlight its accuracy in identifying material parameters, as well as its robustness to measurement noise. We will discuss the choice of datasets, but also demonstrate how data from multiple experiments can be combined to improve resolution. Finally, we will show that our approach provides a natural way to utilise data from the nonlinear regime, and extends to higher-dimensional data sets where spatial data within a sample might be available.

Asynchronous Any Time Virtual VP45

Development of a lab simulation process to evaluate melt fracture of underwater pelletized polymer

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Newer generation polyethylene products are improved in performance over traditional grades by a combination of structure design strategies including lower levels of long chain branching (LCB), increasing molecular weight (MW), or narrowing molecular weight distribution. All these strategies tend to increase production challenges, especially the risk of severe pellet melt fracture (PMF). Conventional critical shear stress analysis has proved to be ambiguous to identify resins that could exhibit severe melt fracture in the underwater pelletization process used in commercial manufacturing conditions. As a result, a lab simulation approach was developed. This approach involves 1) the development of a lab extruder with underwater pelletizer setup that operates at relevant conditions to replicate pellets as made on commercial production lines and 2) a Laser confocal Scanning Microscope (LSM) analysis to measure the roughness of the pellets and thus quantify PMF. The combination of these two technologies provided a workflow to predict PMF of new product designs to be produced in commercial production plants. Furthermore, the workflow can be used to make recommendations to mitigate PMF through material design and appropriate polymer processing aid (PPA) technology. This study describes the validation of a designed simulation workflow and its capability to replicate pellets made in commercial production using two commercial polymers that represent the typical upper and lower end of melt fracture situations expected.

Asynchronous Any Time Virtual VP46

Advances in rheo-optical methods

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Simultaneous use of rheological and optical techniques, i.e. of rheo-optical methods, is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. In this paper, new rheo-optical techniques as well as new applications of existing methods are reported. Microscopy and rheo-confocal microscopy provide direct visualization of material under flow. A combination of microscopy techniques with a dual motor rheometer in counter-rotation mode allows the observation of structures at the stagnation line. A rheo polarized imaging techniques called SIPLI (shear induced polarization light imaging) combines a visualization technique with measurements of local stresses through the detection of the birefringence. By employing parallel-plate geometries, different shear rates are present throughout the sample, from a maximum shear rate at edge of the sample to a zero shear rate in the center of the plate. With SIPLI the whole plate is observed and the birefringence can be displayed over the full range of shear rates within one single experiment. Applications include structure alignments and shear induced phase transitions of different materials such as block copolymers, nano-crystalline cellulose, and polymer melts. Spectroscopic techniques such as IR or Raman are used for detecting chemical change during curing reactions or conformational changes during phase transitions. The phase transition from the crystalline to liquid state for different polymers was monitored by rheo-Raman spectroscopy. Special emphasis has been given to an accurate temperature control over a large temperature range in order to take full advantage of the potential of the various rheo-optical techniques.

Asynchronous Any Time Virtual VP47

Non-linear transient stretching and relaxation of highly deformed vesicles reveals a deflation-dependent bending modulus

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Vesicles are membrane-bound soft containers that play a key role in biological processes. In this talk, we present new results on the non-equilibrium stretching and relaxation dynamics of phospholipid vesicles in precisely defined flows. Automated flow control (via a Stokes trap) is used to expose freely suspended vesicles to precisely controlled, time-dependent strain rate schedules in flow. In this way, we directly observe non-equilibrium vesicle shapes as a function of reduced volume, viscosity contrast, and Capillary number using fluorescence microscopy. Using this approach, we study the non-equilibrium stretching dynamics of vesicles, including transient and steady state stretching dynamics in extensional flow. Remarkably, vesicles are found to be highly deformable objects that undergo reversible deformation in the bending-dominated regime with deformed aspect ratios of >20-50 in repeated stretch-relax cycles. Quantitative analysis reveals that the steady-state deformation of vesicles in flow exhibits power-law behavior as a function of reduced Capillary number. We further developed an analytical model to determine the bending modulus of lipid membranes based on non-equilibrium steady-state conformational stretching data. Remarkably, our results show that phospholipid vesicles exhibit a deflation-dependent bending modulus, such that the membrane bending modulus decreases significantly as a function of reduced volume. Finally, we identify two distinct relaxation processes for vesicles stretched to high deformation, revealing two characteristic time scales: a short time scale corresponding to bending relaxation and a long time scale governed by membrane tension. Overall, our results provide new insights into the flow-driven shape dynamics for vesicles using new experimental methods in automated flow control and the Stokes trap.

Asynchronous Any Time Virtual VP48

Saliva rheology and its effect on aerosol generation during sneezing

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Aerosols and droplets that are produced upon sneezing, coughing, or speaking can lead to the transmission of contagious diseases such as COVID-19, influenza, and tuberculosis. The mechanism of droplet formation during sneezing has been previously documented, revealing that the mucus volume is initially expelled as a flat sheet, which destabilizes into filaments that subsequently break up into droplets [1]. Less than 1% of the total salivary mass is composed of mucins, a high molecular weight protein that renders mucus viscoelastic. The presence of mucins influences the dynamics of filament stretching by retarding the onset of droplet formation. The process of aerosol formation during sneezing is systematically replicated using an impinging jet setup, where the collision of two liquid jets forms a thin fluid sheet that can subsequently fragment into ligaments and droplets [2]. Experiments are conducted with human saliva provided by different donors, and the resulting sheet morphologies are compared to commercially available saliva substitutes. We quantify the effect of viscoelasticity via oscillatory shear and extensional rheology experiments. Due to the radial flow profile that is established within the sheet, extensional stresses dominate over shear stresses. We summarize our results in terms of the dimensionless Weber, Reynolds, and Deborah numbers. We find that for a given solution, the sheet-to-ligament and the ligament-to-aerosol transitions are primarily determined by the Weber number. The magnitude of this transition Weber number is directly correlated to the elasticity of the solution, quantified by the Deborah number. This is particularly relevant for human saliva, since the Deborah numbers among donors can differ by up to two orders of magnitude. Thus, higher ejecta velocities and a diminished saliva elasticity facilitate the formation of aerosols upon sneezing.

[1] B. E. Scharfman et al., Exp Fluids 57, 24 (2016). [2] J. W. M. Bush and A. E. Hasha, J. of Fluid Mech., 511 (2004).

Asynchronous Any Time Virtual VP49

Spinning a yarn of the molecular rheology of natural silk spinning: Sticky reptation in extensional flow

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The rheologically-triggered transition, from semi-dilute protein solution to ordered fibre of natural silk, motivates an examination of the remarkable, and evolved, system of its molecular rheology. Polymer persistence, entanglement structure and electrostatics all combine with the nano-rheologically structured spinning duct of silk-worms, and the flow history of the spinning process, to create a sensitive flow-induced trigger for fibre formation. A theoretical and computational study of minimal models for silk protein solutions demonstrates immediately that the usual approach of considering the ensemble-averaged conformational properties of the chains, while successful in understanding the rheology in start-up extensional flow of ordinary entangled polymers, is strongly violated in a number of other cases. These include the minimal model for silk solutions: associating (sticky) polymers in extensional flow (as well as linear polymers in shear and entangled ring polymers). Here, we develop Coarse-grained simulations solve the conformational Brownian dynamics of entangled and unentangled sticky polymers, while the strain-dependent opening and closing of intermolecular associations are treated using a kinetic Monte Carlo algorithm. In the linear flow regime, we show through simulation and scaling arguments that the network weakens the dependence of the sticky-Rouse diffusivity on the sticker lifetime from the usual -1 power-law relation to a -4/5 power. In the non-linear flow regime, we find a large dispersity of chain conformations of both sticky and non-sticky linear polymers in shear flow. We also confirm the onset of an emergent (non-Gaussian) power-law tail of the stretch distribution of sticky polymers in extensional flow below the stretch transition, suggesting a highly energy-efficient route to nucleation of solid fibers.

Asynchronous Any Time Virtual VP50

Rheology and direct write printing of chitosan - graphene oxide nanocomposite hydrogels for differentiation of neuroblastoma cells

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We report the synthesis, characterization, rheology, and direct-write printing of chitosan - graphene oxide (CH - GO) nanocomposite hydrogels at a varying concentration of GO in 3 and 4 wt% CH polymeric gels. Rheological characterization of CH - GO hydrogels shows that an addition of only 0.5 wt% of GO leads to a substantial increase in storage modulus (G'), viscosity, and yield stress of 3 and 4 wt% of CH hydrogels. A three-interval thixotropy test (3ITT) shows that 3 wt% CH with 0.5 wt% GO hydrogel has 94% recovery of G' after 7 sequential stress cycles and is the best candidate for direct-write printing. Neuronal cell culture on 3 wt% CH with 0.5 wt% hydrogels reveals that GO promotes the differentiation of SH-SY5Y cells.

Asynchronous Any Time Virtual VP51

Diffusion of proteins in the continuous phase of block polymer liquid crystals

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Development of approaches to confine, crowd, and stabilize proteins within the aqueous, continuous, interstitial spaces in block copolymer micellar liquid crystals require an improved understanding of the dynamics of protein diffusion through these complex matrices. Pluronic [PEOm-

PPOn-PEOm] liquid crystals provide a thermoreversible and versatile template for development of these applications. Proteins are first dispersed in an aqueous Pluronic solutions, which are liquid at low temperature (T < ~ 10°C). On heating to near room temperature and higher the block copolymers self-assemble into micelles, which arrange into ordered crystalline lattices. The aqueous continuous phase of these crystals acts as a nanostructured template which hinders the mobility of the dispersed proteins - the proteins are confined to the aqueous interstitial pockets. The properties and size of the aqueous pockets between micelles can be engineered by changing polymer architecture, concentration, additives, and temperature. The mobility of the proteins within this aqueous phase will depend on more than geometry of the dynamic, nanostructured material. In this work we use Fluorescence Recovery After Photobleaching (FRAP) to quantity the mobility of fluorescently labeled proteins (Bovine Serum Albumin - BSA) within the continuous phase of Pluronic liquid crystals. We characterize a range of concentrations (Cgel - 2xCgel) and temperatures (25-55°C) over time scales of ~24 hours. We find the diffusivity of BSA to decrease by up to 4 orders of magnitude as the polymer concentration is increased from the gel concentration, Cgel, to 2xCgel. Contrary to the expected increase in diffusivity with increasing temperature, we observe a decrease in diffusivity in some cases. Diffusion in these systems cannot be explained as transport through a bulk viscous media. The properties of the micellar corona impact the proteins' ability to move through micellar brushes as they diffuse between interstitial sites. Here, we use rheological studies to explain t

Asynchronous Any Time Virtual VP52

Millifluidic bulge test reveals local and bulk mechanical properties of engineered biofilms

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Biofilms - communities of bacterial cells associated with their extracellular polymeric matrix - are complex materials whose features span many length scales, ranging from bulk cohesive material properties, to mesoscale structural and compositional heterogeneity, down to the microscopic cellular morphology and cell-cell interaction chemistry. Engineered biofilms have the potential to provide materials that change mechanical, optical or transport properties in response to their environment.

We are interested in studying their mechanical properties without excessively disrupting their structure and interactions. We developed a method to gently lift a biofilm onto a disk (3mm dia.) with a circular opening to create a freely suspended specimen (1.5mm dia.). Elevated pressure is imposed beneath the biofilm and the resulting dome-like shape is recorded using optical coherence tomography. Image analysis of the cross section allows for average estimates of bulk properties, while analysis of the stress and strain fields in volumetric images provides spatial resolution. The bulge test imposes equibiaxial extension near the top and varies to approximately constant width extension near the clamped edges, observable in spatially resolved measurements.

Coupling our method with genetically engineered *E. coli* K-12 DH10B, we compare biofilms expressing elastin like polypeptides with or without the ability to form disulfide bonds and find that the former leads to films that are stiffer, more homogeneous, and can sustain roughly six times the maximum stress (2.5 vs 18 kPa) prior to failure.

Our method requires only microliters of material, causes minimal disruption to the film structure, and allows for estimates of both average properties as well as local heterogeneity as a function of cell-cell interaction chemistry.

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Asynchronous Any Time Virtual VP53

Mechanical pre-metastatic lung terraforming by breast cancer-derived extracellular vesicles

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Tumor microenvironment-mechanics greatly affect tumor-cell characteristics such as invasion and proliferation. We and others have previously shown that following chemotherapy, tumor cells shed more extracellular vesicles (EVs), leading to tumor growth and even spread, via angiogenesis and the mobilization of specific bone marrow derived cells contributing to metastasis. However, physical, mechanobiological, and mechanostructural changes at pre-metastatic sites that may support tumor cell seeding, have yet to be determined. Here, we collected tumor-derived extracellular vesicles (tEV) from breast carcinoma cells exposed to paclitaxel chemotherapy, and tested their effects on tissue mechanics (e.g. elasticity and stiffness) of likely metastatic organs in cancer-free mice, using shear rheometry. Cancer-free mice were injected with saline or with tEVs from untreated cells and lung tissue demonstrated widely variable, viscoelastic mechanics, being more elastic than viscous. Contrastingly, tEVs from chemotherapy-exposed cells induced more uniform, viscoelastic lung mechanics, with lower stiffness and viscosity; interestingly, livers were significantly stiffer than both controls. We observe statistically significant differences in softening of lung samples from all three groups under increasing strain-amplitudes and in their stiffening under increasing strain-frequencies; the groups reach similar values at high strain amplitudes and frequencies, indicating local changes in tissue microstructure. Evaluation of genes associated with the extracellular matrix and fibronectin protein-expression revealed potential compositional changes underlying the altered mechanics. Thus, we propose that tEVs, even without cancer cells, contribute to metastasis by changing microstructures at distant organs. This is done partially by altering the composition and mechanostructure of tissues to support tumor cell invasion and seeding.

Barenholz-Cohen et al., Int J Cancer 147(10), 2924-2933 (2020).

Asynchronous Any Time Virtual VP54

Determining the yield stress of a biopolymer-bound soil composite for extrusion-based 3D printing applications

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Biopolymer-bound Soil Composite (BSC) is a novel class of construction materials with potential use in extraterrestrial infrastructure development and more sustainable construction on Earth. Little is known about the rheological properties of this new material and its suitability for Extrusion-based 3D Printing (E3DP). This paper presents methods for testing BSC yield stress to assess the material's pumpability and buildability. Based on experimental results, mixture design guidelines are established to produce BSC mixtures suitable for E3DP. Finally, hydrodynamic and frictional yield stress models are proposed for predicting the pumpability, extrudability and shape stability of BSC based on soil volume fraction.

Asynchronous Any Time Virtual VP55

Physical aging in chocolate subsequent to thermal and mechanical rejuvenation

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Under quiescent conditions, thermodynamically out of equilibrium materials evolve as a function of time to attain progressively lower free energy states - a process termed as physical aging. On the other hand, rejuvenation is a process in which, in principle, the structure formed during physical aging reverts. Soft glasses are widely reported to undergo rejuvenation on the application of a strong deformation field (mechanical rejuvenation). Instead, structure build-up during aging in polymer glasses can be erased by raising their temperature above the glass transition temperature. Interestingly the microstructural change because of thermal and mechanical rejuvenation is known to be different as system explores different sections of the phase space in each type of rejuvenation. Molten chocolate is a dense colloidal suspension containing fat that is known to undergo microstructural evolution under ambient conditions. In this work, we study the evolution of rheological properties of a commercially available chocolate bar after the application of thermal and mechanical rejuvenation. We carry out stress relaxation experiments at different time elapsed (t_w) since thermal or mechanical rejuvenation. Considering the time for stress decay to half of its initial value ($t_{½}$) as a measure of the relaxation time, we study the effect of both the rejuvenation fields on subsequent physical aging. We see a power law dependence of relaxation time on aging time ($t_{½} \sim t_w^{\mu}$). Very interestingly, physical aging after the thermal rejuvenation shows a much stronger power law dependence than the mechanical rejuvenation.

Asynchronous Any Time Virtual VP56

Drying-induced stratification in complex mixes of dairy proteins

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The evaporation of a colloidal dispersion is characterized by solute accumulation at the air-liquid interface, leading to the formation of a gelled skin. From the preliminary colloid deposit to complete solidification, the development of this layer affects the overall drying process and final sample morphology. The mechanisms governing skin formation in drying colloidal suspensions remain currently not fully clarified, especially in complex polydisperse systems. This work investigates droplet skin formation in a binary system of dairy proteins, i.e. whey proteins isolates (WPI), and native phosphocaseinates (NPC). A single-droplet approach was used to explore droplet morphology evolution and drying kinetics as a function of WPI relative percentage compared to the overall protein content (WPI%R). The observation of the evaporation stages highlighted the separate role of WPI and NPC on droplet characteristics, ranging from skin buckling (WPI%R=20%) to rigid convex shell (WPI%R=50%). Moreover, evaluating drying kinetics and sol-gel transition characteristic times highlighted WPI main impact above a critical value (WPI%Rc), resulting in a rigid skin with high resistance to buckling. Such enhanced mechanical properties suggested WPI external segregation during skin formation, whose evidence was provided by the direct observation of dry skin section structure. The hypothesis of protein stratification by size was corroborated by the agreement with recent predictive models on the evaporation of bidisperse model colloidal suspensions. Finally, the organization of protein molecules throughout the interface gelification process was also investigated by interfacial rheology tests, stressing significant similarities between ageing- and drying-induced gelled interface behavior above WPI%Rc. This study contributes to a better understanding of the drying mechanisms occurring in binary colloidal systems. Moreover, these outcomes are potentially valuable for the optimization of milk powder production in the dairy industry.

Asynchronous Any Time Virtual VP57

Application of high pressure shear rheology to assess CO_2 gas bubble nucleating proficiency of native starch particles and dispersed proteins

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Gas bubble nucleation and its control is one of the most important parameter in industrial foaming applications defining the physical and chemical properties of the end product. It is possible to enhance this processing step by adding gas bubble nucleation supporting agents. In this work, the

potency of corn and potato starch as bubble nucleating agents as well as whey protein concentrates and isolates for low-temperature high pressure (HP) foaming applications have been evaluated. In a first work step, the physical properties of the starches were assessed using scanning electron microscopy (SEM), Washburn rise method, nitrogen adsorption, H_g porosimetry as well as light scattering and compared to those of talcum, a well know and widely used nucleating agent in non-food systems. Secondly, the effect of the addition of these starch particles on CO_2 gas bubble nucleation in highly viscous watery hydroxy-methyl-propyl-cellulose dispersions was determined applying HP rheology. Results of the surface properties evaluation suggested that the investigated native starch particles are suitable natural nucleating agent for HP foaming applications but are less efficient than talcum particles. The applied HP rheology technique developed to measure the critical supersaturation revealed, that the starches can compete with the talcum. Moreover, it was shown that the CO_2 gas bubble nucleation was dependent on the source of whey proteins, the concentration of these proteins in the investigated dispersions as well as on the applied shear rate. These findings also allowed to validate the suitability of HP rheology to investigate gas bubble nucleation under defined shear conditions thus, enabling new insights into the mechanism of this process for low-temperature foaming applications in food and pharmaceutical product systems.

Asynchronous Any Time Virtual VP58

Propagating high stress fronts responsible for shear thickening in a cornstarch suspension

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Rheological measurements of dense suspensions often reveal dramatic shear thickening, but only provide measurements of average quantities. Evidence is accumulating that shear thickening is associated with large spatiotemporal fluctuations. Here we describe direct measurements of spatially resolved stress at the boundary of a sheared cornstarch suspension, showing persistent regions of high local stress that propagate in the flow direction. The persistence of these regions enables a detailed description of their structure, including the profile of boundary stress, the non-affine velocity of particles at the boundary of the suspension, and a measurement of the relative flow between the particle phase and the suspending fluid. The propagating fronts fully account for then increase in viscosity with applied stress reported by the rheometer.

Asynchronous Any Time Virtual VP59

Extensional stress-relaxation measurements on wheat flour dough – The key to finalizing the Fractional K-BKZ framework?

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Wheat flour dough is a viscoelastic material with a multi-scale structure. On a microscopic level it consists of a gluten matrix in which starch granules and a variety of minor components are dispersed. The complex interplay of interactions that takes place on this microscopic level results in a macroscopic rheological behavior of dough that is difficult to model accurately. A better understanding of dough rheology is highly desirable in view of the link between dough rheological properties and final bread quality. The linear rheology of dough can be accurately described using the fractional Maxwell model (FMM). By extending the FMM with the K-BKZ equation, the non-linear extensional behavior can be captured as well, at least from a qualitative point of view, although quantitatively an overestimation of the extensional stress growth is predicted. To overcome this limitation, a suitable damping function can be included into the Fractional K-BKZ framework to account for strain-softening at large strains. Conventional shear stress-relaxation measurements, which are typically used to circumvent the difficulties associated with extensional experiments, fail to provide an adequate damping function. Here we show that extensional stress-relaxation measurements performed on a highly-viscous material such as bread dough allow determination of an extensional damping function. Incorporating this damping function into the Fractional K-BKZ framework allows us to account for the disruption in gluten-starch interactions when dough is exposed to extensional deformations.

Asynchronous Any Time Virtual VP60

Colloidal gelation in foam: Probing the impact of elastic continuous phases on foam mechanics

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We explore the evolution of the mechanical properties of a foam containing colloidal particles that undergo a sol-gel transition. This enables us to investigate the effect of an elastic continuous phase on foam mechanics, probing a wide range of elastic moduli within a single experiment. Right after production of the foam the mechanics is controlled by the elasticity of the bubbles, while the contributions of the continuous phase become dominant as the colloidal particles form a gel. Remarkably, we find that we can describe the entire evolution of the foam mechanics by considering additive elastic contributions of the coarsening bubbles and the gelling continuous phase, provided that we assume that gelation occurs significantly faster in the foam than in the bulk.

Asynchronous Any Time Virtual VP61

Delayed elastic and ageing creep response of foams

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Liquid foams distinguish themselves among soft jammed materials in that intermittent rearrangements constantly reconfigure the bubble packing. Thus, any small applied stress causes a slow creep deformation beyond the Hookean strain. Here, we show that the creep response comprises two power-law regimes, well separated by a transient relaxation that slows down with waiting time. The short-time branch is quasi-stationary and we identify it as a delayed elastic response, since it is recoverable upon releasing the stress. The other branch is the asymptotic behaviour of a non-stationary contribution to creep and is irreversible. Remarkably, a unique exponent governs both power-laws and the increase of the relaxation time, consistent with ageing in Soft Glassy Rheology just above the glass transition.

Asynchronous Any Time Virtual VP62

An essential factor of perfluoroalkyl surfactant attributing to efficacy in firefighting foams

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Perfluoroalkyl surfactants are routinely used to make aqueous film forming foams (AFFF) for class B fire suppression due to their superior ability to quickly knockdown the flame and form a vapor barrier. However, due to environmental and toxicity concerns regarding the persistence of these chemicals, they are quickly getting regulated in the US, Europe, and Australia. These regulatory measures necessitate the exploration of an alternative surfactant system to match the performance of the perfluoroalkyl surfactants yet be environmentally benign. Of the several factors that govern foam performance in fire suppression, here we focus on the stability of the foam blanket over the fuel surface. Two simple model aqueous foams, one made from a perfluoroalkyl surfactant and one from a silicone polyether surfactant, are compared with regard to their stability in contact with heptane as a model fuel oil. The observed foam stabilities are explained in terms of the equilibrium phase behavior of the system water-surfactant-heptane. It is demonstrated that the fundamental enabling factor that makes perfluoroalkyl surfactant perform exceedingly well in stabilizing foams on hydrocarbon fuel oil is its oleophobicity. For hydrocarbon or silicone surfactants, propensity for the surfactant phase to solubilize hydrocarbon oil and be solubilized in the oil destabilizes the foam. This is particularly so if the surfactant's PIT (phase inversion temperature) range falls within the application temperature range.

Asynchronous Any Time Virtual VP63

Simulating foam and bubble suspensions using an extended Stokesian dynamics approach with bubble interaction

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Bubbles suspended in a fluid affect the suspension rheological properties relative to the base fluid alone. Generally, the viscosity of the suspension increases as the volume fraction of the bubbles is increased. A current application, and motivation for this study, is in wellbore cements used for hydrocarbon extraction and carbon sequestration. In these settings, the gas bubbles are dispersed into the cement to reduce the density as well as improve the properties for specific conditions or wellbore issues. A bubble interaction was developed and used with a Stokesian dynamics approach to numerically simulate the behavior of many bubbles suspended in a Newtonian fluid. We account for the nature of bubbles by allowing for slip on the bubble surface, the deflection on the bubble surface, and a bubble-bubble pairwise interaction that represents the surfactant physics; we do not account for bubble compressibility. The parameters describing the bubbles are chosen to represent more realistic physics of bubble interactions.

Asynchronous Any Time Virtual VP64

Controlling the morphology of polymeric foams: An experimental and numerical investigation

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Cell morphology of thermoplastic polymeric foams is a key factor for the performance of the final product, e.g., in terms of mass and energy transport, acoustic absorption, catalytic, impact, and cushioning properties. In particular, three possible foam morphologies exist, namely, with closed cells, closed cells with broken bubble walls, and open cells. In the gas foaming technology, a physical blowing agent, such as carbon dioxide or nitrogen, is used to form bubbles at high pressure in a softened polymer. As a consequence of a pressure quench, these bubbles grow in the liquid matrix until they impinge and possibly break the thin liquid films among them. If film breakage happens, the broken film may retract due to the interplay of surface tension, liquid viscosity, and elastic stress accumulated by the polymeric liquid during bubble growth. This, in turn, determines the final morphology of the foam. In this work, we experimentally study the morphology of polymeric foams obtained by gas foaming as a function of the process conditions and of the rheology of the liquid matrix. In addition, we perform three-dimensional direct numerical simulations in order to support the experimental findings and rationalize the effects of the process parameters and of the polymeric matrix rheology on the viscoelastic stress accumulated in the liquid at the end of bubble growth, and thus on the expected morphology of the foam.

Asynchronous Any Time Virtual VP65

Nanometric sized ions as foam Stabilizers

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In the last years, it has been shown that nanometer-sized ions, or nano-ions (NIs), with low charge density strongly adsorb to interfaces covered by hydrated moieties, e.g. at micellar surface of sugar-based or polyethoxylated surfactants.[1-3] NIs can also bind to the cavities of macrocycles, e.g. cyclodextrins.[4,5] The strong binding of NIs with electrically neutral and polar hydrated systems in the mM rconcentration range was described as a "superchaotropic" effect [1,4,6] in comparison with the more classical chaotropic effect of smaller ions such as iodide or thiocyanate.[7] Recently, superchaotropic nano-ions were also shown to behave like ionic surfactants when mixed with non-ionic surfactants in water.[8] Here, we show that the superchaotropic NIs, the polyoxometalate SiW12O404- (SiW) and ionic boron clusters - strongly stabilizes non-ionic surfactant foams. The foam stabilization by NIs was found to be even better than the stabilization observed by addition of ionic surfactants such as sodium dodecyl sulfate (SDS). Both DS- and SiW12O404- incorporates into the foam films produced with a polyethoxylated surfactant (Brij-O10). SiW12O404- adsorb within the polyethoxylated chains of Brij-O10 due to the superchaotropic effect whereas SDS anchors in the hydrophobic chain of the Brij-O10 due to the hydrophobic effect. It is noteworthy that SiW is not surface active and does not foam in water on the contrary to SDS. Nevertheless, adding SDS or NaSiW to a Brij010 foam (0.5 mM) close to the equimolarity slow down liquid drainage and bubble Ostwald ripening as revealed by image analysis and conductivity measurements. Furthermore, as SiW12O404- adsorbs to the non-ionic surfactant foam films they become charged, thicker and more stable, hindering film rupture as revealed by small angle neutron scattering (SANS). The use of superchaotropic nano-ions as new foam stabilizers is herein discussed.[9]

Keywords: foam film, neutron scattering, drainage, nano-ion

Asynchronous Any Time Virtual VP66

Foam coarsening under steady shear: Interplay between bubble rearrangement and film thinning dynamics

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Aqueous foams are unstable and age by drainage and coarsening. Today, these effects are well described, as well as their impact on foam properties. For instance, the foam viscoelastic properties evolve in time as a consequence of coarsening which tends to increase the mean bubble size. Here, we investigate the reverse coupling, and study if and how the continuous flow of a foam can impact its dynamics of coarsening. We introduce a new protocol in which brief oscillatory measurements are inserted within a steady shear, allowing us to monitor the relative variation of the bubble size with time, and as a function of the applied shear rate. It turns out that the coarsening rate is strongly impacted by the applied shear : this rate is continuously reduced above a critical shear rate, which decreases itself with the bubble size. This coarsening rate reduction can only be interpreted as the result of out-of-equilibrium and shear-dependant film thicknesses, being higher than at rest. The critical shear rate, above which films are sustained at higher thickness than at equilibrium, emerges from the competition between the rate of rearrangements and the time required to drain a thick film created during the rearrangement. We thus report here first experimental proofs and measurements of out-of-equilibrium film thicknesses within a sheared foam, and on the impact this shear has on coarsening.

Asynchronous Any Time Virtual VP67

Evaporation and atomization of ultra-stable emulsion droplets

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Evaporation and atomization of multicomponent droplets are fundamental to numerous industrial applications ranging from spray drying and ink-jet printing to spray combustion in gas turbine and internal combustion engines. In particular, the evaporation characteristics of microemulsions, a class of liquid-in-liquid dispersions which are thermodynamically stable emulsions, play an important role in the field of pharmaceutics, drug delivery, material synthesis, coatings, and fuels. We employ a non-intrusive technique to study the water-in-oil microemulsions by externally heating acoustically levitated droplets. The evaporation of droplets in a contact-free environment allows us to mimic the physical processes in the aforementioned applications. The objective of this work is to understand the evaporation and atomization mechanisms of acoustically levitated water-in-oil microemulsion droplets. The isolated single droplets are heated using a continuous laser and high-speed imaging is used to visualize the evaporation and breakup dynamics. The modes of droplet atomization is primarily governed by the volatility differential between the dispersed and the continuous phase, laser irradiation intensity, the relative composition of the constituents, the size and physical properties of the parent droplet. The microemulsions are characterized using dynamic light scattering (DLS) and rheometry. An effort has been made to understand the role of microemulsion composition and the influence of base oil in the emulsion formulations (from aliphatic to aromatic) on the evaporation dynamics and distinct modes of atomization. Furthermore, the effect of laser irradiation intensity on the dynamics of key physical phenomena such as vapor bubble growth and ligament-mediated breakup has been explored.

Asynchronous Any Time Virtual VP68

Microstructure and interfacial rheology of ellipsoids at interfaces - Role of surface modification

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In this contribution, we present our work on the self-assembly and surface rheology of ellipsoids at oil-water and air-water interface. We consider monolayers of (i) pristine hematite ellipsoids and (ii) hematite ellipsoids whose surface is partially and fully modified by the adsorption of oleic acid. Our results showed contrasting self-assembly of ellipsoids which are partially surface modified when compared to ellipsoids of homogeneous surface chemistry. For the same system, interfacial rheology is studied using Bi-cone geometry attached to a rotational rheometer. It is observed that for a given surface coverage, the storage and viscous modulus of monolayer of surface modified ellipsoids are much higher than the monolayers of bare ellipsoids. Finally, we show the efficacy of oleic acid modified ellipsoids in effecting emulsion phase inversion and formation of non-spherical emulsion drops.

Asynchronous Any Time Virtual VP69

Structure-rheology relationship of β-lactoglobulin's quaternary structure through interfacial rheology

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In this study, we utilize interfacial rheology to investigate the implications of the quaternary structure of β-lactoglobulin (BLG) on its adsorption properties at dodecane/water interfaces. The subphase solution conditions including the ionic strength, salt type and temperature were tuned to vary the relative amounts of two native BLG species, namely, the monomer and its smallest aggregate, the dimer. Unfolding of BLG molecules at the interface triggers the formation of disulfide linkages between pairs of molecules through free thiol groups are located at cys121. In this way, monomeric BLGs can only pair up to form discrete assemblies of two BLG molecules (non-native dimers) that are not interconnected with each other and this is reflected in the absence of a viscoelastic layer in solutions with high monomer concentrations. In contrast, native dimeric BLGs are capable of forming two thiol bonds allowing the formation of extended networks. Indeed, a higher concentration of dimers increases the final interfacial elastic strength of the network. While such bifunctionality has been observed for the bacterial protein BslA, we believe such fundamental structural correlations of many other proteins could be unearthed using interfacial rheology in order to understand the physiological purposes of their multimeric forms.

Asynchronous Any Time Virtual VP70

Effect of aromatic and non-aromatic solvents in the interfacial viscoelasticity of Brazilian asphaltenes

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Asphaltenes are known to be surface-active molecules that aggregate under certain conditions like temperature, pressure, and composition, causing large cost to the production and refining of crudes. Operational problems like the plugging of pipelines, wells and facilities can generate fouling and impair oil production, leading to undesirable shutdowns. Besides, the efficiency of the desalting process of crudes, in which corrosive salts are removed from the oil phase through a liquid-liquid extraction, relies on how asphaltenes and other natural compounds change the surface properties of oil-water interfaces. In this study, we create a set of novel protocols using a shear rheological study to measure in situ changes of Brazilian (BR) asphaltene films under the addition of distinct solvents. We link the evolution of interfacial microstructure with the molecular packing of asphaltenes and their aggregation dynamics. Moreover, we also investigate the yielding behavior of the interface by disrupting asphaltene aggregates upon different shear rates. A Langmuir trough is employed to obtain typical pressure-area (p - A) isotherms and to support our rheological analysis. Finally, we use scanning electron macroscopy (SEM) and 1H NMR and 13C NMR experiments to determine the morphology and structure of asphaltenes, respectively. Our findings indicate that BR asphaltenes are a polycondensate aromatic island-type structure that form reversible films when polar solvents are injected at a previous asphaltene layer. Furthermore, our protocols show that non-polar solvents may lock up asphaltene nanoaggregates in mixture and, consequently impair their interfacial activity. We find that the network growth and BR asphaltenes self-assembly is directly related to the aromatic content.

Asynchronous Any Time Virtual VP71

Drag on a spherical particle at the air-liquid interface: Interplay between compressibility, Marangoni flow and surface viscosities

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Particles at interfaces play an important role in a large range of industrial and biological processes. In the majority of these processes the interface is complex, i.e. it exhibits a position- and time- dependent surface tension and/or rheological interfacial stresses, where the latter are possibly deviatoric. Due to the coupling of the interface to the bulk and the intricate interplay between the different physical mechanisms that induce interfacial stress, understanding and predicting the flow dynamics of a particle translating at an interface is not trivial. We numerically investigate the dynamics of a spherical particle embedded symmetrically in a planar air-liquid interface. The interface is assumed to remain planar, and the particle translates tangentially to the interface. Moreover, the interface is endowed with a concentration-dependent surface tension and viscous stresses are added using the Boussinesq-Scriven model. The finite element method is employed to solve the fully coupled set of flow- and transport-equations. We first perform a thorough analysis of the role of mesh- and domain-size for an incompressible interface. We then systematically investigate the role of a non-uniform interfacial tension and interfacial viscosities, paying special attention to interfacial compressibility. For inviscid interfaces, the motion of the particle induces a gradient in surface concentration, which in turn drives a Marangoni flow in the opposite direction, increasing the drag on particle. Our numerical method allows simulations for a large range of Marangoni and Péclet numbers, and we show how these can induce incompressiblity of the interface. We then investigate the role of interfacial shear- and dilatational viscosities, and show how incompressibility of the interface can also be introduced by a large dilatational viscosity. Finally, we systematically investigate cross effects where both Marangoni stresses and interfacial viscosities play a role, and we elucidate their intricate coupling.

Asynchronous Any Time Virtual VP72

Super resolution microscopy to study rheological transitions during egg-white cooking

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Food materials transition through different physical states during processing and cooking. Food rheology is a very helpful tool used to explain molecular mechanisms occurring during these transitions inside food matrices. However, more quantitative tools at the microstructural level are needed to gain a complete multi-length scale perspective (molecular-micro-macro), which is key to achieve a deeper understanding of structure-function relationships in food and soft materials. The application of super resolution (SR) microscopy techniques offer the opportunity to study materials microstructure more in depth, since it allows the recollection of new regimes of microstructural data while being minimally invasive. The objective of this session is to show how food microstructural data can be correlated with rheological transitions of non-Newtonian food fluids. This is shown through visualizing and quantifying the microstructure of egg-white cooked at varying temperatures and times. Images of the egg-whites with different rheological parameters were taken with a dual 'confocal and SR system' and processed with image deconvolution and quantification software. Variations of 3?C in the cooking temperature of egg-whites generated materials with different rheology, which were correlated with the SR microstructural data. Correlations were found between the particle counts and particle density data of the SR images and the elastic modulus (G') of the egg-whites cooked at different temperatures. Also, the microstructural analysis found two different aggregation mechanism corresponding a initial logarithmic G' increase phase followed by a linear increase of G' phase during egg-white cooking. These results show how SR microscopy can help gain deeper understanding of the rheological transitions that non-Newtonian food fluids undergo during cooking. This level of structure-function understanding can lead to new developments that can respond to current global food challenges, like a current demand of egg-white replacers.

Asynchronous Any Time Virtual VP73

Colloid-polymer mixtures revisited: Assessing the role of macromolecular depletant

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Recent Monte-Carlo simulations and mean-field density functional theory suggest that the organization of ring polymers close to walls differs from that of their linear counterparts [I. Chubak et al., Mol. Phys. 116, 2911-2926 (2018)]. Their density profile features pronounced oscillations which lead to a much stronger depletion force for rings compared to (typically used) linear polymers at the same size ratio. Here, we test this theoretical result and explore further the role of macromolecular architecture of the depletant. We use the established PMMA hard spheres at an intermediate volume fraction (0.44). By adding linear or ring polymer of the same molecular weight or size as depletant and systematically increasing its concentration, we investigate the formation of gel and examine its viscoelastic properties by means of linear and nonlinear shear rheological measurements. We focus in particular on probing the onset of gelation and the strength of the resultant gel. Our results indicate that, in the presence of rings gelation takes place at smaller concentrations and the resulting gels are much stronger compared to the respective gels based on linear chains. Our unambiguous results point to the importance of polymer molecular structure in influencing interactions and consequently gelation in colloid-polymer mixtures and open the route for further investigations using branched polymers and soft colloids, which we currently pursue.

Asynchronous Any Time Virtual VP74

Evaporative shape transformations in polymeric sessile droplets

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Droplets of aqueous polyethylene glycol (PEG) form high aspect ratio residue structures depending upon evaporation rate, molecular weight, and concentration. Previously, the effect of substrate and contact angle on this phenomenon had been unknown. Here it is shown that increasing substrate wettability and decreasing droplet size both promote the formation of pillar deposits. Images collected with the Dynamic Fluid-Film Interferometry (DFI) apparatus developed in the Fuller Lab at Stanford University suggest that the unique characteristic of PEG leading to this behavior during drying is the contraction of a desiccated solute skin formed at the three-phase contact line and propagating toward the apex of the droplet. Contraction of this skin increases pressure inside the droplet and forces fluid flow orthogonal to the substrate.

Asynchronous Any Time Virtual VP75

Influence of surface roughness on the yielding of thermo-reversible colloidal gels

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The microstructural and solid-liquid transition of colloidal gels has been intensively researched using various characterization methods in the past [1,2]. In the present work we investigate the effect of surface topography on the yield stress and thixotropy. To this end, thermo-responsive octadecyl coated silica particles were synthesized in a controlled and reproducible manner using click-like chemistry to graft the stabilizer to particles with concave, convex and no surface features. The thermo-responsive nature allows to delete the influence of mechanical history, as gelation can be induced by decreasing the temperature inside the measurement cell. This model system is utilized to compare the initial yielding behavior of colloidal gels with primary particles of different surface topographies. Rheological measurements show that surface roughness delays the structural yielding due to interlocking of the particles, in addition to influencing the thixotropy as roughness counteracts flow induced cluster densification.\\ [1] Gopalakrishnan, V., and C. F. Zukoski. "Yielding behavior of thermo-reversible colloidal gels." Langmuir 23.15 (2007): 8187-8193. [2] Chan, Hubert K., and Ali Mohraz. "Two-step yielding and directional strain-induced strengthening in dilute colloidal gels." Physical Review E 85.4 (2012): 041403.

Asynchronous Any Time Virtual VP76

Assessing rheological properties of highly-filled polymers for material extrusion additive manufacturing of metallic parts

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Material extrusion additive manufacturing of highly filled polymer is a very recent process for the manufacture of metallic parts, but there are very few studies on the influence of the material composition on the rheological properties. The feedstock is composed of metallic powders (65 vol.%), paraffin wax, stearic acid, and ethylene vinyl acetate (EVA).

In this study, rheological properties of two feedstocks with different EVA types are investigated over the shear rate range experienced by the material during the process. One EVA has 40 vol.% of vinyl-acetate (VA) and the other 28 vol.%. Viscosity as a function of shear rate is measured with a capillary rheometer at high shear rate (200 to 2000 s^{-1}) and with a rotational rheometer at lower shear rates (0.01 to 100 s^{-1}) using plate/plate and concentric cylinder configurations. The viscosity values for one feedstock are repeatable, but differs a lot according to the measuring system used. Moreover, according to the VA% of the EVA, rheological properties seem to differs significantly.

It is assumed that the flow induced by a specific rheometer configuration and the VA% of EVA in the feedstock will affect the state of dispersion of the powders in the material, thus the rheological values obtained. Therefore, changing the VA% of EVA, or the type of flow undergone by the material could enable to tailor the rheological properties required for a desired 3D printing application.

Asynchronous Any Time Virtual VP77

Active particles in external fields

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External fields can act as a mechanism by which the orientation and speed of active particles is controlled. For example, in viscosity gradients, active particles tend to reorient to align against the gradient and then move in this steady-state orientation with a speed that is different from that in the absence of the field. In this talk, we detail how the boundary conditions on the particle can significantly change the dynamics of active particles in viscosity gradients. More generally, we show how manipulating the speed and orientation of active particles (in the presence of noise) allows one to control the accumulation of active matter. We find that accumulation depends on the competition between the strength of the reorientation and the speed changes. For weak reorientations, the particles accumulate in the regions of low speeds but for strong reorientations, the particles align themselves along or against the field and accumulate downstream or upstream relative to the field.

Asynchronous Any Time Virtual VP78

On the inverse quenching technique applied to gelatin solutions

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Gelatin gels are known to be non-equilibrium systems, due to the continuous growth and shuffling of the junction zones throughout all accessible time scales. For this reason, performing rheological experiments on a distinct gel microstructure, characterized by a definite number of junctions, is a challenging task. Inspired by the inverse quenching technique applied in the past to semi-crystalline polymers, we here apply an unusual thermal history to an aqueous solution of gelatin in the semi-concentrated regime (6.67%w pig-skin gelatin), in order to freeze the system in a metastable condition for a time sufficiently long to perform a rheological characterization. The solution, initially kept in the sol-state at 60°C, is rapidly cooled below gelation temperature, and isothermal gelation is started at 10°C. After soaking at this low temperature for a given time, the

sample is rapidly heated (inverse quenching) up to a value in the range 24-29°C, where kinetics are monitored. If the waiting time at low temperature and the inverse quenching temperature are suitably chosen, sample elasticity will remain stationary for a relatively large time window, and rheological experiments will then be reliably performed.

Asynchronous Any Time Virtual VP79

Nonlinear shear rheometry of unentangled polymers

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Decoding the dynamics of polymers in fast flows is a relevant challenge. On the experimental side, fast flows are prone to flow instabilities and require suitable setups to collect reliable data. On the theoretical side, phenomena such as monomeric friction reduction and finite chain extensibility must be considered for understanding nonlinear dynamics. In the past years, many research efforts were devoted to exploring nonlinear dynamics of entangled systems. Elongational data at high Weissenberg number were obtained owing to experimental setups such as the filament stretching rheometer. On the other hand, the cone-partitioned plate rheometry allowed to circumvent effects of edge fracture, and to perform shear start-up experiments at high rates. At the same time, tube-based models were implemented for successfully describing the dynamics of polymer melts and concentrated solutions. Recently, unentangled polymer melts are attracting considerable interest. Unentangled systems are relatively easier to predict, as orientation and stretch occur simultaneously above the Rouse time. However, the data available are scarce because of the associated experimental challenges. For example, in shear flow, the available range of rates for nonlinear tests, comprised between the inverse of the Rouse time and the shear rate at which glassy modes come into play provoking transducer resonance, is quite narrow. Secondly, at high shear rates, instabilities such as edge fracture occur. Matsumyia et al. successfully measured the nonlinear start-up elongational rheology of unentangled melts. In this work we present careful data sets on nonlinear start-up shear experiments on unentangled polystyrene melts. The data are collected by means of cone-partitioned plate setups. The shear thinning behaviour and the validity of the Cox-Merz rule are discussed.

Watanabe et al. Macromolecules 2021, 54, 3700-3715; Matsumiya et al. Macromolecules, 2018, 51, 9710-9729; Ianniruberto and Marrucci, Macromolecules, 2020, 53, 4, 1338-1345.

Asynchronous Any Time Virtual VP80

Determination of the molecular weight distribution of ultra-high molecular weight polyethylene from solution rheology

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The rheological determination of material properties of polymers (molecular weight distribution, degree of branching, etc) is not always easy to pursue. In particular, when dealing with Ultra-High Molecular Weight (UHMW) polymers, the rheological measurements can be affected by experimental limitations (shear fracture, torque overload, temperature investigation range, loading problems). Diluting the polymer melt into an appropriate solvent [1] may overcome, or at least limit, these experimental issues. In this perspective, rheology can be used as a tool to relate the macroscopic viscoelastic response of polymer systems to their molecular architecture. The aim of this work is to determine the Molecular Weight Distribution (MWD) of a UHMW Polyethylene (UHMWPE) by extrapolating it from the linear viscoelastic response of UHMWPE solutions in a suitable solvent, namely, Low Molecular Weight Polyethylene (LMWPE). The pure melt is dissolved in a LMWPE and the rheological measurements are performed in a concentrated regime. Once we verified the scaling laws of the main rheological parameters (plateau modulus, relaxation time, zero-shear viscosity) as function of concentration, we are able to extrapolate the linear viscoelastic response of the pure melt. The analysis of rheological results is performed by using the time-dependent diffusion/double reptation model introduced by van Ruymbeke [2]. This model allows to determine the molecular wight distribution of the melt starting from the linear rheological behaviour of a melt or solution [3]. The MWD results of the model are compared from those obtained independently on the UHMWPE melt.

References: [1] A. Brem et al., Macrolecules, 53, 5957-5970, 2020; [2] E. van Ruymbeke et al., Journal of Non-Newtonian Fluid Mechanic, 105, 153-175, 2002; [3] K. Chaudhuri and A.K. Lele, Journal of Rheology, 64, 1-12, 2020.

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Asynchronous Any Time Virtual VP81

Frequency dependence and critical transition can be induced by a negligible Van der Waals force in non-Brownian Newtonian suspensions

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Recent experiments report that slowly sheared noncolloidal particle suspensions can exhibit anomalous rate (ω)-dependent complex viscosities in oscillatory shear, despite a constant relative viscosity in steady shear [1]. Using a minimal hydrodynamic model, we show that a weak interparticle attraction reproduces this behavior. At volume fractions φ = 20%~50%, the complex viscosities in both experiments and simulations display power-law reductions in shear, with a φ-dependent exponent maximum at φ = 40%, resulting from an interplay of hydrodynamic, collision and adhesive interactions. Furthermore, this rate dependence is accompanied by diverging particle diffusivities and pronounced cluster formations even at small oscillation amplitudes γ_0. It was previously established that suspensions transition from reversible absorbing states to irreversible diffusing states when γ_0 exceeds a critical value $\gamma_c^+(\varphi)$. Here, we suggest that a second transition occurs below a rate-dependent critical amplitude, $\gamma_c^-(\omega) \leq \gamma_c^+(\varphi)$, in the presence of weak attractions.

1. Martone R, Carotenuto C, Minale M, 2020, J Rheol 64, 1075 - doi: 10.1122/8.0000077

Asynchronous Any Time Virtual VP82

Mechanical and structural analysis of channel networks in bacterial biofilms

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Bacterial biofilms are formed by communities of microorganisms that are encased by a matrix consisting of self-produced, hydrated extracellular polymeric substances. Biofilm formation is observed in a large variety of microorganisms and provides a protected mode of growth. Recent advances show that biofilms are structurally complex, dynamic systems that exhibit different morphologies depending on the environmental conditions.[1] In certain growth conditions, large three-dimensional structures, which can be defined as channels, are found within biofilms. These channels show low resistance to liquid flow and therefore enable transport by advection.[2] Recent works identify the role of interfacial energy and mechanical instabilities as driving forces during biofilm morphogenesis[3], but the exact mechanism of channel formation is still unclear. Our work represents a step towards understanding the physical process of channel formation within a microbial biofilm.

We study how the adhesion of the biofilm to the substrate influences the formation of channels inside *Pseudomonas aeruginosa* biofilms grown under flow in microfluidic devices. We quantify the mechanical properties of the biofilm with active microrheological techniques. Our results show that biomass production, adhesion to the substrate and rheological properties control a mechanical buckling instability, which triggers the formation of folds and wrinkles. These three-dimensional structures can be identified as hollow channels in which bacterial movement is greatly facilitated and which rapidly increases the effective volume occupied by the biofilm. Combining methods and concepts from biology and material science sheds light on the physical process of channel formation inside bacterial biofilm grown in flow and enables us to predict and control the biofilm morphology.

[1] Flemming et al., The perfect slime. IWA Publishing, London, 2017
[2] Asally et al., PNAS, 109(46):18891-18896, 2012
[3] Yan et al., eLife 2019;8:e43920, 2019

Asynchronous Any Time Virtual VP83

Entrance flow of unfoamed and foamed Herschel-Bulkley fluids

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The present study investigates extrusion processing of unfoamed and foamed cocoa butter (CB) crystal-melt suspensions (CMS) with varying crystal volume fraction Φ_{SFC}. The yield stress to wall shear stress τ_0/τ_w of CB CMS was fitted with the Herschel-Bulkley Papanastasiou (HB-P) model. Foamed CB CMS behaved fluid-like for $\Phi_{SFC} \leq 11.9\%$ and according to a brittle porous solid for $\Phi_{SFC} > 11.9\%$. The dimensionless entrance pressure loss n_{en}/α as a function of dimensionless shear stress τ^* was higher for foamed compared to unfoamed CB CMS at $\Phi_{SFC} \leq 11.9\%$ and lower for foamed compared to unfoamed CB CMS at $\Phi_{SFC} > 11.9\%$. The Φ_{SFC} dependent difference in n_{en}/α was attributed to the crystal confinement in the die entrance flow which is increased in the case of elastic gas bubble deformation and decreased in the case of plastic gas pore collapse. The computational fluid dynamics (CFD) simulated flow of unfoamed and foamed CB CMS through an abrupt circular 20:1 contraction with the HB-P model was compared with experimental results by quantitative entrance flow visualisation (QEFV). Differences in measured and simulated τ^* and critical yielding radius R_{crit} were related to the ability of the HB-P model to describe the viscous flow in the die and the limitations the HB-P model to describe elastic stress contributions in the die entrance flow. Furthermore, the QEFV derived half center incidence angle θ as well as the entrance flow shear- and elongational rates γ_{ef}, ε_{ef} were derived and used to establish a model predicting the Bagley entrance pressure loss ΔP_{Bag} and calculate an entrance flow characteristic shear- and elongational viscosity $\eta_{ef,\ shear}$ and $\eta_{ef,\ elongation}$.

Asynchronous Any Time Virtual VP84

Interfacial rheology of phospholipid monolayers

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The membrane fluidity of phospholipid bilayers plays a central role in many biological processes, e.g. for cell homeostasis. Membranes not only compartmentalize the cytoplasm and various organelles, but they are also relevant for cell signaling where fine-tuning of the membrane fluidity is a necessity. The formation of metastatic cancer cells relies on an increase in membrane fluidity, which represents just one of many diseases related with membrane fluidity dysfunction. One approach to measure the investigate the mechanical properties of phospholipid bilayers is to investigate the interfacial rheology phospholipid monolayers-one leaflet of the lipid bilayer-under relevant conditions. Furthermore, monolayers have a relevance of their own as they coat the alveoli and prevent lung collapse. Therefore, phospholipids are used in pulmonary lung surfactant replacements for premature infants as well as for adults (acute respiratory distress syndrome). We investigate monolayers of various phospholipids at the water-air and buffer-oil interface, controlling temperature and surface pressure. Their linear viscoelastic regime is probed with oscillatory interfacial shear rheology by the interfacial needle stress rheometer (ISR), which is a macroscopic technique.[1] The lipid mixtures under investigation consist of phosphatidylcholines with saturated (palmitoyl) and unsaturated (oleoyl) fatty acids leading to different melting temperatures of the hydrophobic tails. At sufficiently high surface pressures, the saturated lipids pack efficiently and form liquid condensed phases leading to crowded membranes. The phases can undergo various shape instabilities depending on their size and balance of attractive and repulsive interactions between the lipids. The phase behavior is imaged simultaneously to the rheological measurement by a fluorescent microscope mounted on the ISR.

[1] D. Renggli, A. Alicke, R. H. Ewoldt, and J. Vermant, J. Rheol., vol. 64, no. 1, pp. 141-160, Jan. 2020.

Asynchronous Any Time Virtual VP85

Fast flows on linear and branched wormlike micelles

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Surfactant molecules assemble in water into supramolecular aggregates, referred to as micelles. The micellar morphology can be tuned by changing some parameters in the system (i.e. salinity, pH, and temperature). The most efficient way to induce morphological and/or structural changes is adding complex salts. The latter can penetrate the micellar core, affecting the effective size of the surfactant molecules, thus inducing a morphological transition from spherical micelles into elongated ones, linear or branched, entangled or unentangled. We report shear startup data on solutions of entangled linear and branched wormlike micelles, differing in concentration and type of two binding aromatic sodium salts. The surfactant molecule is Cetylpiridinium Chloride, at fixed concentration (100mM). Sodium Salycilate and Diclofenac Sodium are used as binding salts, at different concentrations (40-70mM). We proved that the type of salt and its packing effectiveness at the micellar interface are crucial for the dynamics of the wormlike micelles. More specifically, we found that linear wormlike micelles behave similarly to ordinary polymers in fast shear flows, exhibiting pronounced overshoots as well as tiny undershoots in transient shear viscosity, before approaching the steady state. The analogy is emphasized by successfully comparing data with predictions of a constitutive equation, recently adopted for ordinary entangled polymers. Concerning the branched structure, the experimental results in start-up flow strongly depend on the type of salt. In specific cases, the surfactant solutions show flow instabilities and strain hardening. A possible mechanism for the onset of these singularities is proposed.

Asynchronous Any Time Virtual VP86

A numerical study of extensional flow-induced crystallization in filament stretching rheometry

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A finite element model is presented to describe the flow, resulting stresses and crystallization in a filament stretching extensional rheometer (FiSER). This model incorporates nonlinear viscoelasticity, nonisothermal processes due to heat release originating from crystallization and viscous dissipation as well as the effect of crystallization on the rheological behavior. To apply a uniaxial extension with constant extension rate, the FiSER plate speed is continuously adjusted via a radius-based controller. The onset of crystallization during filament stretching is investigated in detail. Even before crystallization starts, the rheology of the material can change due to the effects of flow-induced nucleation on the relaxation times. Both nucleation and structure formation are found to be strongly dependent on temperature, strain rate and sample aspect ratio. The latter dependence is caused by a clear distribution of crystallinity over the radius of the filament, which is a result of the nonhomogeneous flow history in the FiSER. Therefore, this numerical model opens the possibility to a priori determine sample geometries resulting in a homogeneous crystallinity or to account for the nonhomogeneity.

Asynchronous Any Time Virtual VP87

Lubricant effect of graphene in polystyrene

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Graphene has attracted a lot of interest due to its outstanding mechanical properties but also its barrier properties and electrical conductivity. Some studies recently highlighted a new potential use for graphene as a processing aid agent. Indeed, while adding rigid nanoparticles to a thermoplastic matrix usually leads to an increase in the viscosity of the resulting composite, it has been demonstrated recently that some layered nanoparticles such as graphene can, on the contrary, induce a decrease in the viscosity when added in low amounts. This processing aid effect, also called lubricant effect, is still rarely studied, and not yet completely understood. In this work, the effect of the dimension of graphene nanoparticles on their lubricant effect in polystyrene is studied. To do so, nanocomposites containing 0 to 2 wt% of graphene were produced by melt mixing. Graphene grades with different particle sizes were used. The rheological properties of the nanocomposites were evaluated by carrying out small amplitude oscillatory shear tests and capillary tests, showing a decrease in viscosity when graphene is added to polystyrene. It was shown that this decrease in viscosity is dependent on the dimensions of graphene nanoplatelets.

Asynchronous Any Time Virtual VP88

Ultrasonic dispersion and time evolution of concentrated cellulose nanocrystal suspensions characterized by rheology

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Cellulose nanocrystals (CNCs) are biobased nanoparticles with interesting mechanical and optical properties. However, the necessary condition to take advantage of such properties is the absence of agglomeration. Unfortunately, the drying step following their extraction leads to the formation of strong agglomerates. Thus, a dispersion step in suspension prior to their use or integration in polymer matrices is unavoidable. This is usually achieved using a highly powerful tool: an ultrasonication probe.

Whereas an optimized ultrasonic dispersion protocol for small volumes of CNC aqueous suspensions at intermediate concentrations (60 mL - 3.2 wt%) was previously detailed (Girard et al., 2020), the limitation of this technique remains on processing higher CNC concentrations or larger volumes of suspension. Indeed, the ultrasonic efficiency decreases when viscosity and volume increase. Understanding CNC suspension evolution during and after ultrasonication helps provide guidelines to address these challenges.

This work focuses on the concentration limitation. A rigorous rheology study was carried out to characterize concentrated CNC suspensions (6.4wt%), i.e. concentrations at which a gel is obtained. Compared to lower concentrations, these suspensions also present a yield stress, which makes their analyses trickier. The viscosity build-up after sonication demonstrates network formation over time. This behavior is compared across two sample types: never-dried CNC suspensions and the more commercially ubiquitous spray-dried CNC, to validate that a well-dispersed state can be achieved at high concentration starting from dry powder.

A system to process larger volumes will be suggested with rheological on-line measurements to assess the dispersion state. This whole agglomeration and dispersion problem is encountered for other kinds of nanoparticles. As such, the results of this study could be transposed widely.

Asynchronous Any Time Virtual VP89

Rheological implications of pH induced particle-particle association in aqueous suspension of an anisotropic charged clay

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Kaolinite particles are geometrically anisometric and electrostatically anisotropic. Until recently, the charge of both basal faces of kaolinite was assumed to be independent of pH, and the isoelectric point (IEP) of the edge surface was thought to occur at pH 4-6. Therefore, kaolinite suspensions were expected to have an edge-face association at low pH. However, recent atomic force microscopy (AFM) studies have shown that the kaolinite alumina basal face and edge surface carry a pH-dependent surface charge with an IEP at pH 5-6 and ~ 3, respectively. Here, we revisit the modes of particle association in kaolinite suspensions and apply Derjaguin-Landau-Verwey-Overbeek (DLVO) theory to study the rheological implications of surface charges of various kaolinite faces from recent AFM-based studies. Specifically, aging within the linear viscoelastic region, small amplitude oscillatory shear behavior (strain amplitude and frequency response), and critical stress behavior were studied as a function of pH. Kaolinite suspensions (40 wt.%) exhibited two-step structure recovery after shear rejuvenation and two-step yielding at pH less than the IEP of the alumina basal face. In addition, the storage modulus (G') and critical stress required to stabilize the flow followed non-monotonic behavior as a function of pH. At low pH, the silica face-alumina face mode of association was dominant rather than the edge-face microstructure. A peak in the G' vs pH curve at pH 4.5-5 was correlated with the silica face-alumina face attraction estimated from DLVO theory, which passes through a maximum at approximately the same pH. Based on these observations, we propose a new state diagram for kaolinite suspensions in the pH-concentration space.

Asynchronous Any Time Virtual VP90

Alteration of soft glassy dynamics in aqueous suspensions of an anisotropic charged swelling clay through pH changes

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Owing to their anisotropic surface charge and anisometric shape, colloidal range sodium-montmorillonite (Na-Mt) particles in suspension exhibit thixotropic yield stress at very low solids concentrations. In this talk, we will present the aging behavior of Na-Mt suspensions as a function of pH and clay concentration. The temporal evolution of the storage modulus (G') was stronger in the subnatural (pH <9.5) than supernatural (pH >9.5) pH regime. Horizontal shifting of the aging curves in the sub- and supernatural regimes led to aging time-H+ concentration and aging time-OH- concentration superposition, respectively, which was linked to microstructural differences between the two pH regimes. An aging time-Na-Mt concentration superposition was also observed in both pH regimes, and the impact of pH-governed aging on this viscosity bifurcation behavior was explored. The critical stress associated with the viscosity bifurcation behavior increased linearly with G' but with different slopes for sub- and supernatural pH regimes, signifying the complexity of thixotropic yield stress systems. We postulate that positively charged patches on the Na-

Mt particle edge merge with the characteristic surface as a function of H+ ions in the system. This leads to a strongly associated microstructure at low pH and a relatively weak but associated microstructure at natural pH.

Asynchronous Any Time Virtual VP91

Yielding of model viscoplastic interfaces in shear and compression: Landmark observations and constitutive modelling

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Colloidal particles are widely employed to provide Pickering stability to high interface systems. Their colloidal nature makes them prone to irreversibly adsorb at interfaces, and the flexibility to tune interactions makes them ideal candidates as model systems to understand the behavior of more complex interfaces. Typically, they are used to fully cover the surface of bubbles and droplets, though it has been recently shown[1] that the existence of an interfacial yield stress at sub-monolayer coverages suffices to resist bubble dissolution (and the main driving force for Ostwald-ripening). Analogously to bulk materials, the viscoplastic nature can be achieved by different material design routes; specific to interfaces as an extra handle to tune interactions are capillary forces that arise from contact line variations due to e.g. shape or roughness. However, differently than their 3D counterparts, these 2D materials have the advantage of being compressible, which means that we can experimentally interrogate the full tensorial nature of yielding for constitutive modelling. Here, we used both i) flocculated particle interfaces that behave as 2D-gels and ii) dense particle interfaces close to monolayer coverage that resemble glassy systems. By using custom-built interfacial rheology set ups we investigated the transition from linear to nonlinear behavior in both shear and compressional/dilatational deformation modes. We report the main features observed during yielding, for the first time in isotropic compression, and discuss these in relation to designing complex interfaces. In addition, we also propose and verify a simple constitutive model to account for viscoplasticity that can potentially give important insights also for bulk materials.

[1] Beltramo et al, PNAS (2017)

Asynchronous Any Time Virtual VP92

Droplet-based microfluidic tool to quantify viscosity of concentrating multicomponent protein solutions

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Accurate knowledge of the viscosity of concentrated protein solutions is essential for the manufacture and delivery of protein therapeutics. Conventional methods for viscosity measurements require large solution volumes, which is limiting, especially during the early stage of protein development. In this work, a droplet-based microfluidic device is developed to quantify the viscosity of protein solutions using only micro-liters of sample during concentration. Particle tracking is used to probe viscosity allowing for smaller volumes and rapid characterization. The use of an in situ approach during controlled concentration of a solution allows for larger portions of composition space to be characterized during a single experiment. The technique is validated and parameter space is verified using well-studied lysozyme and BSA solutions. Comparison to models for the viscosity of these characterized materials is performed and used to demonstrate the potential of the technique. This approach will allow the impact of different excipients and additives on the viscosity of the protein solutions to be efficiently characterized.

Asynchronous Any Time Virtual VP93

Processing irreversibly adsorbed, solvent-responsive nanoparticles at the oil-water interface

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PEO-coated nanoparticles have been shown to be surface active at fluid-fluid Interfaces. The adsorption of PEO-grafted particles can be controlled by controlling the PEO layer through "salting out" out the PEO with different ionic species. The interfacial properties of solvent-responsive, core-shell nanoparticles can be tuned with interfacial processing. In this work, we compare the impact of changes in PEO solvent quality in the bulk to those for particles already adsorbed at oil/water interfaces. Particles adsorb irreversibly to an oil/water interface from a neat suspension in pure water; interfacial tension ($\gamma \sim 22$ mN/m) and dilatational modulus ($E' \sim 10$ mN/m) of the interface change negligibly as it is processed with pure water or increasing concentrations of salt (in this case Na_2SO_4). At lower surface coverages of the particles (larger γ), interfaces show compressional reversibility. At greater surface coverages (lower γ), large-amplitude compressions result in a complex, nonlinear stress response. For the same interface, the extent of compression required to induce the nonlinear response increases with increasing electrolyte in the bulk. Assuming that this state occurs at the same critical surface coverage for all interfaces, the corresponding decrease in particle size due to the "salting out" of the polyethylene oxide shell is of the same order of magnitude as data from small-angle neutron scattering. The irreversibility of the adsorption and salt-responsive mechanical response of these particles show that this system would be ideal to study interfacial, particle-particle interactions within the context of complex phenomena like wetting or coalescence.

Asynchronous Any Time Virtual VP100

Effect of specific surface area on the rheology of graphene nanoplatelet-filled PEO composites

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As the demand for graphene-based materials increases, rigorous and convenient characterization techniques are needed to adequately describe the properties of graphene and its derivatives, to maximize the benefits of its superior material properties for proposed applications. In addition to conventional characterization techniques, the use of rheology can greatly supplement the information obtained about these nanomaterials in terms of a qualitative correlation with the specific surface area (SSA). In this work, we use rheology to probe the microstructural characteristics of graphene nanoplatelets (GNPs), produced through the thermomechanical exfoliation of graphite, by studying the effect of the specific surface area of GNPs when dispersed within a model polymer matrix - poly(ethylene oxide). The rheological properties of GNPs with four different SSA ranging from 175 to 430 m^2/g were investigated and compared to the starting graphite material. By fitting the complex viscosity data, the aspect ratios of these plate-like fillers were estimated to range from 22 to 83 and 6 to 27, based on the Utracki model and Krieger-Dougherty model respectively, for low to high GNP SSA. The rheological and electrical percolation threshold concentration decreased with increasing SSA, which is attributed to higher filler-filler interactions associated with increasing SSA, leading to the formation of a space-filling network. The yield stress values obtained for high filler content samples upon fitting the complex viscosity data to the Berzin model verify the formation of a percolated filler network. The complex viscosity, elastic and viscous moduli of the samples increased with SSA, demonstrating the enhanced filler-filler and polymer-filler interactions associated with increasing SSA. It was also seen that the enhancement in rheological properties was more dramatic beyond an SSA of 175 m^2/g. Hence, we show that rheology can be a useful bulk characterization tool to quantify the process of graphite exfoliation.

Asynchronous Any Time Virtual VP101

Pickering interfacial photocatalysis of o-Xylene

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Recently, surfactant-free Pickering emulsions have been receiving significant attention in interfacial catalysis. Small droplets in these emulsions can serve as microreactors and can also provide large interfacial area for the chemical reactions. In this study, we exploit Pickering emulsions for interfacial catalysis of o-Xylene via in situ photocatalytic degradation. To this end, commercially available fumed titania nanoparticles are used as Pickering emulsion stabilizers and photocatalysts. The effect of homogenization speed, emulsification time, pH, and oil phase volume on the emulsion properties are first studied. Photocatalytic reactions are carried out in a specially designed experimental setup consisting of small quartz tubes in non-stirring conditions under UV-light irradiation. The emulsified reaction system is observed to result in efficient degradation of o-Xylene compared to conventional catalysis carried out in bulk mode. We believe water-insoluble organic pollutants such as o-Xylene laden wastewater can easily be treated in few hours in an energy-efficient manner with the help of Pickering interfacial photocatalysis.

Asynchronous Any Time Virtual VP102

Analytical modeling of interfacial diffusion for symmetric bilayer entangled polymer films

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This study uses the double constraint release model with chain stretching effect (DCR-CS) to predict the interfacial diffusion for symmetric bilayer entangled polymer films at an iso-thermal condition. The DCR-CS model features double reptation, convective constraints release, and segmental stretching. Polystyrene with two different molecular weights (PS 200K, PS 390K) was used to validate the model prediction of the interfacial diffusion at 130 deg C. By changing the Rouse Weissenberg number in extensional dominant flow from 1 to 20 in extensional dominant flow, the stretching ratio increased from 39% to 93% of the maximum stretching ratio for PS 200K. The stretching ratio varied from 40% to 90% for PS 390K, which has nearly double the molar molecular weight. In the shear dominant flow, the variation of the Rouse Weissenberg number from 1 to 20 caused an increase in the stretching ratio from 26% to 54% of the maximum stretching ratio for PS 200K where the same changes of the Rouse Weissenberg number resulted in the maximum stretching ratio changing from 25% to 54% for PS 390K. Using the obtained values for the transient stretching ratio, the interfacial diffusion values of the polymers in a bilayer configuration were calculated and compared to the values reported for PS 667 in the literature (Qiu & Bousmina, J. Rheol. 43(3),1999). The model predictions for PS 667 showed significant deviations from experimental values. To increase the accuracy of the DCR-CS model predictions, sensitivity analysis for the dependency of the correction function of the reptation relaxation time at the entanglement density was performed. The analysis of the results showed that a substantial improvement could be achieved at the power-law index (n) equal to 2 (0 represents the original DCR-CS model). Furthermore, our analysis of the effect of initial entanglement density on stretching ratio and subsequent interfacial diffusion implies negligible changes in the transient stretching values and the interfacial diffusion.

Poster Session

Symposium PO
Poster Session

Organizers: Gwynn Elfring and Jeff Richards

Wednesday 6:30 Ballroom 1-2-3-4 PO1

Helical locomotion in yield stress fluids

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Microorganism's locomotion is common in various biological environments and affects several aspects of our life, including reproduction, infection and the marine ecosystem. The prime example includes swimming of Helicobacter pylori (H. pylori) in gastric mucus that may lead to ulcer. In the acidic environment of the stomach, gastric mucus exhibits a strong yield stress behavior that protects the stomach from invasion of bacteria. In this work, we investigate the locomotion of a 3D printed helical swimmer in a model yield stress fluid based on crosslinked polyacrylic acid. The swimmer is actuated in a uniform magnetic field via a custom-made rotating Helmholtz coil. We show that below a critical threshold, the helical swimmer cannot propel itself forward in the yield stress fluid and this critical threshold strongly depends on the swimmer pitch angle. In addition, once the swimming is underway, the dynamics of the swimming is strongly controlled by the pitch angle. At low pitch angles, the swimming speed is much smaller than a Newtonian fluid suggesting that the yield stress hinders the swimming. Surprisingly, at larger pitch angles, the swimming speed is much higher than the swimming speed in the Newtonian fluid indicating that yield stress may facilitate the locomotion. We use Particle Image Velocimetry (PIV) to resolve the flow field particularly, the yield surface, around the swimmer at different conditions.

Wednesday 6:30 Ballroom 1-2-3-4 PO2

Can micro-pillared surfaces affect the viscoelasticity and attachment strength of Pseudomonas aeruginosa biofilms?

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A better understanding of bacterial biofilms formation and viscoelasticity is essential for their prevention or control. While biofilm properties are heavily influenced by variety of environmental conditions, the role of modified surface textures and their mechanical properties has been less studied. It is known that surface texture can alter swimming patterns of platonic bacteria. When biofilms have been grown on textured surfaces changes in formation behaviors have been observed. Micro-pillared surfaces have been used to probe internal stresses within biofilms. However, to our knowledge, the effect of surface texture on viscoelasticity has yet to be explored. In this work, we specifically study how micro-pillared surfaces of varying density and size modify viscoelasticity.

Pseudomonas aeruginosa biofilms are grown on the micro-pillared surfaces inside PDMS microchannels. Using a unique fabrication technique, we are able to control both the density and size of the pillars. The growing biofilms are embedded with fluorescent particles which allow characterization of viscoelasticity through multiple particle tracking passive microrheology. Initial results show that at wide densities and pillar sizes, biofilm viscoelasticity at 48 hours is unaffected by the texture surfaces despite changes in formation behavior. However, as spacing decreases greater changes in biofilm viscoelasticity are expected.

Wednesday 6:30 Ballroom 1-2-3-4 PO3

Rheological characterization of Candida albicans fungal biofilms

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Fungi such as *Candida albicans* exist as biofilms that present as viscoelastic materials. Although methods to measure properties such as yield stress, yield strain and moduli have been developed for bacterial biofilms, similar methods are lacking for fungal biofilms. Here we present a method to measure the mechanical rheology of fungal biofilms and then use it to probe differences among mutant strains of *C. albicans*. The methods include a growth protocol appropriate to the long culture times of fungal species (~14 days), and which allows their biofilms to be transferred to the rheometer without morphological disruption. Rheological testing is performed using parallel plate geometry. Gap height, evaporation rate, experimental duration, and sample radius were varied to demonstrate method performance. Small-amplitude oscillatory shear and non-linear creep tests were performed to measure the biofilm's linear elastic (G') and viscous (G") moduli as well as yield stress. For a wild-type strain G' and G" were nearly independent of frequency, with magnitudes of 18,000 ±1100 Pa and 1,700 ±140 Pa, respectively, at a frequency of 1 rad/s. The yield stress, measured by a variable strain amplitude method, was 850 ± 60 Pa. The linear creep response, fitted to a Jeffrey's model gave a characteristic relaxation time of 810 ±19 s and a linear creep viscosity of 8.4 × 10^6 ±1.8 × 10^5 Pa s. The method was used to characterize the rheological properties of three chitin synthase mutants. Comparison of the morphology and rheology of the mutant strains demonstrates that chitin deposition in the fungal cell wall influences the cell shape and rheological properties of the biofilm. The method developed here is generally applicable and its use is important on both a fundamental and practical level because discovering how genotypic, phenotypic, and environmental factors impact the material properties of these microbial communities can have implications for understanding fungal biofilm growth and remediation.

Wednesday 6:30 Ballroom 1-2-3-4 PO4

Surface layer and bulk viscoelasticity of human airway mucus

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The airway surface bi-layer (ASL) lines the respiratory tract, simultaneously trapping inhaled particulates and facilitating their removal from the lung. The ASL consists of a mucus layer on top of the periciliary layer. Mucins, large gel-forming glycoproteins are responsible for the characteristic physical properties of mucus and are critical to its function. Secreted mucins, which possess both hydrophilic glycosylated domains and hydrophobic globular domains, interact with a wide range of proteins and nucleic acids within mucus. The hydrophobic domains: 1) promote self-association in the bulk phase; and 2) make mucins air-surface-active, inducing strong adsorption at the air-mucus interface with formation of a thin, viscoelastic skin layer that effectively separates the mucus layer itself into two distinct layers. Measuring the modulus of mucus using multiple rheometric geometries with varying surface-to-volume ratios, we measure different apparent viscosities with different contributions of surface to bulk. A simple model deconvolutes these contributions, permitting assessment of the bulk and surface properties. Surfactants are shown to reduce the associative interactions of mucins, lowering the overall viscoelastic modulus.

Wednesday 6:30 Ballroom 1-2-3-4 PO5

Biomass microbeads as sustainable rheological modifiers for personal care consumer products

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Plastic microbeads are commonly used as exfoliants and as rheological modifiers to improve viscosity, bulking, and film formation of personal care consumer products (PCCPs). While 95-99.9% of these beads are removed by sedimentation processes during wastewater treatment, trillions of these microplastics enter the environment daily in the US alone. Spherical microbeads made from biomass are a viable alternative to eliminate this source of microplastic pollution, and also present an opportunity for passive environmental remediation via toxin adsorption and capture. We synthesized an array of biomass microbeads by precipitating solutions of microcrystalline cellulose and Kraft lignin dissolved in ionic liquids (ILs) into an anti-solvent. Microbead size, symmetry, and rheological and mechanical properties strongly depend on both formulation parameters (biomass composition, concentration in IL) and processing parameters (nozzle size, anti-solvent, extraction solvent). Lignin incorporation reduced die swelling during processing, affording access to smaller microbeads; however, the Young's modulus of lignin-containing beads obtained via mechanical compression was also reduced. Additional shear recovery experiments on various microbeads in a model detergent system demonstrate that rheological properties can be well controlled by tailoring microbead formulation, which can be used to inform the production of stable and environmentally friendly alternatives to plastic microbeads.

Wednesday 6:30 Ballroom 1-2-3-4 PO6

Using bi-disperse microrheology to measure human mesenchymal stem cell remodeling of hydrogels on multiple length scales

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Hydrogels can improve wound healing by delivering additional cells to aide in the healing process. Human mesenchymal stem cells (hMSCs) are commonly delivered due to their role in coordinating healing. For hydrogels to deliver hMSCs, they must enable migration out of the gel and into the wound. This requires understanding how hMSCs modify rheology across length scales. hMSCs break cross-links using matrix metalloproteinases (MMPs), migrate several microns and eventually degrade the bulk hydrogel. How each scale is remodeled must be considered when designing a scaffold. To measure length scale dependent remodeling and correlate rheology with motility, we use bi-disperse multiple particle tracking microrheology (MPT). Bi-disperse MPT measures Brownian motion of two different sized particles simultaneously to quantify length scale dependent structure and rheology. We encapsulate hMSCs in a poly(ethylene glycol)-based hydrogel that is degraded when cross-links are cleaved by MMPs. We measure three length scales: 0.5 and 2.0 and 4.5 μm. We measure that the 2.0 μm length scale is more remodeled than the 0.5 μm length scale. We identify cytoskeletal tension (CST) as the source of differences in remodeling by inhibiting it and measuring similar remodeling on each scale. We then quantify how hMSCs apply force by measuring if particles have directed motion, measuring that 2.0 μm particles are directed towards specific regions in the field of view while 0.5 μm particles are undirected. Regions where 2.0 μm particles are directed are where force is applied by CST. We measure that 2.0 and 4.5 μm scales are remodeled more than the 0.5 μm scale for the same cellular speed. These results indicate that larger particles are trapped in a partially degraded gel which is pulled by the cell while 0.5 μm particles diffuse through the network. This work measures remodeling across length scales and can improve material design to direct hMSCs to wounds using length scale dependent structure.

Wednesday 6:30 Ballroom 1-2-3-4 PO7

Earwax deters crawling insects and aids in self-cleaning

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The production of earwax among mammals is ubiquitous, but its purpose is still poorly understood. We hypothesize that one of the roles of earwax is to deter insects from crawling into the ear. In this experimental study, we use plate-plate rheometry and creep testing to measure the material properties of human, pig and sheep earwax. We find earwax is viscoelastic, with the elasticity of the human tendon. It also exhibits shear-thinning behavior whose physiologically relevant viscosities range from caulk to corn syrup. Earwax reduces fire ant adhesion, reducing body velocity by a factor of two, and dramatically increasing the chance of slipping during a vertical climb. Exposure to air causes earwax to dry and become brittle, facilitating self-removal once it loses its slippery properties.

Wednesday 6:30 Ballroom 1-2-3-4 PO8

Rheological characterization of electrosprayed inulin-poly(vinyl) alcohol microparticle suspensions for therapeutic applications

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Inulin is a prebiotic fiber that has been used as a dietary supplement in cancer therapy. There is growing interest to administer inulin as encapsulated microparticles as a means of supporting its efficacy. Electrohydrodynamic processing (EHDP) is a commonly used method to produce such nano- and microparticles by applying large electric potentials between polymer solution droplets and a collector plate. Earlier studies have hypothesized that the rheological properties of inulin samples are linked to its therapeutic efficacy. Here, we produce inulin microparticles via EHDP using poly(vinyl) alcohol (PVA) as a supporting polymer and characterize its rheological properties as a suspension in water. The ratio of inulin to PVA and the PVA molecular weight is varied. In the first part of the study, we measure the transient rheology of inulin/PVA and pure PVA particle suspensions over the typical time of digestion (approximately 4 hours). We find that the moduli of PVA particle suspensions reached steady-state after approximately one hour while that of inulin/PVA particle suspensions continued to increase through the experiment duration. We investigate and identify that the source of this time-dependence is primarily driven by inulin. In the second part, we seek to understand differences in the steady-state rheology of these microparticle suspensions vs solutions containing equivalent concentrations of inulin and PVA. Frequency sweep measurements show, in all cases, that the storage and loss-moduli of particle suspensions is 10-fold greater relative to their solution form. Their flow-curve shows strong shear-thinning up to shear rates of 10^2 s^{-1} while the solutions predominately display a plateau viscosity. We attempt to correlate this time dependent rheology, enhanced moduli, and shear-rate thinning to in vitro inulin release studies to better understand how these microparticle suspensions may be used for delayed or continued release of inulin as therapeutic measures.

Wednesday 6:30 Ballroom 1-2-3-4 PO9

Tuning the extent of protein and biofilm deposition on surfaces with liquid layers

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The colonization of abiotic surfaces with living organisms is a complex interaction between the organism, the surface, and the environment that is difficult to untangle. For example, recent work in catheter-associated urinary tract infections (CAUTI) has shown that fibrinogen (Fg) is released during catheterization and deposited on the catheter surface, coating it and forming a platform for colonization by CAUTI-associated pathogens. Yet the extent of the role that environmental Fg plays remains unclear. In this work, we use bio-inspired liquid-infused surfaces to create a system in which the extent of protein deposition, and by extension biofilm formation, can be directly tuned. Control is accomplished by modulating the amount of liquid infused into a permeable polymer bulk, and by extension the amount of liquid presented at the surface. This in turn affects the interaction of the bacteria with the surface, with more bacteria colonizing surfaces where more protein is present. The results demonstrate that liquid-infused surfaces can be a useful tool in untangling complex interactions in the colonization of abiotic surfaces by living organisms.

Wednesday 6:30 Ballroom 1-2-3-4 PO10

Immiscible liquid-coated materials for bioseparations

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Bioseparations, such as liquid and aerosol filtration, are most often performed with the use of porous materials. However, porous materials can be prone to biofouling and other types of surface adsorption. In this work, we present bio-inspired liquid-coated surfaces as a new approach to separation materials that resist fouling. Liquid-coated filters can be created by immobilizing a water immiscible liquid on the surface of commercially available synthetic filtration membranes. By chemically matching the infusing liquid to the filtration membrane, the stable liquid layer that is formed produces a dynamic, mobile surface that resists the adhesion of contaminants. For water purification, 0.45 µm pore diameter

polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) filters were tested using omniphobic perfluoropolyether coating liquids. We measured the continuity of the surface liquid layer by testing how easily a water droplet could begin to move the surface, as well as the anti-adhesion properties of the surface liquid layer through quantifying the speed of droplet movement at a static angle of inclination. The results indicate that the PTFE membranes could sustain a more consistent functional liquid layer, with an approximately 75% lower sliding angle and 70% faster droplet movement at a fixed angle than the PVDF. For aerosol filtration, we tested liquid-coated commercial PTFE and HEPA filters for their efficiency in capturing and releasing aerosolized Escherichia coli for analysis. We determined that bacteria trapped on the liquid-coated filters could be removed with increased efficiency compared to bare controls. The use of liquid coated materials in bioseparations opens new doors for the creation of dynamic filtration strategies.

Wednesday 6:30 Ballroom 1-2-3-4 PO11

Fabrication of vascularized polymers with fugitive ink 3D printing

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Nature relies on vascular systems to permit chemical communication between the surface and underlying tissues of an organism. In this work, we replicated such bi-directional communication in polymeric hydrogels to create a non-living system with similar properties using a technique known as fugitive ink 3D printing. Fugitive ink 3D printing utilizes a sacrificial component that can be easily removed from the system by altering a physical characteristic such as temperature, pH, etc. For fabricating these vascularized polymers, the co-block polymer Pluronic F127 serves as an excellent filament due to its change in viscosity from a paste-like state at higher temperatures (30°C) to a liquid-like state at lower temperatures (4°C). Vascularized polymers were fabricated in three steps. First, paste-like Pluronic F127 was printed in the desired pattern at higher temperatures. Next, a molten hydrogel was poured over the pattern and allowed to cool to lower temperatures. Lastly, the liquid Pluronic F127 was evacuated from the polymer via vacuum suction. Preliminary tests on the resulting vascularized polymers showed that a test signal (dye) placed at the surface could be collected after diffusing through to a carrier liquid placed in the vascular channels at concentration in agreement with theoretical models. Tests with E. coli as a model living system showed that the bacterial cells could be spatially and temporally controlled at the surface by introducing antibiotics into the vascular channels. This work lays the foundation for the fabrication and use of vascularized polymers as a means to permit chemical communication between a living surface layer and an external user.

Wednesday 6:30 Ballroom 1-2-3-4 PO12

No sagging, no cry

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We test hypotheses of rheological property requirements and sensitivities for direct ink write 3D printing of suspended lattice structures, motivated by the fabrication of implantable scaffolds for bone regeneration after fracture. We focus on gravitational sagging of extruded end-supported horizontal cylinders and experimentally explore shape retention as a function of yield stress, complex moduli, thixotropy, and extensional viscosity. The primary component of the ink formulations is hydroxyapatite (HAp) particles (2-5 micron diameter) which is the main mineral of bone. Additionally, inks contain particles of polymethyl methacrylate (PMMA, sized 10-15 microns to create porosity), and polymeric components hydroxypropyl methylcellulose (HPMC, derivative of cellulose molecules), polyacrylic acid (PAA), and polyethylenimine (PEI); the latter two being polyelectrolytes that serve as electrostatic binding agents. A custom-built 3D printer, equipped with a laser scanner, is used for quantitative analysis of the interplay between ink rheology and sag to arrive at a rheology-sag-resistance map. This map will assist in ink design to achieve higher cell penetration within tolerable sagging distance and serves as a guide to other direct-write 3D printing processes to consider the sensitivity of shape retention to rheology beyond just the yield stress.

Wednesday 6:30 Ballroom 1-2-3-4 PO13

Coalescence of passively trapped droplets in a microfluidic device with and without confinement

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The dynamics of coalescence of droplets can enlighten fundamental physics of emulsion stability. For surfactant-stabilized emulsions, the presence of heterogeneity (solid surface, particles, bubbles etc.) can greatly change the time scales for coalescence. We investigate the coalescence of two droplets, one of which is in adherence to a solid surface. A microfluidic chip with droplet generator and a passive hydrodynamic trap is fabricated. The T-junction generates micron-sized water in oil droplets that travel downstream and are trapped by the hydrodynamic forces. The continuous generation of droplets ensures a series of coalescence occurs at the trap. This is captured using a high-speed camera and the images are analyzed to measure the film drainage time and incoming velocity. The concentration of surfactant and the degree of confinement is also varied, and coalescence is quantified as a function of non-dimensional film drainage time, surfactant concentration, and capillary number.

Wednesday 6:30 Ballroom 1-2-3-4 PO14

Simultaneous characterization of thermophoresis and fluid properties using multiple particle tracking microrheology

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Thermophoresis is the phenomenon that particles in a fluid migrate in a temperature gradient. Until now, no agreement has been found on the underlying physics of thermophoresis, however applications utilizing thermophoresis are numerous. A particularly important application is bioseparations. The work presented here characterizes fluids in a microfluidic device to simultaneously measure thermophoresis of dispersed fluorescent tracer particles and rheological properties of the continuous phase using multiple particle tracking microrheology (MPT). MPT measures the Brownian motion of the embedded probe particles and relates this to rheological properties. We develop a method to characterize the unidirectional motion induced by a 1D thermal gradient (parallel to the channel walls) and at the same time, perpendicular to the thermophoretic motion, tracer particles undergo independent Brownian motion, enabling MPT. Using MPT, the one-dimensional particle mean-square displacement is measured enabling the calculation of the diffusion coefficient and the temperature-dependent fluid viscosity. The thermophoretic motion is characterized by quantifying particle velocity and calculating the thermal diffusion coefficient. A better understanding of the relationship between thermophoresis and material properties will allow for optimization of microfluidic devices designed for effective and efficient bioseparations. A timely application is the advancement of devices used for viral diagnostic tools, enabling the implementation of thermophoretic enrichment methods for virus detection.

Wednesday 6:30 Ballroom 1-2-3-4 PO15

The rheology of methane and carbon dioxide hydrates at extreme high pressures

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Gas hydrates have been an active research topic due to their occurrence in the oil and gas industry. As a result, much of the body of knowledge focuses on water-in-oil emulsion gas hydrate systems. Recently, however, technologies that take advantage of gas hydrate properties have sparked new research motivation. Most of these technologies require flow systems and do not involve oil-based systems. Based on these facts, the need for the characterization and elucidation of the shear rheology of gas hydrate systems from pure water systems is apparent. This study explores pure water hydrate systems of methane (CH4) and carbon dioxide (CO2) at pressures between 0 and 30 MPag. The viscosity of the system was measured at a constant shear rate and at temperatures between 0 and 10?. The effect of temperature on the viscosity of CH4 hydrate systems was one order of magnitude larger than the pressure effect on viscosity in most of the pressure range. The pressure effect on the viscosity of CO2 hydrate systems was up to one order of magnitude larger than that of the CH4 hydrate system, likely as there was more gas present in solution due to CO2's higher solubility in water. The time to reach maximum viscosity in CH4 hydrate systems was found to decrease by at least a factor of two as pressure increased from 10 to 15 MPag. Several systems with high driving forces for hydrate formation did not form gas hydrates within the 24-hour timeframe. These driving forces were up to 4.1 MPag and 2.07 MPag for the CH4 and CO2 systems, respectively. The key system limitations to the formation of hydrates were categorized as either arising from kinetic, diffusion, and/or heat effects. The presented data and analysis are a significant contribution to the currently sparse characterization of high pressure-low temperature shear rheology of these energy materials, which is crucial to the design and development of new technologies that make use of gas hydrate properties.

Wednesday 6:30 Ballroom 1-2-3-4 PO16

Use of thermal analysis and rheometry to study the properties of crude oil

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Crude oil is typically extracted as a single organic liquid phase from the reservoir. However, during transportation, a drop in the temperature can cause the higher molecular weight paraffins or waxes to separate into the solid phase. The temperature at which the first wax crystals appear during cooling is commonly known as the wax appearance temperature (WAT). Once below the WAT, the crude oil can form a gel-like structure. Breaking down this structure to restart and maintain flow may often require energy- and cost-intensive approaches. This poster will focus on characterizing crude oil and related fuels using thermal and rheological analysis at different temperatures above and below the WAT in the context of flow assurance. The thermal analysis section will focus on Modulated DSC ® (MDSC) as a technique to measure WAT with improved sensitivity and reduced supercooling. The rheometric studies comprise of viscosity measurements above the WAT, rheological changes during outwaxing (through flow, oscillation and OSP), and yield stress measurements below the WAT. Note: Modulated DSC ® is a registered trademark of TA Instruments.

Wednesday 6:30 Ballroom 1-2-3-4 PO17

Exploring secondary flows while building high-fidelity tools for complex viscoelastic behavior in precision manufacturing

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Secondary flows driven by viscoelasticity in irregular ducts are revisited with the aim of creating effective tools for multilayer extrusion. Efficient 2.5D calculations of single and multi-mode Giesekus and Phan-Thien-Tanner constitutive models detail the development of corner flows in rectangular channels; with the capacity to explore full 3D simulations. This is a starting example in the building of these tools upon high fidelity open-source codes in providing key information for process development and design. The knowledge discovery enabled by tailored computational tools can be indispensable to accelerated precision grade multilayer manufacturing. More generally, throughout the process steps of transport, distribution, coating or film formation, and solidification, 2.5D and similar viscoelastic computations can provide key insights into secondary flows, elastic flow instabilities, and other anomalies. Application to rolling bank coating flows and other recirculating patterns is underway. As a result, material characteristics and process remediations that enhance or diminish the defect-causing instabilities or secondary flows can be detailed as part of processing development and design.

These examples are offered as a means of bringing fundamental rheology knowledge to process practitioners where it can be combined with experiential process knowledge to accelerate high-fidelity manufacturing. The computational model bridge between rheological research and manufacturing process design advantageously becomes an integral part of the iterative procedure of model hypothesis and verification towards customized knowledge discovery for optimal process design, operability, and window of control information.

References:
Yue, Dooley, Feng, "A general criterion for viscoelastic secondary flow in pipes of noncircular cross section," J. Rheol. 521 (2008).
Holmes, Fa´vero, Osswald, "Modeling Viscoelastic Secondary Flows in Three-Dimensional Noncircular Ducts,", PE&S 52(8) (2012).

Wednesday 6:30 Ballroom 1-2-3-4 PO18

Elastic instabilities in confined geometries

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Polymeric flow through confined geometries is relevant in industrial applications such as enhanced oil recovery, microbial mining, groundwater remediation, and biological processes such as drug delivery, particles and cells transport during respiration and fertilization. Large elastic stresses induced due to confined geometries lead to elastic instabilities in the viscoelastic flows. We study viscoelastic instabilities in the confined geometries made of series of expansion-contraction obstacles and cylinders. The accumulation of polymeric stress as polymeric chains advect through closely placed obstacles creates strands of high polymeric stress. These strands act as a barrier for the flow crossing the regions, which leads to flow separation and formation of multiple flow states. The formation of strands of polymeric stress regulates the macroscopic transport of fluid and particles in realistic porous media.

Wednesday 6:30 Ballroom 1-2-3-4 PO19

Oreology: Fracture and flow of “milk’s favorite cookie”

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Understanding the flow behavior of food ingredients and products has widespread impact on economies of production, public health, and individual diets. Though unstudied compared to starches, doughs and condiments, sandwich cookies present an ideal model of parallel plate rheometry, in which a fluid sample (the cream) is held tenaciously but temporarily between two parallel plates (the wafers). When the wafers are counter-rotated, the cream deforms, flows and fractures, leading to separation of cookie halves. To address this gap, we introduce Oreology (/?ri?'?l?d?i/), from the Nabisco *oreo* for "cookie" and the Greek *rheo logia* for "flow study," as the study of the flow and fracture of sandwich cookies. We measure linear and nonlinear mechanics of the eponymous oreo and probe the dependence of post-mortem cream distribution on the kinematic protocol used to separate wafers. A bespoke 3D-printed fixture (PLA; Ender 3) holds wafers on a DHR3 rheometer with a rubber band-powered clamp to transfer torsion without cracking brittle wafers.

Results show adhesive failure in which nearly all (95%) cream remains on one wafer after failure. We ascribe this to the production process, as we find that the cream-heavy side is uniformly oriented within most boxes of oreos. The full failure event has elasto-visco-plastic nature, with a linear elastic modulus of 110kPa, yield stress of 10kPa and yield strain of 10%, followed by cream rupture at 30% failure strain. Mechanics are independent of rate and direction, and consistent for Original, Double and MEGA Stuf cookies and for Golden and Dark Chocolate varieties. However, failure can be altered when the cream is reflowed to promote adhesion/soften cream, such as by moderate heating (>30°C or ~12s in a microwave), after which cream splits more evenly by cohesive failure. Future studies may examine other sandwich-variety cookies, such as custard creams, macarons, and ice cream sandwiches. At-home tests are encouraged to contribute to this incipient field of study.

Wednesday 6:30 Ballroom 1-2-3-4 PO20

Shear banding and wall slip in polymer wormlike micelles

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Shear banding, the separation of flow into distinct regions of structure and viscosity, is well- studied in wormlike micelles (WLMs) and often accompanied by some degree of wall slip, a phenomenon where the velocity of a fluid at moving surface is less than the solid boundary. Despite their frequent association, the role of wall slip in shear banding instabilities is still not fully understood. Some work suggests wall slip is only present at early times in the evolution of the shear bands whereas other work has shown prolonged wall slip. To better understand the relationship between these phenomena, we use a model system of WLMs exhibiting slow dynamics, formed from triblock poloxamers with polyethylene oxide (PEO) end blocks and polypropylene oxide (PPO) midblocks. Previous work on poloxamer WLMs established the clear presence of wall slip across a range of shear rates. As shear rate increases, the flow transitions from a region with only wall slip to both shear banding and wall slip, but the criteria governing this transition is unclear. Here, the interplay between shear banding and wall slip is studied via a combination of rheology and particle tracking velocimetry. Concentric cylinder geometries with varying inner cylinder radii and surface finishes are used to access conditions with varying wall slip. Additionally, using prior knowledge of the variation of poloxamer WLM structure and properties with temperature, material relaxation time is tuned, probing the impact of the WLM relaxation time on wall slip and banding as well. The interplay of wall slip and shear banding across the range of geometries and relaxation times examined here provides new insights on the role of wall slip on shear banding instabilities.

Wednesday 6:30 Ballroom 1-2-3-4 PO21

Shear banding in poloxamer wormlike micelles (WLMs) with slow dynamics

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Shear banding is a flow instability where, beyond a critical stress or shear rate, a homogeneous fluid flow separates into distinct regions or "bands" of viscosity and underlying structure. Although shear banding has received considerable attention, the mechanism of shear band formation is unclear. Suggested mechanisms in literature include nucleation and growth and disentangle-re-entanglement, but the criteria for selecting one mechanism over another for a given material and flow are unknown. We explore these mechanisms by studying the shear banding evolution of wormlike micelles (WLMs), the archetypical system for these instabilities, across a variety of flow conditions. Here, long, entangled micelles are composed of triblock poloxamers with polyethylene oxide (PEO) end blocks and polypropylene oxide (PPO) midblock, which rearrange and break on slow timescales (t~3000 seconds). As shear bands are localized structures that vary in both space and time, we use a combination of time-dependent nonlinear rheology and spatiotemporal flow small angle neutron scattering (flowSANS) to characterize shear band formation and evolution. The slow dynamics of this system increase the temporal resolution of shear band development relative to the relaxation time, providing new insights on the microstructural evolution of both transient and steady state shear bands. The mechanism of shear band formation in these systems is a function of applied shear rate, where transient shear banding appears to follow the nucleation and growth mechanism, while steady state shear banding follows the disentangle-re-entanglement mechanism. These differences in mechanism help to distinguish transient and steady state shear banding.

Wednesday 6:30 Ballroom 1-2-3-4 PO22

Droplet-on-fiber: Rheological assessment

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The goal of this study is to manufacture and characterize droplet-on-fiber through a dipping process. The withdrawal of the fiber from a liquid solution will result in a coating due to the balance between the viscous drag and the capillary rise. The thickness of the layer depends upon various parameters of the fluid (viscosity, dynamic modulus, solid loading, surface tension) and dipping process (withdrawal speed, fiber material and diameter). Above a threshold thickness, hydrodynamic instability will trigger the formation of droplets. Controlling the process parameters will determine the liquid volume in the droplet and its morphology. Such a facile droplet formation technique will be less resource intensive than existing methods and can produce droplets of various sizes and shapes in a short amount of time.

This work investigates hydrogel droplet formation for biomedical application, which is a commonly used biocompatible material. Extruded polylactic acid (PLA) fiber is considered as the substrate for droplet adherence. Crosslinking agent is sprayed after fiber withdrawal to facilitate the gelation process which will create a robust gel spheroid. The focus of this study is on the shape fidelity and reproducibility of the droplet formation by varying the dipping fluid composition. The aspect ratio between droplet diameter and wetting length is defined as a quantifiable shape-fidelity index which is reported in this work. By varying the dipping fluid composition, the relationship between the viscosity of the dipping fluid (alginate) and the PLA fiber can be identified. The observations made throughout this study will allow for further development of this dipping process, as well as determine the optimal concentration of alginate to achieve reproducible droplets with the desired morphology for cell spheroid formation.

Wednesday 6:30 Ballroom 1-2-3-4 PO23

Introducing the role of brittility to the soft materials

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Many soft materials show the transition from solid-like behavior to liquid-like behavior, but how this yielding transition occurs can vary significantly. Understanding the physics behind this transition is of great interest for the behavior of biological, environmental, and industrial materials, including those used as inks in additive manufacturing. For some materials, the yielding transition is smooth and gradual while others yield abruptly. We refer to this abrupt yielding as being "brittle". The key signatures of brittle yielding include a stress overshoot in steady-shear-startup tests and a sharp increase in loss modulus during oscillatory tests. We are able to account for brittility in our recently proposed continuum model for yield stress materials (Kamani et al., Phys. Rev. Lett. 126, (2021)). The original formulation of the model describes the unrecoverable plastic viscosity as being dependent on the total strain rate; plastic flow is aided by the rate at which elastic deformation is acquired. We account for brittility by modifying the contribution of the recoverable component to the total strain rate, which impacts the rate at which yielding occurs. The model results are successfully compared to results of different rheological protocols from a number of model yield stress fluids having different microstructures, indicating the general applicability of the phenomenon of brittility for such soft materials. Our study shows that the brittility of soft materials plays a critical role in determining the rate of yielding transition, and provides a simple tool for understanding its effects under various loading conditions.

Wednesday 6:30 Ballroom 1-2-3-4 PO24

Measurement and prediction of oozing in PSAs

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Pressure-sensitive adhesives (PSA), which are a key component of graphic labels, tapes, medical dressing and a wide range of other applications, are soft and highly viscoelastic making them conformable to deformation and pressure. While this property is critical to achieving tackiness and improving processability of PSAs, one of the biggest disadvantages is that they are prone to creeping flows, i.e. increasing deformation with time under pressure. In the graphic and label industry, roll-side oozing of the adhesive can occur at various stages like during the lamination process, die-cutting or matrix stripping operations, or on laminates under storage in abnormal temperatures or humidity (based on geographic location). As this can cause serious problems with processing disruption and final application, there is a need for a reliable method to predict the creeping behavior of PSAs under different temperatures, relative humidities and pressures to provide proper guidance for material handling. In this poster, we present a systematic approach of experimental and mathematical modeling to characterize and predict the viscoelastic behavior of PSAs under different conditions of roll pressure and temperature. Using compression creep and linear oscillatory shear rheology, we build a master curve for different pressures and temperatures that is then fitted with a linear viscoelastic model. To test the effect of different surface friction from the backing liner and facestock, we design a custom compression test of a disk shaped sample whose deformation profile is captured on a video camera. Using a finite element model and a semi-analytical approximation of the mechanics of ultra-thin laminates over a large domain, the measured bulk adhesive rheology is used to systematically analyze level of oozing under the effect of different surfaces. The method developed here will be highly useful as guidance for storage and processing conditions in manufacturing plants for existing and new PSA formulation.

Wednesday 6:30 Ballroom 1-2-3-4 PO25

Characterizing rheological behavior of dispersions and paints using Orthogonal Superposition

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Viscoelastic properties of dispersions and weak structured fluids can be investigated using Superposition techniques. In Orthogonal Superposition (OSP), the material undergoes a small amplitude oscillation in the axial direction, orthogonal to a rotational steady shear. OSP can also be used to perform 2D oscillation, in the axial and radial direction. OSP techniques provide valuable information about the change in material structure under shear such as the relaxation time, structure orientation, and thixotropy of the samples without conducting extra tests. Paints, for instance, exhibit complex rheology behavior under shear to achieve demanding performance requirements - brushing, spreading, avoiding drips, surface leveling, etc. Being interested in performance during painting process, paint industries can use OSP to measure storage and loss modulus under the same shear rates used during painting. Therefore, the OSP data can be used to establish a new relationship between the formulation, the change in the microstructure, and the performance of dispersions. In this study, multiple structured fluids were investigated to highlight the potential applications of the OSP technique. The orthogonal measurements are presented in conjunction with both steady shear and oscillatory viscosity measurements in a modified Double Walled Couette geometry.

Wednesday 6:30 Ballroom 1-2-3-4 PO26

Characterizing yield using Orthogonal Superposition under controlled shear stress

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Orthogonal Superposition (OSP) is a rheological technique for characterizing viscoelasticity under non-linear flow conditions. Previously used to map changes in microstructure as a function of shear rate, OSP can now be performed under controlled shear stress, in addition to shear rate.

Stress-controlled OSP provides a novel approach to investigate "Yield Stress," traditionally characterized using either steady shear, or oscillatory rheology. Steady-shear rheology provides an indication of stress needed to achieve bulk flow, but is fundamentally limited to conditions beyond the initial yield, and lacks insight into viscoelasticity. Oscillatory measurements into the non-linear regime (LAOS) probe structural changes under deformation, but do not replicate the same shear history a sample encounters in its end-use application. OSP combines SAOS and steady shear stress for direct observation of viscoelastic behavior before, during and after yield. Thixotropic effects can also be observed under shear stress, to improve insight into yield stress as a time-dependent phenomenon.

Wednesday 6:30 Ballroom 1-2-3-4 PO27

Temperature controlled droplet-based extensional rheometry for characterizing thermoresponsive materials

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Understanding the extensional rheology of polymer solutions is essential for determining the sprayability and printability of a wide range of industrially relevant materials such as coatings, printing inks, and agricultural sprays. However, solution extensional rheology remains challenging due to instrumentation constraints. Recently, Dripping-onto-Substrate (DoS) extensional rheometry has enabled the characterization of low viscosity ($\eta_0 < 20$ mPa·s), low elasticity ($\lambda_E < 1$ ms) fluids without major pre-deformation, which can disrupt test fluid microstructure. However, to date, DoS measurements have been limited to ambient conditions. In this work, we develop temperature controlled DoS rheometry for the first time and demonstrate its utility by characterizing the temperature-dependent extensional behavior of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (Poloxamer 234, P234) in 0.9 M NaF solutions as a model system known to exhibit a pronounced thermal response. To enable heated DoS measurements, we built a custom temperature control chamber in which the nozzle, substrate, and enclosure are heated with custom PID controllers. At room temperature (T = 23 °C), P234 solutions are composed of spherical micelles and exhibit inertiocapillary (IC) behavior in DoS measurements. Above the sphere-to-rod transition temperature (29 °C), the spherical micelles elongate into cylindrical micelles, which continue growing with increasing temperature. Heated DoS measurements of P234 reflect this structural change; as temperature is increased, break up times increase and IC behavior transitions towards viscocapillary behavior. Above 32 °C, the formation and growth of rods also results in elastocapillary behavior. The new temperature control capabilities presented herein add key capabilities to DoS measurements, broadening the range of materials and processing conditions this technique can be used to study.

Wednesday 6:30 Ballroom 1-2-3-4 PO28

Improving analysis methods for Dripping-onto-Substrate (DoS) extensional rheology measurements

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Dripping-onto-Substrate (DoS) extensional rheology can be used to measure the capillary-driven thinning of a variety of fluids, including polymer, micellar, and protein solutions. The thinning of a liquid bridge is recorded by a high-speed camera, and custom scripts convert images to the minimum radius profile which can then be fit to obtain extensional rheological properties. However, data analysis methods for DoS may be inconsistent or visually-based, which makes analysis prone to human error. For example, trials can have considerable variation in symmetry of the filament and contact angle on the substrate. Additionally, visual selection of the startpoint frame can dramatically change the total break-up time, adding uncertainty when comparing trials. While these subtleties may be less important for fluids exhibiting elastic-like behaviors, these issues are non-trivial when analyzing low viscosity and low elasticity fluids. In this work, we develop metrics for assessing quality of DoS measurements, and analyze correlations between parameters such as symmetry, contact angle, and aspect ratio. Our automated scripts can detect patterns in liquid bridge images, automatically determine the thinning startpoint, and give quantitative metrics for parameters like filament symmetry. By incorporating automated data analysis and quantitative metrics to analyze data quality, more consistent measurements and analysis between DoS trials are obtained.

Wednesday 6:30 Ballroom 1-2-3-4 PO29

Tandem NIR/rheo cure monitoring of chemical conversion and rheology

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NIR data can successfully be obtained from a coating curing on a rheometer plate, enabling simultaneous collection of both spectroscopic and rheological data and allowing for direct correlation of key rheological figures of merit with chemical conversion. By combining NIR with cure rheology, we were able to obtain new insights into the relationship between chemical conversion and rheological behavior for a demonstration coating system, particularly as a function of cure temperature.

Wednesday 6:30 Ballroom 1-2-3-4 PO30

High temperature dynamic mechanical analysis of glass and damascene steel in flexure mode up to 950 °C

Matthias Walluch[1], Daniela Ehgartner[1], Abhishek Shetty[2], Christopher Giehl[3], and Denis Schuetz[1]
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Dynamic mechanical analysis (DMA) is a powerful method to characterize viscoelastic properties and phase transitions for a wide range of materials. Currently, it is mainly used to characterize polymers via determination of storage and loss moduli (E or G) to investigate the effect of temperature and to detect transitions of the mobility on a molecular level (e.g. the glass transition temperature). While production and application temperatures for polymers are usually limited to several hundred degrees, material properties of glasses and metals require characterization at temperatures exceeding 600 °C. This contribution introduces a modular setup based on Modular Compact Rheometer (MCR), linear measuring drive and convection temperature device which enables the characterization of materials at temperatures up to 950 °C. Application examples are presented to show the use of DMA in flexural mode (three-point bending) on glass and damascene steel (with the typical complex, layered laminate structure). The results provide data on stiffness, damping properties, inner structure and softening as affected by temperature. DMA on glass reveals the effect of the oscillatory frequency on the material's properties. The temperature of softening and other viscoelastic features experiences a significant shift when changing this parameter. This underlines the advantage of DMA for material characterization and process optimization. Further, it highlights its strength compared to other thermo-analytical methods like Dynamic Scanning Calorimetry (DSC), where only static conditions can be simulated. In case of damascene steel, DMA enables to track the hardening and tempering curves of both the individual steel components and the complex layered laminate, thus providing an TTT diagram of the laminated material. Further, using different cuts (orientations) of the laminate it is possible to understand how the microlayers of the two steels interact in regards to their complex moduli and phase transitions.

Wednesday 6:30 Ballroom 1-2-3-4 PO31

Shear cessation in the pre-yielding and post-yielding of dense soft solids

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A range of soft materials, including foams, emulsions, and microgels, exhibit a transition between solid-like and liquid-like deformation behavior as the applied deformation is increased beyond some threshold. This transition from elasticity to flow is known as yielding, and the way in which it progresses is of great practical importance in many engineering applications. Here, we simulate the steady shear startup of a non-Brownian jammed suspension, whose flow curve is described by the Herschel-Bulkley form. The transient behavior of our material shows a stress overshoot followed by a steady shear plateau. Throughout this transience, we perform an iterative series of flow cessation simulations as the strain increases to probe the progression of yielding. This is accessed through the resulting stress relaxation behavior of this suspension at each point in time. We find that the material is able to relax a greater percentage of its shear stress as it goes through yielding, indicating that the material has become more favorable to the acquisition of unrecoverable strain, as the shear cessation tests hold the total strain constant. We find the stress relaxation curve fits a stretched exponential form, and can extract a time scale (τ_σ) accordingly. The maximum value of τ_σ occurs before the system yields or stress overshoot, which may indicate the onset of shear banding. We show the differences in the material microstructure at the onset of shear banding and the steady-state using the particle displacement distributions. We also study the dependence of τ_σ on shear rate, age of the sample, and system size. Further, we compare our simulation results with that of experiments on Carbopol to identify a critical shear rate above which the main dissipation in the system is due to plastic rearrangements and/or solvent viscosity.

Wednesday 6:30 Ballroom 1-2-3-4 PO32

On extrapolation of dynamic data to obtain the limiting steady-state compliance

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From linear viscoelasticity, it is known that the steady state recoverable shear compliance $J_{e,0}$ for viscoelastic fluids can be found from dynamic data. In using this relationship, the two limiting values η_0 and G'/ω^2 are needed, both of which will have error-often significant error. These relative errors add in calculating $J_{e,0}$, which severely reduces the value of the method. An obvious and useful fix for viscoelastic fluids is to substitute G''/ω for η_0 giving the easier problem of finding the limit of $G'/(G?)^2$ at zero frequency. Better yet, it appears that many of the empirical relationships used for finding η_0 are suitable for this extrapolation, as will be shown using data over ~5 decades of frequency for three polymer melts.

Wednesday 6:30 Ballroom 1-2-3-4 PO33

Time-resolved microstructural changes and macroscopic sequence of physical processes in large amplitude oscillatory shear of model soft gels

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The flow and deformation behavior of soft particulate gels are incredibly useful due to their ability to reversibly yield, i.e. transition between solid-like and fluid-like behavior, when sufficient deformation is applied. While the microscopic dynamics and macroscopic rheology of these systems have been studied separately in detail, the development of direct connections between the two has been difficult, particularly with regard to the non-linear rheology. To bridge this gap, we perform a series of large amplitude oscillatory shear (LAOS) numerical measurements on model soft particulate gels at different volume fractions using molecular dynamics simulations. In the model, particles interacting with a combination of a two-body short-range attraction, and a three-body bending stiffness term spontaneously self-assemble into disordered network of soft gels at relatively low volume fractions ($\varphi<20$ %).

To capture the constitutive physics occurring in the nonlinear rheology of the gels, we utilize the sequence of physical processes (SPP) framework to define time-resolved dynamic moduli. By tracking the changes in these moduli through the period, we can distinguish transitions in the material behavior as a function of time. Our goal is to establish the microsopic origin of the non-linear rheology by connecting the changes in dynamics moduli to the corresponding microstructural changes during the deformation including the non-affine displacement of particles, and the breakage, formation, and orientation of bonds.

Wednesday 6:30 Ballroom 1-2-3-4 PO34

Comparison of sequence of physical processes and Chebyshev decomposition methods to evaluate and interpret large amplitude oscillatory shear (LAOS) response of hard, soft and semolina flour dough

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Wheat flour doughs have unique viscoelastic properties strongly depend on the origin of the flour, protein content, gliadin/ glutenin ratio, mixing condition. In this study, the nonlinear viscoelastic rheological properties of dough samples originated from hard, soft and semolina wheat flours are compared. These dough samples have been selected because they have specific applications like cake, bread, and pasta etc. LAOS measurements have great potential to mimic mixing and manufacturing processes including large and rapid deformations. Chebyshev decomposition and sequence of physical processes methodologies are utilized to extract meaningful quantitative measures from complicated nonlinear stress response. Three different dough samples were prepared by mixing semolina, hard and soft wheat flour with deionized water in a 300 g of Brabender Farinograph bowl at 30 °C according to AACCI method 54-21. Each flour dough samples have brought to 500 BU line and all dough samples are taken out from the farinograph at dough development time. The parallel-plate geometry of the DHR-3 rheometer was used in the strain range of 0.01%-300% at a frequency of 10 rad/s. The Fourier transformation of the raw oscillations, their reconstruction, the Lissajous curves and non-linear LAOS rheological parameters were obtained using the TRIOS software of TA instruments. The extraction of transient moduli and analysis of sequence of physical processes are done by Matlab and SPP-LAOS freeware. In the nonlinear viscoelastic region where the applied strain is large, stiffening ratio($S>0$) and thickening ratio ($T<0$) suggests that all of the yogurt samples exhibit strain stiffening and shear thinning behavior. SemD samples showed the highest resilience with higher yield strain due to its higher protein quality than that of hard and soft wheat dough samples. Higher dough strength of SemD sample has been attributed with glutenin content and the ratio of HMW/LMW.

Wednesday 6:30 Ballroom 1-2-3-4 PO35

How to make medium-amplitude oscillatory shear stress (MAOStress) measurements

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We report the first-ever complete measurement of MAOStress material functions, using PVA-Borax, a transiently crosslinked polymer network, and a stress controlled rheometer having an electronically commutated (EC) motor. Moreover, we outline experimental limit lines and their dependence on geometry and test conditions. These MAOStress measurements enable us to test theoretical interrelations between MAOStress and MAOStrain material functions derived by Lennon et al.[1]. Using our previously published MAOStrain data of PVA-Borax[2], we find good agreement between the inter-relation prediction and our measurements. Similar to the benefit of linear viscoelastic interrelations, we show how this weakly-nonlinear interrelation is useful for extending experimental accessibility and providing corroborating evidence for credible MAOStress and MAOStrain, which reveal material physics beyond linear viscoelasticity but at weakly-nonlinear conditions that are accessible to theory and detailed simulation[3].

[1] K. R. Lennon, G. H. Mckinley, and J. W. Swan, "Medium amplitude parallel superposition (MAPS) rheology . Part 1?: Mathematical framework and theoretical examples," J. Rheol., vol. 551, no. 64, p. 551, 2020. [2] N. A. Bharadwaj, K. S. Schweizer, and R. H. Ewoldt, "A strain stiffening theory for transient polymer networks under asymptotically nonlinear oscillatory shear," J. Rheol., vol. 61, no. 4, pp. 643-665, 2017. [3] R. H. Ewoldt and N. A. Bharadwaj, "Low-dimensional intrinsic material functions for nonlinear viscoelasticity," Rheol. Acta, vol. 52, no. 3, pp. 201-219, 2013.

Wednesday 6:30 Ballroom 1-2-3-4 PO36

Protorheology: Visual evidence and inference

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Protorheology [1] is the first thing we all do to assess rheological properties: poke, stir, stretch, squish, scoop, drop, or simply observe flow and deformation in a natural setting. However, the link between these observations and specific rheological properties is not always clear, and rarely quantified. Yet, a wealth of insight is possible from these simple observations, including estimates of viscosity, critical stress for nonlinearity (e.g. yield stress), elastic modulus, creep compliance, relaxation time, normal stress difference, extensional viscosity, thixotropic timescales, and more. Here we survey and compare protorheology flow scenarios and some common index tests to outline (i) how to map photo and video observations to evidence of different rheological phenomena and (ii) how to quantitatively infer rheological properties (understanding limitations), from the most useful and common observations. We argue for increased use of documented visual evidence and quantitative inference alongside reported rheological properties. This approach benefits the researcher by providing insight for choosing rheometric test conditions and provides important

corroborating evidence for interpreting measured rheological properties and the assessment of bad data. Additionally, we outline how these methods compose a collection of recipes for "do-it-yourself" rheometry that is useful for coursework and instruction prior to, or in the absence of, access to rheometers, with examples from the University of Illinois Urbana Champaign during the Spring Semester of 2020.

[1] We could call this many things. We choose the term *protorheology* from *proto* (first in time) which evokes related usage in the terms *prototype* and *protohuman*. These are things not fully formed, and with limitations, but from which much can be learned.

Wednesday 6:30 Ballroom 1-2-3-4 PO37

Psychorheology through transient recovery rheology: Importance of timescales

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Consumer products such as food, cosmetics, toys, or other devices rely on having a viscoelastic behavior that is pleasant on the senses. However, the relation between the perception of soft materials and their physics, also known as psychorheology, is not well understood, and materials are often developed through trial-and-error rather than designed by rheology. In this work, recovery rheology is used via a series of creep and recovery tests to decompose measured strains into a recoverable and unrecoverable component. These tests allow us to build a transient view of traditional rheological metrics. The metrics are tracked with respect to two independent time axes - a creep time and a recovery time. Instantaneous material properties are examined and found to rapidly change at short times, suggesting that timescales are the most important aspect of human perception. The methods in this work provide a basis for finding relevant psychorheological measures, in contrast with typically used steady-state measures that are often inadequate in capturing the realities of perception.

Wednesday 6:30 Ballroom 1-2-3-4 PO38

A complete rheological formalism built on the concept of recovery

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Many rheological formalisms come from the concepts of inelastic fluid dynamics where deformations are always unrecoverable. We build a new formalism based on the ideas of recovery, which are ubiquitous in viscoelastic fluids. Our new formalism contains two contributions to arbitrary deformations, which therefore encompasses the traditional approach as a special case. The introduction of the two deformation gradients leads to two distinct measures of strain and strain rates, each based on recoverable or unrecoverable behaviors. The construction reveals the importance of performing recovery experiments and highlights the information gained from understanding the fundamental nature of those measurements. We performed transient nonlinear recovery measurements on a cetyl pyridinium chloride/sodium salicylate (CPCl/NaSal) solution, and the resultant rheological material functions allow the development of a new viscoelastic constitutive model, which consists of nonlinear viscous and elastic terms. We compare the model's predictions with the rheological measurements, and given the simplicity of the model, reasonably good agreements are found in the experimental data obtained from a range of different deformations. The present findings suggest a clear correlation exists between microstructural evolution and recoverable and unrecoverable components. A new direction is also provided to explore the relation between rheological material functions and material responses under different dynamic flows.

Wednesday 6:30 Ballroom 1-2-3-4 PO39

Automatic construction of rheological master curves

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We construct master curves by applying Gaussian process regression to model experimental data sets and then maximum a posteriori estimation to shifting parameters that "best" bring the statistical models derived from these data sets into registry with one another. We apply this methodology to various rheological data sets that exhibit parametric self-similarity, including time-temperature superposition of polymers and time-cure superposition of gels. The statistical framework for data superposition provides uncertainty estimates for the shifting parameters with minimal added computational cost, and is robust to experimental noise. Finally, we employ this automated approach to make forward predictions of data at an unmeasured state. This method for master curve construction, and subsequent forward predictions, is data-driven and non-parametric, and may be applied in a computationally efficient manner to a wide variety of data superposition problems.

Wednesday 6:30 Ballroom 1-2-3-4 PO40

Kinetics of solvation using Time Dissolution Evolution (TiDE) rheometry

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Textiles have been used by humans for millions of years, and organic fibers still are often preferred over synthetic fibers for their flexibility, strength, durability, and water-repellency. However, the underlying cause of such durability also prevents recyclability: due to strong interchain hydrogen-bonding interactions, the main ingredient of cotton - cellulose - does not dissolve in common solvents, and over 80% of all cotton-based

goods end up in landfills. As a possible remedy, ionic liquids progressively solvate cellulose by disrupting hydrogen bonds, which can allow a solvent-based recycling process. But, in order to create an economically viable recycling process, cellulose fibers must not be degraded by the process, and relevant kinetics and solution strength must fall within reasonable processing windows, even for highly concentrated (>5%) solutions. We take advantage of this interesting material to develop a rheometric framework for understanding the kinetics of dissolution of a macromolecule from powder to entangled solution.

We monitor the dissolution of cotton-based textiles in 1-ethyl-3-methyl-imidazolium acetate (EMIMOAc) from chopped fiber to homogeneous dispersion using small amplitude oscillatory shear (SAOS) rheometry. Due to the changing entanglement structure during dissolution, standard time-temperature superposition is inappropriate, and we instead develop a new method of Time Dissolution Evolution (TiDE) to understand and predict this cellulose rheology for a series of cellulose concentrations (0.5-12%) and degrees of polymerization (500-2500). The time-evolving SAOS measurements are described using regression to the Baumgaertel-Schausberger-Winter (BSW) relaxation spectrum model. This results not only in kinetic information but also in observability of the majority of the material relaxation spectrum. The resulting solvent-specific information is useful to guide processing of cellulose into new synthetic fibers, and to inform limits to recycling based on time and viscosity.

Wednesday 6:30 Ballroom 1-2-3-4 PO41

Quantifying thixotropy using step-rate tests and kinetic structure-based constitutive modeling

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Complex rheological phenomena like thixotropy pervade fluid-based industrial materials, including paints, coatings, adhesives, and sealants, among others. The objective of the current work is to develop and assess fast methods to measure thixotropic rheological properties of these complex fluid systems. The proposed test conditions use step shear tests and simulate the mechanical shearing history that these fluids would typically undergo during either processing or application. The thixotropic recovery and breakdown data are analyzed using structure kinetics-based constitutive equations that use a superposition of two different stretched exponentials for modeling the thixotropic transients, which is an ad-hoc modification of the mathematical model originally proposed by Wei et al. (J. Rheol., 2018). This method is effective in both fitting and predicting the thixotropic behavior of many application relevant materials under typical processing and testing conditions. Using the techniques developed here would give the user a handle on low-dimensional, easily accessible thixotropic material properties such thixotropic timescales, degrees of stress and viscosity changes due to shearing. One will be able to quantify both viscoelastic and thixotropic properties and their relative importance in material behavior.

Wednesday 6:30 Ballroom 1-2-3-4 PO42

Creeping flows of smooth and rough colloids

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Creep and yielding in dense colloidal suspensions are thought to arise from the slow relaxation of cage dynamics and particle friction. However, the precise mechanism through which interparticle friction affects the slow recovery and rate-dependent creep of dense suspensions is not well understood. Here, we report the strain and strain rate response of a series of dense suspensions composed of fluorescent colloids with tunable roughness suspended at high volume fractions (0.60-0.64) in a refractive index-matching squalene. The hard sphere poly(methyl methacrylate) colloids (diameter~1-1.2 µm) are grafted with a layer of poly (12-hydroxystearic acid), and roughness is introduced by the addition of a crosslinking molecule during the nucleation step of the synthesis. Confocal laser scanning microscopy is used to determine the particle shape and volume fraction in the solvent to account for swelling. Dense suspensions are loaded onto a stress-controlled rheometer equipped with a cone-and-plate geometry, which applies steady shear stresses above and below the yield stress of the bulk material (~0.01-0.05 Pa). Experimental observations indicate the presence of suspension memory and avalanche-like fluidization behaviour, particularly for suspensions of rough colloids near the yield stress. These results suggest that the geometric frustration caused by surface roughness generates long-lived contacts between nearest neighbour colloids, and that the slow relaxation of these contacts are responsible for hysteresis, irrecoverable properties, and stochastic fluctuations in the strain behaviour.

Wednesday 6:30 Ballroom 1-2-3-4 PO43

Extensional rheology of colloid-polymer mixtures with depletion attractions

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Extensional deformation of particle-laden complex fluids is ubiquitous in industrial processes such as fiber-spinning, extrusion, and injection molding. Prior studies in a mixture of colloids and non-adsorbing polymer, a model for interparticle attractions, revealed that polymer size and dispersity can affect the shear rheology of colloid-polymer mixtures. Here, we study the effect of depletant size and dispersity on the extensional rheology of model colloid-polymer mixtures using a dripping-onto-substrate (DoS) protocol. We use a model colloidal system of methacrylate copolymer particles with dimethylacrylamide copolymer brushes. The particles are suspended at constant volume fraction of $\Phi=0.40$ in refractive index and density matched 80 (w/w)% glycerol in water mixtures with added NaCl for electrostatic screening to achieve nearly hard-sphere interactions. Depletion attractions between the colloids are introduced by adding polyacrylamide with different molecular weight and dispersity.

We characterize the extensional properties such as extensional viscosity (η_E) and relaxation time (λ_E) from the filament-thinning dynamics. We compare the λ_E scaling of three different polyacrylamides with and without the presence of particles as a function of normalized concentration in free volume (c/c*). Depending on the size and dispersity of the depletants, the λ_E scaling can either follow or deviate from the λ_E scaling of the polymer solutions. These results will allow us to further understand the role of polymer size distribution in the extensional rheology of colloid-polymer mixtures, which represent simplified models of suspensions used in practical applications.

Wednesday 6:30 Ballroom 1-2-3-4 PO44

Probing plastic rearrangements in colloidal gels during creep

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A mechanistic understanding of yielding of colloidal gels is of both fundamental and practical interest, especially in view of the widespread use of these materials. The emergence of a yield stress is attributed to the formation of a percolated colloidal network. Only a few rheo-confocal studies focused on the microstructural evolution during yielding[1]. However, due to their limited spatio-temporal resolution, these studies could, as yet, not provide a complete image of yielding at the colloidal network level.

Using a homemade ultrafast rheo-confocal setup[2], we investigate the microstructure of a colloidal gel under constant shear scanning a 35 µm x 35 µm x 20 µm 3D voxel stack each second. Inspired by how structural rearrangements of particles trigger the yielding of colloidal glasses, we focus on the plastic rearrangements of particles of PMMA-g-PHSA in a model depletion gel under shear below or near the yield stress yielding. Image processing methods and particle tracking can be used to determine the local strain field stemming from plastic events and their propogation. We study the influence of the volume fraction and the depletion strength on such basic plastic events. We focus on the rearrangements before yielding, inspired by rheo-DLS experiments as precursors of yielding[3], in order to assess their impact on the subsequent macroscopic yielding.

1 : B. Rajaram et A. Mohraz, Soft Matter, **2010**, *6*
2 : G. Colombo *et al.*, Korea-Australia Rheology Journal, **2019**, *31*
3 : S. Aime *et al.*, PNAS, **2018**, *115*

Wednesday 6:30 Ballroom 1-2-3-4 PO45

Time dependent rheological behavior of particulate suspensions: Portland cement vs silicon carbide

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The effect of shear history on the flow behavior of aqueous-based particulate suspensions of Type I-II portland cement and ß-silicon carbide, of similar particle size distribution (PSD), was studied using cyclical flow curve rheometry and interpreted with respect to zeta potential and particle settling measurements. Whereas cement particles react (hydrate) with time, silicon carbide is completely inert in water. Three pastes formulations were used: one with deionized water, one with 0.15 % (by mass) polycarboxylate comb polymer solution, and one with 0.15 % ammonium polymethacrylate solution. The non-reactive ß-silicon carbide was found to display similar time-dependent rheological characteristics as compared to the cement for about the first two hours after contact with water. Comparative results show that a thixotropic to anti-thixotropic transition occurs for both reactive and non-reactive particle types, suggesting that physical particle-associations, e.g., flocculation/de-flocculation-related structural changes, are dominant in young cement pastes rather than hydration-related structure changes. Thus, it is difficult to separate the effect of hydration related changes in cement from physical particle-related effects using only flow curve measurements during the first two-hour period from the time of mixing. Results further imply that the state of dispersion of the particles in a dilute suspension is not a good predictor of rheological behavior in dense suspensions.

Wednesday 6:30 Ballroom 1-2-3-4 PO46

Characterization of powders from non-cohesive to cohesive through rheological means

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Next to water, powders are considered the most common raw material. Powder behavior impacts a number of industries, such as the food, paint coating, and pharmaceutical industry to name a few. Depending on the process a powder can either be the initial raw product, intermediate additive, or in some cases the final desired end product. However, the characterization of powders is greatly influenced by a number of both external and/or internal parameters making it difficult to predict powder behavior. The parameters include volumetric flow, consolidation, temperature, humidity, as well as applied torque or shear. A series of techniques were investigated in order to further classify powder behavior under varying external conditions.

Wednesday 6:30 Ballroom 1-2-3-4 PO48

Rheological signatures in colloidal gels of oppositely charged particles

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In this contribution, we consider a study of rheology of colloidal gels formed via electrostatic-heteroaggregation of colloidal particles of opposite polarity. Such colloidal gels find applications in personal care, pharmaceutical, paints, foods, and paper industries. The interactions between the particles dictate the microstructure of such gels, in turn influence their rheological response. In this work, hetero-aggregated gels of spherical nanoparticles at intermediate and higher concentrations are studied using rheology. The scaling exponent of the storage and loss vs. volume fraction is found to be much higher indicating that such gels consist of much strong percolated network of particles. With increasing strain amplitude, two step yielding is observed for gels at higher concentrations. Yielding behaviour is further investigated using steady shear, rheo-microscopy and large amplitude shear rheology. The viscoelastic non-linearities are studied using Lissajous elastic curves and the data is compared with steady shear rheology tests. The overall goal of this study is to provide insights into mechanism of gel formation, microstructural features, and stability of oppositely charged particle gels.

Wednesday 6:30 Ballroom 1-2-3-4 PO49

Impact of silica nanorod concentration on the nonlinear rheology of aqueous poly(acrylamide)-nanoparticle suspensions

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Recently, thorough optimization of nanoparticle synthesis procedures has introduced new methods to produce a wide variety of anisotropic structures on multiple length scales[1]. The combination of anisotropic nanoparticles and inducing larger-order anisotropy of these particles further increases the anisotropy of materials and can introduce complex macroscopic properties including impacts on the rheological properties, thermal and electrical conductivity[2], optical[3] or mechanical properties[4]. In this study, we examine the ability to vary the size and shape of silica nanorods and the resulting impacts on the steady shear rheological behavior of suspensions in aqueous poly(N-isopropyl acrylamide) solutions. Varying the tetraethoxysilane[5] content can vary the length:diameter ratio between 2 and 15 and influence the shape and homogeneity of particles. Rheological results demonstrate that each method influences the static microstructure-demonstrated by varying yield stresses, flow curves and nonlinear rheology-such that the combination of induced and nanoparticle anisotropy can be used for even finer tuning of rheological properties. This work serves to expand the foundation of the next generation of polymer-nanoparticle composite literature, specifically by demonstrating the functionality of suspensions of silica nanorods in aqueous polymer solutions.

[1]Grzelczak M, et al., Chem. Soc. Rev., 37 (2008).
[2]Ziyin L, et al., ACS. Appl. Mater. Interfaces, 5 (2013).
[3]PK, et al., J. Phys. Chem. B, 110 (2006).
[4]Knauert ST, et al., J. Polym. Sci. Pol. Phys. (2007).
[5]Murphy RP, et al., Langmuir, 32 (2016).

Wednesday 6:30 Ballroom 1-2-3-4 PO50

Rheological characterization of high-solids, drilling fluids by flow loop

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In underground tunneling, drilling fluid is constantly pumped into and out of the hole to remove rocks, soil, and other debris, and this mixture of fluid and solids are called "cuttings". Cuttings are a complex fluid that can be challenging to pump and rheologically characterize due to entrained solids that can vary in size from colloidal to centimeter in scale. In Horizontal Directional Drilling (HDD), drilling fluid is typically pumped through a center pipe within the hole, flows out of a cutterhead, mixes with rock, soil, and debris, and circulates back to the hole entrance through the annular space between the center pipe and the hole wall. Soil solids are removed to prevent clogging and buildup that lead to inefficient HDD operation. However, as hole length increases, pressures needed to circulate cuttings back to the surface can increase beyond that which the hole wall can withstand, leading to a fracture of the ground and loss of circulation. The rheological properties of the cuttings have a significant effect on the pressures required to maintain this circulation, but rheological measurements of the solids-laden cuttings are challenging to obtain. With conventional rheological measurements, the rapid settling of solids, and larger solids that approach the measuring gap of traditional rheometer geometries make measurements unfeasible. In this work we describe the implementation of a custom-built flow loop capable of characterizing the rheological properties of high solids concentration cuttings. The solids tested are composed of clay and sand with particle size, molecular composition, and clay-sand ratio specific to the site of tunneling. The drilling fluids tested are composed of bentonite clay in water and exhibit reversible shear-thinning behavior. Turbulent pressure-drop and flow rate data are collected from the flow loop and fit to non-linear relationships between friction factor, Reynolds number, and power-law parameters to characterize cuttings rheology as a function of solids concentration.

Wednesday 6:30 Ballroom 1-2-3-4 PO51

Dynamic magnetochromatic response of concentrated suspensions of Janus particles

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The promise of Janus particles as bulk additives for responsive complex fluids has been limited by the inability to scale up Janus particle functionalization. Particles having the high fidelity and monodispersity in both size and surface functionalization are fabricated utilizing particle monolayer formation and physical vapor deposition (PVD). Using Automated Langmuir Blodgett deposition, particle monolayers are fabricated on roll-to-roll substrates at meter per minute rates, overcoming the typical rate-limiting step for functionalization. Light transmittance of suspensions of Janus particles ranging from 1 - 50 microns in diameter subjected to both uniform and non-uniform oscillatory magnetic fields is measured. While larger Janus particles have faster response due to a larger magnetic force and slower relaxation due to Brownian rotation, smaller particles assembled into chains of particles give a significantly larger change in contrast due to their larger change in projected area along the light path. Their combined gravity-driven motion gives even more complexity to their orientation response. Janus particles dispersed in thermoreversible yield stress fluids also results in hysteresis response that suggests new modes of engineering of magnetically responsive complex fluids.

Wednesday 6:30 Ballroom 1-2-3-4 PO52

Study of the depletant concentration on the rheology of concentrated nanoemulsion

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Nanoemulsions are metastable colloidal dispersions with a wide range of applications in food, cosmetic, and pharmaceutical industries due to their unique structural properties. Gelation in nanoemulsions can effectively be used to expand the nanoemulsion applications as rheology modifiers and to design highly structured porous materials. In this research, we study the colloidal gelation of concentrated nanoemulsion with the oil volume fraction of 50% and 60% in the presence of depletant molecules. The rheological properties of the concentrated nanoemulsions are studied at different concentration of polyethylene glycol diacrylate (PEGDA) as the depletant. The gelation behavior and the structure-flow relationship of nanoemulsions are examined through flow curve and oscillatory shear measurements. These results offer a foundation for controlling the properties of colloidal systems and nanoemulsion-templated porous materials.

Wednesday 6:30 Ballroom 1-2-3-4 PO53

Drainage via stratification in micellar foam films

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Drainage via stratification happens on freestanding films of soft matter due to confinement-induced structuring and layering of supramolecular structures like micelles. Stratifying micellar thin films exhibit coexisting shades of gray and step-wise thinning, because stratification in micellar films proceeds by the growth of thinner domains at the expense of surrounding thicker film. The local volume conservation leads to the formation of nanoscopic ridges at the moving front, and the ridge often undergoes an instability leading to nucleation of nanoscopic mesas, that grow, move and coalesce over time. The shape and size of ridges and mesas in stratifying films are visualized and analyzed using interferometry, digital imaging, and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). In this contribution, we analyze the shape evolution of nanoscopic topographies in stratifying films in an effort to develop a comprehensive understanding of drainage by stratification in micellar foam films, including the role played by the contribution of supramolecular oscillatory structural forces to disjoining pressure.

Wednesday 6:30 Ballroom 1-2-3-4 PO54

Normal stresses at the yielding point

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Non-null normal stresses in shear flows are present in all complex fluids. This work investigates the normal stress differences in the of elasto-viscoplastic materials in the vicinity of the yielding point. The goal is to better determine the stress state that is required to cause yielding. This class of materials are found in several industries such as oil, farmaceutical, food and others. Due to the complexity of the experiments needed to characterize this behavior, a procedure to measure the normal stresses while the fluid undergoes steady and transient rheological tests under shear was developed using the ARES-G2 rheometer. A hair gel, a highly concentrated emulsion and a Carpobol dispersion were tested. First, it was observed that residual stresses in viscoplastic materials deeply affect the measurements of the normal stresses. Considering low shear rates, for all materials studied, substantially high values of normal stresses in comparison to the shear yield stress are observed. Additionally, for the Carpobol dispersion, the influence of the interfacial tension surrounding normal stress measurements for high shear rates is presented. The highly concentrated emulsion displays interesting results as, for high shear rates, the shear stress is larger than the normal stress, in contrast with results from the other two fluids. For the hair gel, positive normal stresses were seen at early times in the constant shear rate experiments. Among other findings, it was seen that the time needed to reach a steady state while measuring normal stresses is significantly longer than that required to obtain a steady shear stress.

Wednesday 6:30 Ballroom 1-2-3-4 PO55

Poroelasticity of confined hydrogel films

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Thin gel films coat almost every interior surface of the human body, protecting and lubricating the underlying tissue. Understanding the mechanical properties of these natural materials is important for biomedical applications such as implants, but biological gel layers are difficult to study directly. An alternative approach is to use synthetic polymer hydrogels as model systems. However, due to the experimental challenges of studying soft, thin films, few studies have investigated hydrogel films of biologically relevant thicknesses. Here, I present an adaptation of the Surface Forces Apparatus (SFA) technique that enables simultaneous measurement of film thickness and normal force for gels of biologically relevant film thicknesses. Indentation and creep experiments were performed on polyacrylamide gel films of thickness 10-100 µm and high levels of confinement-the ratio of contact width to film thickness-to match biological contact geometries. The results are described by a poroelasticity model analogous to a Kelvin-Voigt viscoelasticity model. Changes in solvent quality are shown to drive a transition from viscous to elastic behavior that is well described by polymer scaling theory. These findings demonstrate that viscous dissipation is amplified by confinement and that the apparent stiffness of confined, hydrated gels is dominated by fluid flow through the polymer network.

Wednesday 6:30 Ballroom 1-2-3-4 PO56

Exploration of slide-ring gelation kinetics using rheology

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This work utilizes aspects of chemo-rheology to understand the gelation behavior of slide-ring gels. Slide-ring gels are synthesized from polyrotaxanes, which are macromolecules threaded through a macrocycle and possess a mechanically bonded ring-on-string architecture. The resulting macroscopic properties of such an unusual microstructure are extremely soft gels which exhibit 2 time-dependent plateaux attributable to the rubber elasticity and "sliding" elasticity. Limited work exists on understanding the effects of factors contributing to the kinetics of gelation. We employ small amplitude oscillatory shear to characterize the gelation in situ by monitoring the viscoelastic properties. Observing the elastic and viscous moduli in real-time provides information about gelation time and completion of gelation. We investigate the effect of temperature and cross-linker concentration on the process. A modified Hill equation is fit to the data to better model the gelation behavior. Finally we present the case for using classic rubber elasticity theory to estimate the effective strand density in this peculiar system.

Wednesday 6:30 Ballroom 1-2-3-4 PO57

Modulating the rheology of collagen-based hydrogels using morphology-controlled tannic acid particles

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Hydrogels are porous three-dimensional structures with polymeric cross-linked networks which has the provision for sufficient water and nutrient flow for cell proliferation to stimulate the regeneration of defective tissues. Compared to surgical scaffold implantation, injectable hydrogels can be easily applied by minimal invasive techniques to form a self-standing hydrogel. Naturally derived polymer, collagen has been widely employed as injectable hydrogel since it inherits the structural and functional cursors to accelerate tissue formation, however it shows poor mechanical properties. The use of biodegradable tannic acid particles provides a useful approach to improve the rheology of these systems while its inherent antibacterial and anticarcinogenic nature adding to the gel functionality. Polyphenolic tannic acid particles could potentially interact with collagen through their hydroxyl and carboxyl groups allowing us to modulate the rheology. In this study we examine how liquid as well as particulate tannic acids impact the rheological properties of collagen-based hydrogels. Liquid and tannic acid particles of different shapes are synthesized and incorporated into collagen in this regard. While samples exhibit solution-like features at storage conditions (4ºC), they transform into gels under physiological temperatures (37ºC). The sol-gel transition in terms of temperature and time are monitored as a function of tannic acid concentration and morphology. Interestingly, particulate tannic acid incorporation exhibits the largest increase in elastic modulus with shape playing a secondary factor. Measurement of yield stress using the elastic stress method also reveals a similar trend. These results are interpreted in terms of the underlying interactions of the tannic acid with collagen, as examined using other analytic approaches.

Wednesday 6:30 Ballroom 1-2-3-4 PO58

Tuning rheological and structural transitions in ABA/BAB poloxamer hydrogels

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Poloxamer P407 is an ABA triblock polymer widely used in the biomedical field due to its biocompatibility and thermoreversible gelation in water. Temperature increase triggers self-assembly of P407 in water into micelles which can enclose hydrophobic small molecules. Further

increases in temperature result in rheological transitions corresponding to micelle ordering into complex phases including face-centered cubic (FCC)-packed structures. However to maintain mechanical integrity in drug delivery applications, development of bridged micellar structures is desired. One potential route for achieving micellar bridging is by incorporating BAB triblock reverse poloxamers (RPs) into P407 systems to induce bridging via the hydrophobic endblocks. Here, we show that the addition of RPs to P407-based systems can drastically affect the mechanical properties, structure, micellization and gel transition temperatures. To reduce unfavorable PPO-water interactions, dangling PPO blocks from the RPs associate with each other, resulting in a physically-bridged network across the micelles. Increasing the extent of bridging through RP incorporation reduces the inter-micelle potential, resulting in the FCC-packed micelles transitioning to a BCC-packing and eventually a breakdown in crystalline structure. Utilizing a combination of rheology, differential scanning calorimetry (DSC), and small-angle x-ray scattering (SAXS), we demonstrate how RP length, composition, and concentration effects the thermal transition and structures of these materials. This understanding allows for the development of thermo-responsive materials with optimal mechanical properties for a wide-variety of applications.

Wednesday 6:30 Ballroom 1-2-3-4 PO59

Rheological properties of phase transitions in polydisperse and monodisperse colloidal rod systems

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Rheological modifiers are used to tune the rheology of products, including in products that change state during end-use. To effectively use rheological modifiers the material structure and rheological properties must be well understood. Hydrogenated castor oil (HCO) is currently used as a rheological modifier in home care products, but this rod is polydisperse, which could produce complex heterogeneous structures. To determine the effect of polydispersity on rheological modification, this work characterizes gelation of HCO and polyamide (PA), a monodisperse colloidal rod, using multiple particle tracking microrheology (MPT). In MPT, fluorescent probe particles are embedded in the sample and their Brownian motion is measured. Our system consists of a colloid (HCO or PA), a surfactant (linear alkylbenzene sulfonate, LAS), and a non-absorbing polymer (polyethylene oxide, PEO). PEO is used to drive gelation through depletion interactions. We measure these materials as depletion interactions are increased and gel the system. MPT data are analyzed using time-cure superposition to determine the critical values at the phase transition. We determine that the critical relaxation exponent is dependent on LAS:colloid, but PA and HCO have similar critical value. The critical relaxation exponent is lower for LAS:colloid=16, indicating a tightly associated network, than LAS:colloid>16, indicating a loosely associated network. This difference is due to a difference in the zeta potential between these two systems, which indicates that the strength of the electrostatic force changes when LAS:colloid is varied. This changes the starting material structure and leads to different gel evolution. This study shows that, for both systems, the rheology and microstructure during gelation depends on LAS:colloid, but polydispersity does not affect gelation evolution. This work will inform future product design by providing guidance to specify desired rheology and minimize trial-and-error experiments.

Wednesday 6:30 Ballroom 1-2-3-4 PO60

Magneto-rheological studies on the role of hydration in anomalous magnetically-induced block copolymer ordering

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The directed assembly of block copolymers via external stimuli is central to improving structural control and expanding viable applications of the materials. In particular, magnetic fields have emerged as a promising new external stimuli for processing block copolymers. Yet directed assembly of block copolymers via magnetic fields suffers from limitations including the need for large applied fields (> 6 T) or anisotropic constituents such as crystalline blocks. Recent work has demonstrated the anomalous disorder/order transition of poloxamer micellar solutions under weak magnetic fields and without the need for anisotropic constituents. This project seeks to understand the mechanism behind this anomalous transition with the goal of furthering BCP processing and advanced materials design. This presentation focuses on the role of micelle hydration in the magnetically-induced disordered/ordered transition. Hydration of the micelles was varied via solvent quality, relative block solubility, hydrogen bond strength, and ionic strength to elucidate the proposed ordering mechanism. The current hypothesized mechanism focuses on a magnetically-induced change in polymer solvent interactions which results in an alteration in the hydration of the PEO corona and/or the PPO core. The hydration and size of the micelles under various solvent and environmental conditions were observed via X-ray scattering following magneto-rheological studies. Parameters extracted from magneto-rheology studies such as plateau modulus and critical transition time provide insight into the role of hydration on the kinetics of the magnetically-induced transition.

Wednesday 6:30 Ballroom 1-2-3-4 PO61

Role of glass fiber on the crystallization of poly(ether ether ketone)

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The isothermal quiescent and flow-induced crystallization of poly(ether ether ketone) (PEEK) has been investigated using fast scanning calorimetry (FSC) and oscillatory shear rheometry. We extended our work on the crystallization of PEEK and focused on glass fiber reinforced PEEK composites. FSC data indicate that the presence of glass fiber in the PEEK melt inhibits the quiescent crystallization kinetics, perhaps from a steric hinderance effect of glass fiber. Small-amplitude oscillatory time sweep results suggest that with shear flow, the presence of glass fiber accelerates the crystallization of PEEK. A correlation to specific work was explored. With a refined understanding of the effect the applied work has on the crystallization of PEEK and glass fiber reinforced PEEK, improved models are developed for the isothermal crystallization, with and without prior shear flow. These models can be used to predict the rate of crystallization of PEEK and its glass fiber composites relevant for commercial application in industry.

Wednesday 6:30 Ballroom 1-2-3-4 PO64

Dynamics of entangled linear polymers at fast deformations: Influence of matrix viscoelasticity

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To deeply understand the nonlinear viscoelasticity of linear entangled chains we performed start-up shear experiments on four diluted melts and four binary blends of long polystyrene chains (PS 820kg/mol) with varying the concentration and molar mass of the matrix chains. Similarly to published experimental results, we find that in the elastic regime of deformation (i.e., at $\gamma\text{`}\tau_R (M)\gg 1$) there is a fractional power-law scaling of the transient viscosity maximum vs the shear rate. We also find that the steady-state viscosity exhibits stronger strain-softening behavior as the entanglement density increases, which can eventually lead to macroscopic shear-banding. Regarding the Cox-Merz rule validity we find that, within experimental error, it is confirmed with the exception of two bidisperse blends having high molecular weight matrices. We attribute this failure to possible edge instability and fracture. Our experimental findings are compared against a nonlinear version of the Time Marching Algorithm (TMA) that couples the dynamics of orientation, stretch and constraint release (CR). The nonlinear TMA does a reasonable quantitative job in describing the nonlinear shear steady-state data, provided that the contribution of the matrix (short chains) to the overall polymer stress is accounted for. This work identifies future directions to fully predict the different relaxation dynamics under transient flow.

Wednesday 6:30 Ballroom 1-2-3-4 PO65

Interfacially compatibilized PI/PDMS blends with reduced octadecylamine-functionalized graphene oxide

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In this work, we investigate the interfacial compatibilization effect of reduced octadecylamine-functionalized graphene oxide (ODA-GO) on the morphological and rheological properties of immiscible homopolymer blends of polydimethylsiloxane (PDMS) and polyisoprene (PI). We prepared droplet-matrix blends with a PI:PDMS ratio of 30:70 or 70:30 and interfacially localized ODA-GO stabilizer loadings from 0.1% to 1%. Blends were examined by optical microscopy and rheometry. Experiments reveal that the compatibilization effects of interfacially localized ODA-GO are symmetric, with PI and PDMS-continuous blends. Both blends show typical droplet-matrix morphology with stabilized round drops that do not stick together. On the other hand, for higher ODA-GO content, smaller drops observed for PI-continuous blends as compared to PDMS-continuous blend. In oscillatory experiments, although both blends displayed liquid-like behavior and lack of viscosity overshoot, PI-continuous blends deviate more from liquid-like behavior at high ODA content. Moreover, flow-induced coalescence is completely suppressed in the S30 as compared to S70 blends as the ODA-GO loadings is increased from 0.1 to 1 wt%, suggesting to strong interface in S30 as compared to S70 blends. This work provides a strategy for interfacially-compatibilizated polymer blends with specific properties for practical applications.

Wednesday 6:30 Ballroom 1-2-3-4 PO66

Relaxation dynamics of polyelectrolyte solutions

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The relaxation times (τ) of polyelectrolyte solutions are unique in the semidilute unentangled concentration regime as $\tau \sim N^2c^{-1/2}$ is expected by the Rouse model. The concentration dependence of t has been extensively tested using various polyelectrolyte aqueous solutions, mainly for high molecular weights since they exhibit shear-thinning for at least a decade of shear rates; shorter chain do not exhibit enough shear thinning to evaluate t reliably in commercial rheometers. In this study, we used ethylene glycol (EG) and glycerol as solvents instead of the lower viscosity water. EG and glycerol both effectively slow down the relaxation dynamics and allow the relaxation time measurement for lower molecular weights. Five number-average degrees of polymerization (Nn = 140 ~ 9150) of narrow distribution cesium polystyrene sulfonate (CsPSS) solutions are studied in water, anhydrous EG and anhydrous glycerol using X-ray scattering to determine the correlation length and the rotational rheometers to determine the specific viscosity, relaxation time and terminal modulus. A plot of $\xi^3\tau/N^2$ vs. c shows that the relaxation time data can be reasonably reduced to a common curve. The terminal modulus G can be perfectly reduced by plotting G/kT vs. c/Nn. Additionally, time-temperature superposition was applied for CsPSS/glycerol solutions from 25 to -5 ^oC to study the entanglement behavior. Using the overlap parameter Pe, we also estimated the entanglement concentrations of CsPSS in glycerol.

Wednesday 6:30 Ballroom 1-2-3-4 PO67

Rheology of an associating polymer solution: Poly(vinyl alcohol) in water

Colin D. Ditillo[1], Daniele Parisi[1], Seth Lindberg[2], Mark W. Hamersky[2], and Ralph H. Colby[1]
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Multiple grades of poly(vinyl alcohol) (PVA) with varying molecular weight and degree of hydrolysis were investigated to explore the associating effect on the shear rheology of these polymers in aqueous solution. Viscosity measurements on PVA solutions at high concentration showed positive deviation from the predicted specific viscosity scaling of polymer solutions without associations in the entangled regime. This also translates to longer-than-expected relaxation times for these entangled solutions. In dimethyl sulfoxide (DMSO) solvent, the same effect is not seen, and the predicted scalings for the concentration dependences of specific viscosity and relaxation time for polymer solutions without associations are recovered. Having one solvent that avoids association effects (DMSO) is very enabling for quantifying the association effects on rheology in water. Investigations into the effects of degree of hydrolysis and solvent mixture have shown that in ternary solutions, the system becomes very complex, and therefore the particular dominant interactions between hydrogen bonding groups that results in the associations are not yet fully understood.

Wednesday 6:30 Ballroom 1-2-3-4 PO68

"Tying the knot", enhanced recycling trough ultra-fast entangling across ultra-high molecular weight polyethylene interfaces

Fotis Christakopoulos[1], Enrico M. Troisi[2], Nic Friederichs[2], Jan Vermant[1], and Theo Tervoort[1]
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Ultra-high molecular weight polyethylene (UHMWPE) is a high-end engineering polymer. However, the very features that lead to its exceptional properties, i.e. ultra-long macromolecular chains, renders joining two surfaces of this material a tedious and slow process, leading to long welding times and impeding mechanical recycling of UHMWPE. Here we report the anomalous fast joining of UHMWPE interfaces by simply depositing small amounts of nascent disentangled UHMWPE powder at the interface. The time evolution of build-up of adhesive fracture energy in the molten state and the reduction in interfacial slip between two molten UHMWPE layers, reveal an orders of magnitude increase of the rate of interpenetration compared to the dynamics of a regular UHMWPE-melt interface. This ultra-fast self-diffusion mechanism is insensitive to molecular weight, in contrast to reptation-driven diffusion, and provides a direct indication of the entropy-driven "chain explosion" upon melting of nascent disentangled UHMWPE. The usefulness of fast molecular stitching is demonstrated for enhanced recycling of UHMWPE.

Wednesday 6:30 Ballroom 1-2-3-4 PO69

Crosslinking poly(acrylamide-co-diallyldimethylammonium chloride) membrane with glutaraldehyde for fuel cell application

Uchenna Asogwa and Matthew W. Liberatore
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Fuel cells?are?a promising development in energy technology?as they?can?convert fuel to electricity with a minimal carbon footprint. Through electrochemical processes, fuel cells can be?twice as energy-efficient as the internal combustion engine.?While proton exchange membrane fuel cells (PEMFC) are relatively common, hydrogen availability and cost of the platinum catalyst have been a major concern for PEM fuel cells. One way to overcome these challenges is by using Anion Exchange Membrane fuel cell (AEMFC). The essential function of an anion exchange membrane is to conduct anions while being impermeable to the oxidants and fuel used in the fuel cell. Despite the advantages of AEMFC over PEMFC, performance and durability challenges that are influenced by mechanical failure and chemical degradation of anion exchange membranes (AEMs) constitute major concerns with the AEMFC. To address these problems, a robust, and durable thin anion exchange membrane through crosslinking of Poly(acrylamide-co-diallyl dimethylammonium chloride) (PAADMAC) with glutaraldehyde is explored. This study examines the effect of varying glutaraldehyde concentrations in crosslinking water-soluble PAADMAC to form an insoluble membrane. A temperature-controlled variable speed micrometer-adjustable film coater was used?to?control desired film thickness and size.?Final membrane thicknesses ranged from 30?to 50?µm.? Chemical characterization of ion exchange capacity (IEC) and water uptake measurements are completed for each film to measure conductivity levels and swelling behavior of the membranes.? Measured?IEC values ranged from 1.0 to 2.0 mmol/g, similar to?state-of-the-art?membranes. Mechanical tests are carried out using a rheometer to characterize the strength of the membranes under both dry and humid conditions.

Wednesday 6:30 Ballroom 1-2-3-4 PO70

Extensional rheology, pinching dynamics, and processability of polymer solutions

Carina Martinez and Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States

The processability of polymer solutions is determined by the shear and extensional rheology response, pinching dynamics, and interfacial properties. Particularly, dispensing, and liquid transfer to substrates by dripping, jetting, spraying, or coating flows involve capillarity-driven pinching of liquid necks with strong extensional flows. However, due to a lack of suitable techniques, the extensional rheology response of polymeric complex fluids with low viscosity and low elasticity that are industrially relevant in a vast variety of formulations, has not been characterized in adequate detail. In this study, we examine how pinching and interfacial dynamics and the shear and extensional rheological response of polymer solutions are modified by the addition of ionic surfactants and particles or additional interactions. We utilize dripping-onto-substrate rheometry protocols and show that shear and extensional rheology response display contrasting concentration-dependent variation. We elucidate the effect of multiple interactions on the pinching dynamics and extensional rheology response, and we discuss the implications for dispensing of macromolecular complex fluids.

Gallery of Rheology

Symposium GR
Gallery of Rheology Contest

Organizers: Cari Dutcher and Patrick Underhill

Wednesday 6:30 Ballroom Pre Function GR1

Axisymmetric numerical simulations of viscoelastic jet thinning and breakup

Konstantinos Zinelis[1], Thomas Abadie[1], Gareth H. McKinley[2], and Omar K. Matar[1]
[1]Chemical Engineering, Imperial College London, London, United Kingdom; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Droplet formation in a non-Newtonian fluid is central to numerous industrial applications such as spray-drying, atomisation and paint application. The flows associated with spray formation involve large interfacial deformations and complex spatio-temporal dynamics. The aim of the present work is to establish a robust numerical basis for systematic examination of viscoelastic fluid sprays. To achieve this, we begin with two-dimensional axisymmetric simulations of an impulsively-started jet exiting a nozzle and entering a stagnant gas phase. We use an adaptively-refined volume-of-fluid technique to capture the interface and the log-conformation transformation for stable and accurate solution of the viscoelastic constitutive equation. We simulate, for the first time, the entire jetting and breakup process of a viscoelastic fluid, including the flow through the nozzle which results in an initial radial stress distribution that is shown to affect the subsequent breakup dynamics. We validate the numerical simulations against the predictions of linear stability analysis. Subsequently, we explore the effect of shearing flow inside the nozzle on the thinning dynamics of the viscoelastic jet via analysis of the spatio-temporal evolution of the polymeric stresses. We also examine the role of the finite extensibility of the polymeric chains on the breakup process and demonstrate the capacity of the numerical formulation to resolve the elasto-capillary regime as a function of mesh resolution and the finite extensibility of the fluid. Finally, we investigate systematically the dependence of the rate of filament thinning on the axial momentum of the jet and the fluid relaxation time; this permits efficient exploration of the material parameter space, capturing the competing effects of elastic, viscous, and inertial forces on the ejected droplet size distribution.

Wednesday 6:30 Ballroom Pre Function GR2

Starry starry spherulite

Kalman D. Migler, Derek E. Huang, and Anthony Kotula
National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

The recycling of mixed polyolefins is problematic because immiscibility between various plastics leads to brittle materials. To investigate, we image the structure of a blend of high density polyethylene (HDPE) and isotactic polypropylene (iPP) upon heating and melting. This micrograph corresponds to the temperature at which the HDPE is starting to melt (the wispy background) while the iPP is still in its spherulitic crystalline morphology (the yellow/blue droplets). The iPP spherulites evoke the moon and stars of Van Gogh's Starry Night while the HDPE background evokes the stars of his night sky. The image was taken in a shear cell mounted on an optical microscope utilizing both phase contrast methods and a first order 530nm retardation plate.

Wednesday 6:30 Ballroom Pre Function GR3

Patterns of fluorescent quantum dots in polymerizing polymer beads passing through regular arrays of micro tubes under UV radiation

Babkin Iurii, Aniket P. Udepurkar, Simon Kuhn, and Christian Clasen
Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium

UV radiation, that initiates the polymerisation of monomer droplets passing through a staggered array of microtubes, excites fluorescens of quantum dots embedded in the solidifying beads, causing an intricate pattern in the dark.

Wednesday 6:30 Ballroom Pre Function GR4

NanoAmazon: Tropical rainforest of Brazilian asphaltenes

Isabela F. Soares, Eliana P. M. Castaño, and Monica F. Naccache
Department of Mechanical Engineering, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil

Amazon rainforest can be seen from a nanoperspective. We use Scanning Electron Microscopy (SEM) to study the morphology of indigenous Brazilian asphaltenes solubilized in a 80/20 hexadecane-toluene mixture. The original SEM image shows agglomerate particles of asphaltenes after evaporation of the solvents (magnification of 10,0000 times), unraveling a remarkable close-packed pattern that may be caused by the presence of the non-polar solvent hexadecane. Surprisingly, we realized that our SEM images resemble the top view of Amazon rainforest with

interesting spots that could mimic vegetation and rivers. We coloured the SEM micrograph by using Adobe Photoshop 2020, and obtained a treated image of asphaltenes as a tropical forest in nanoscale.

Wednesday 6:30 Ballroom Pre Function GR5

Rolling around a spinning top

Bavand Keshavarz and Michela Geri

Massachusetts Institute of Technology, Cambridge, MA, United States

In this entry for gallery of rheology we show high-speed photographs of both Newtonian and non-Newtonian liquids as they roll around a spinning top.

Wednesday 6:30 Ballroom Pre Function GR6

Reawakening

Andrew S. Ylitalo and Julia A. Kornfield

Chemistry and Chemical Engineering, Caltech, Pasadena, CA, United States

We study bubble nucleation in polymer foams using high-pressure, microfluidic flow-focusing. While bubbles generally nucleate isolated from other bubbles, we sometimes see bubbles nucleate in the wake of larger bubbles as they flow down the channel. These bubbles coalesce, form a new wake, and repeat the cycle.

Wednesday 6:30 Ballroom Pre Function GR7

Emerging patterns in polymers

Toluwanimi Bello and Patrick T. Underhill

Rensselaer Poly Institute, Troy, NY 12180, United States

At high enough concentrations, contact among micelles or block copolymer domains lead to nonspherical shapes. In this limit, the dynamics and assembly of the suspension depend more on the interfaces between objects than the bulk objects themselves. This has similarities with foams and biological tissues in which the interfaces between deformable objects (gas bubbles or cells) play a critical role. When quenched from relatively high temperature (with liquid structure) to relatively low temperature, patterns of spatially ordered structure emerge.

Wednesday 6:30 Ballroom Pre Function GR8

Rheological petals

Fahed Albreiki, Alexander Kubinski, and Vivek Sharma

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

The displacement of a more viscous fluid by a lower viscosity fluid in quasi-two-dimensional flow created in the so-called Hele-Shaw cell is observed to create complex fingering patterns. In this image, snapshots of two fingering patterns were acquired while maintaining identical experimental conditions but using a Newtonian fluid (red) in the first part and a viscoelastic fluid (blue) in the second part. The comparison reveals that incorporating viscoelasticity alters the growth and evolution of the pattern leading to highly complex petals-shapes and branch-like structures, whereas the Newtonian fluid develops a more stable fingertip growth. The viscoelastic fluid used is a model elastic fluid with a low rate-independent shear viscosity.

Wednesday 6:30 Ballroom Pre Function GR9

Transition to turbulence in planar jets: Small amounts of polymer destabilize the flow

Sami Yamanidouzisorkhabi, Yashasvi Raj, Gareth H. McKinley, and Irmgard Bischofberger

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

We use high-speed digital Schlieren imaging to visualize the evolution of Lagrangian flow structures in planar jets entering a quiescent bath of water. The jets have an aspect ratio of 10 at the nozzle; their width is 4 mm and their thickness is 0.4 mm. We investigate the transition to turbulence in jets of water (Newtonian case) and in jets of dilute aqueous polymer solutions (viscoelastic case). For the Newtonian jets, the development of a shear layer instability at the edges of the jet leads to vortex roll up and ultimately to turbulence. A unique inertio-elastic instability at the center of the viscoelastic jets leads to a transition to turbulence at a lower Reynolds number compared to that characterizing the transition for Newtonian jets.

Wednesday 6:30 Ballroom Pre Function GR10

Interfacial rheology and thin liquid films

Alexandra Alicke and Jan Vermant

Department of Materials, ETH Zurich, Zurich, Switzerland

The macroscopic stability of multiphase soft materials, such as emulsions and foams, is directly related to the microscopic stability of the films surrounding its droplets or bubbles. The drainage dynamics of these thin liquid films display an intricate balance between surface and bulk properties. In our research, we are interested in understanding the role of interfacial rheological properties on thin film drainage. For this, we typically carry out microfluidic scale experiments of nanometer-thick draining films and relate their behavior to results obtained from different interfacial rheology techniques. Here, we present a somewhat more literal and ludic representation of our scientific interests - inspired by careful observations during cleaning procedures and as a reminder that science is present even in the most trivial daily tasks. This sequence of macroscopic photographs shows the beautiful interference patterns that arise when a free-standing soap film forms in a double-wall ring geometry used for interfacial rheology. Both glycerol and surfactant were used to slow down drainage by increasing bulk viscosity and enhancing Marangoni flows, displaying a myriad of colors and patterns that reflect the nm-thickness inhomogeneities that emerge

Wednesday 6:30 Ballroom Pre Function GR11

Binary colloidal gel network

Jae Hyung Cho and Irmgard Bischofberger

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

When mixed in water, two different types of polystyrene-poly(N-isopropylacrylamide) core-shell colloidal particles of similar sizes can form a binary gel network due to attractive van der Waals interactions. Our poster displays a confocal fluorescent micrograph of the two types of particles that vary in attraction strength, hence named "strong" and "weak" particles, that form a space-spanning network at the total volume fraction of 1%. The system contains an equal volume of the strong and the weak particles that are labelled with green and red fluorescent dyes, respectively, and that are separately visualized using different filters. As shown in the merged image, the two types of particles are uniformly mixed despite the difference in their attraction strengths. This homogeneous composition of the binary gels allows us to tune their mean attraction strengths, and thus their viscoelasticity, by changing the mixing proportion of the two types [Cho and Bischofberger, Phys. Rev. E 103, 032609 (2021)].

Wednesday 6:30 Ballroom Pre Function GR12

Thread of life: Death and rebirth of a cotton thread

Crystal E. Owens, Jianyi Du, A. John Hart, and Gareth H. McKinley

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

People typically choose to wear clothing that is resistant to degrading from mechanical abrasion, inclement weather, and time. Due to strong hydrogen bonding between cellulose chains, cotton is durable in this way, but for the same reason this naturally-sourced fiber is not recyclable. In our attempts to develop a green solution-spinning recycling process for cotton-based textiles, we discovered the beauty of these natural fibers in the midst of processing steps to destroy and regenerate it. This image shows the result of wet solvent fiber-spinning a cellulose spider-web onto a dish, immediately after rebirth of new solid fibers. Residual ionic liquid gives the fibers a warm (amber) glow, while residual coagulant liquid beads up at regular spacings along the threads.

Please see our related abstracts for more detailed technical information (which we believe is just as beautiful!).

Author Index

Paper Index

Plenary Lectures and Award Presentation

Monday, October 11
8:30 AM
Ballroom 5-6-7

Manipulating the rheology of colloidal gels with embedded active matter
Michael J. Solomon
Chemical Engineering, University of Michigan

Tuesday, October 12
Bingham Lecture, 8:30 AM
Ballroom 5-6-7

Do interfaces matter in rheology?
Jan Vermant
Materials Departement, ETH Zurich

Wednesday, October 13
8:30 AM
Ballroom 5-6-7

Electrified droplets: Instabilities, interactions, and rheology
Petia M. Vlahovska
Engineering Sciences and Applied Mathematics, Northwestern University

Thursday, October 14
Metzner Award Presentation
8:30 AM, Ballroom 5-6-7

Dynamics of physically and chemically reversible polymers
Quan Chen
Chinese Academy of Sciences, Changchun Institute of Applied Chemistry

Social Program and Special Events

Sunday, October 10

Rheology Research Symposium (continued from Saturday, Oct 9)

Welcoming Reception
6:00 PM – 8:00 PM Ballroom 2-3, Pre Function, Tent
Sponsored by TA Instruments

Monday, October 11

Monday Boxed Lunch
11:55 AM – 1:30 PM Ballroom 2-3, Pre Function, Tent

Student-Industry Forum
12:15 PM – 1:15 PM Virtual

Gallery of Rheology Preview
1:30 PM – 4:00 PM Ballroom Pre Function
Asynchronous Viewing Meeting Web App

Student Trivia Night
7:00 PM – 8:30 PM Sea Dog Brewing Co.

Tuesday, October 12

Gallery of Rheology Preview
8:30 AM – 4:00 PM Ballroom Pre Function

Society Business Meeting
12:00 PM – 1:30 PM Ballroom 2 and 3

Awards Reception
6:00 PM – 7:00 PM Ballroom Pre Function, Tent

Awards Banquet
7:00 PM Ballroom 1, 2 and 3

Wednesday, October 13

Gallery of Rheology Preview
8:30 AM – 4:00 PM Ballroom Pre Function

Poster Session and Reception
6:30 PM – 8:30 PM Ballroom 1-2-3-4, Pre Function, Tent
Reception sponsored by Anton-Paar USA

Gallery of Rheology Contest
6:30 PM – 8:30 PM Ballroom Pre Function
Online voting 10 AM – 8 PM ET

The Society of Rheology gratefully acknowledges the generous support of Anton-Paar USA, TA Instruments and Department of Chemical & Biomedical Engineering, University of Maine.