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THE SOCIETY OF RHEOLOGY

88TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Grand Hyatt Tampa Bay
Tampa, Florida
February 12 - 16, 2017

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Meeting Schedule

Monday, February 13, 2017

	A1	*A2*	*WI*	*SC*	*SE*
8:30	E. M. Furst (PL1) - *A2*				
9:20	Coffee Break				
10:00	SC1	BA1	SG1	EF1	SM1
10:25	SC2	BA2	SG2	EF2	SM2
10:50	SC3	BA3	SG3	EF3	SM3
11:15	SC4	BA4	SG4	EF4	SM4
11:40	SC5	BA5	SG5	EF5	SM5
12:05	Lunch Break				
1:30	SC6	BA6	SG6	EF6	SM6
1:55	SC7	BA7	SG7	EF7	SM7
2:20	SC8	BA8	SG8	EF8	SM8
2:45	SC9	BA9	SG9	EF9	SM9
3:10	Coffee Break				
3:35	SC10	BA10	SG10	EF10	SM10
4:00	SC11	BA11	SG11	EF11	SM11
4:25	SC12	BA12	SG12	EF12	SM12
4:50	SC13		SG13	EF13	SM13
5:15	SC14	BA14	SG14	EF14	SM14
5:40	End				

Tuesday, February 14, 2017

	A1	*A2*	*WI*	*SC*	*SE*
8:30	M. Cates (PL2) - *A2*				
9:20	Coffee Break				
10:00	SC15	BA15	SG15	EF15	SM15
10:25	SC16	BA16	SG16	EF16	SM16
10:50	SC17	BA17	SG17	EF17	SM17
11:15	SC18	BA18	SG18	EF18	SM18
11:40	SC19	BA19	SG19	EF19	SM19
12:05	Lunch Break / Society Business Meeting - *A2*				
1:30	SC20			EF20	SM20
1:55	SC21	BA21	SG21	EF21	SM21
2:20	SC22	BA22	SG22	EF22	SM22
2:45	SC23	BA23	SG23	EF23	SM23
3:10	Coffee Break				
3:35	SC24	NF1	MF1	EF24	SM24
4:00	SC25	NF2	MF2	EF25	SM25
4:25	SC26	NF3	MF3	EF26	SM26
4:50	SC27	NF4	MF4	EF27	SM27
5:15	SC28	NF5	MF5	EF28	
5:40	End				
7:00	Awards Reception - *FS*				
8:00	Awards Banquet – *Audubon BC*				

Wednesday, February 15, 2017

	A1	*A2*	*WI*	*SC*	*SE*
8:30	Z. Dogic (PL3) - *A2*				
9:20	Coffee Break				
10:00	SC29	NF6	MF6		SM28
10:25	SC30	NF7	MF7		SM29
10:50	SC31	NF8	MF8		SM30
11:15	SC32	NF9	MF9		SM31
11:40	SC33	NF10	MF10		SM32
12:05	Lunch Break				
1:30	SC34	NF11	MF11	AT1	SM33
1:55	SC35	NF12	MF12	AT2	SM34
2:20	SC36	NF13	MF13	AT3	SM35
2:45	SC37	NF14	MF14	AT4	SM36
3:10	Coffee Break				
3:35	SC38	NF15	SL1	AT5	SM37
4:00	SC39	NF16	SL2	AT6	SM38
4:25	SC40	NF17	SL3	AT7	
4:50	SC41	NF18	SL4	AT8	
5:15	SC42	NF19	SL5	AT9	
5:40	End				
6:00	Poster Session & Reception - *FS*				

Thursday, February 16, 2017

	A1	*A2*	*WI*	*SC*
8:00	E. Van Ruymbeke (AP1) - *A2*			
8:40	SC43	NF20		AT10
9:05	SC44	NF21	SL7	AT11
9:30	SC45	NF22	SL8	AT12
9:55	Coffee Break			
10:25	SC46	NF23	SL9	AT13
10:50	SC47	NF24	SL10	AT14
11:15	SC48	NF25	SL11	
11:40	SC49			
12:05	End			

Session and Room Codes

AP = Award Presentations
AT = Advanced Techniques and Methods
BA = Biorheology & Active Fluids
EF = Emulsions, Foams & Interfacial Rheology
MF = Micro/Nano Fluidics and Probe Rheology
NF = Non-Newtonian Fluid Mechanics & Instabilities
PL = Plenary Lectures
SC = Suspensions, Colloids and Granular Media
SG = Self-assembled Systems, Gels and Liquid Crystals
SL = Solids & Composites
SM = Polymer Solutions & Melts

A1 = Audubon B
A2 = Audubon DEF
FS = Foyer-Stairs/Windows
SC = Sandhill Crane
SE = Snowy Egret
WI = White Ibis

Contents

This publication was generated with macros developed by Albert Co. The contents of this publication were extracted from the database of The Society of Rheology abstract submission web app at http://www.rheology.org/sorabst/. This publication and the program booklet are available at http://www.rheology.org/sor/publications/Meeting_Booklets/. The program and abstracts are also accessible using the responsive web app at https://www.rheology.org/sor172/.

Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Audubon DEF PL1

Microrheology's place in the rheologist's toolbox

Eric M. Furst
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Microrheology is a set of maturing methods and techniques with unique capabilities to aid our understanding of a material's rheological properties or help in the design of new materials. Microrheology uses the movement of colloidal particles in a material, essentially as tiny, "embedded rheometers." The operating regime of microrheology favors samples that are softer and more delicate than those that have played important roles in the development of the field---polymers, glassy liquids, elastomers---these lie outside the operating range of most microrheology methods. But microrheology opens a wide range of samples and conditions which may be difficult, if not impossible, to measure by conventional rheometry. From the studies of Heilbronn, Freundlich, and Seifriz in the early 20th century on, particles have been used to measure rheology in small sample volumes. Today, particle tracking, single-particle interferometry, magnetic bead, and laser tweezer microrheology typically require sample volumes between ~1 and 10 microliters. This opens up many scarce and expensive materials to rheological characterization. Formulations of protein therapeutics and emerging biomaterials are just two examples. Because the acquisition times are short, the small sample dimensions facilitate rapid mass and heat transfer, and the methods can harness microfluidics for sample preparation and manipulation, microrheology enables rapid screening of conditions and compositions to capture the "genome" of a material. Microrheology is growing in its versatility and importance in the rheologist's toolbox.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Monday 10:00 Audubon B SC1

Phase behavior and dynamics of polymer-bridged colloidal latex particle suspensions simulated by a novel hybrid population balance - Brownian dynamics method

Elnaz Hajizadeh, Yu Shi, and Ronald G. Larson
Chemical Engineering, University of Michigan, Ann Arbor, MI 48105, United States

We develop a novel hybrid population balance - Brownian dynamics (Pop-BD) simulation technique to investigate the phase behavior and linear viscoelastic response of the waterborne colloidal latex paint particles with associative thickeners, e.g., hydrophobically modified polyethylene oxide urethanes (HEUR). The Pop-BD method couples a set of population balance equations of the bridge-to-loop exchange of the telechelic HEUR chains on the latex particles with a Brownian dynamics simulation, the latter governing only the dynamics of the latex particles. The radial distribution function, g(r), of the particles, along with direct imaging of particle configurations, suggests that both single- and two-phase solutions can develop, as well as colloidal crystals, depending on the average number of bridges per particle, N_B, and volume fraction of the particles, ?. In addition, we develop an effective potential, U_eff, describing the particle-particle interactions, U_cc, and a HEUR chain stretching potential, U_(s,tot), from which we extract the parameters for a Baxter potential that approximates the net interactions between particles, including the effects of the HEUR bridges. The Pop-BD simulation results for the phase behavior show good agreement with the predictions of the Baxter phase diagram for an equivalent suspension of sticky hard spheres.

Monday 10:25 Audubon B SC2

Interplay of enthalpic and entropic contributions in grafted polymer chains of self-suspended hairy nanoparticles

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Self-suspended hairy nanoparticles have recently drawn significant attention owing to their ability of showing good phase stability in absence of a dispersing medium. Here, we report on the dynamics and structure of PEG grafted silica that show several phenomena like thermal jamming, slow-down of polymer chain dynamics as well as stress overshoot during start-up of steady shear. The entropic attractions between the polymer chains owing to the particle curvature can explain many of the observed behaviors. Further, we show that the attraction force between tethered polymer chains can be manipulated in mixtures of hairy nanoparticles with different polymer chemistry to design materials with unusual characteristics. Specifically, we use blends of hairy nanoparticles with PEG and PMMA polymer corona, which are known to have negative Flory-

Huggins interaction parameter (?). These blends show similar soft glassy rheological behavior, but with a significantly higher plateau modulus and yielding energy. SAXS experiments and DFT analysis further reveal that the grafted polymer chains are highly stretched and interdigitated owing to the favorable enthalpic attractions. As an extension to these ideas, we study hairy nanoparticle blends with polymer chains having positive ? parameter (SiO2-PEG/SiO2-PI). Previous studies on block-copolymers based on polymers with positive ? parameters have shown novel micro-phase separation and self-assembly in contrast to polymer-blends, owing to their higher entropy penalty. In SiO2-PEG/SiO2-PI blends, rheological experiments reveal large reduction of storage modulus and energy of dissipation compared to single component materials. We explain these in terms of a competition between enhanced enthalpic repulsions between incompatible corona chains with the entropic requirement of space filling. More subtle effects of this enthalpy-entropy competition are well captured by quantifying the end-to-end distance (and stretching of the PI chains), and the terminal and a-relaxation dynamics of PI.

Monday 10:50 Audubon B SC3

Polyelectrolyte - particle assembly in mixed hydrodynamic fields

Nikolas Wilkinson, Athena Metaxas, and Cari Dutcher
University of Minnesota, Minneapolis, MN, United States

Water-soluble polymers with ionizable groups, or polyelectrolytes, are used in a number of applications due to the polymers unique ability to form mesoscale structures in solution. There are a number of known potential mechanisms for the mesoscale solute assembly, including charge neutralization, polymer depletion, polymer bridging, polymer adsorption, and patch flocculation, but the impact of time-dependent chemical and hydrodynamic conditions on assembly kinetics and final microstructure still remains largely uncertain. We seek to improve understanding of the dynamics of particle-particle, polymer-polymer, and polymer-particle interactions in complex hydrodynamic flows. Here, we explore assembly dynamics using cationic polyacrylamide, a polymer commonly used in water treatment, and anisotropic Na-bentonite clay particles. We will highlight recent advancements in polymer-particle floc structure visualization that allows for improved understanding of the process variable effects on flocculation (Wilkinson et al., 2016). We will also discuss a novel use of Taylor-Couette (TC) flow, or flow between rotating concentric cylinders, for studying how the hydrodynamics effects assembly and structure of these materials during the flocculation process. TC flow offers a high degree of control over hydrodynamics during the flocculation experiment when compared to traditional flocculation experiments. We will present a new TC cell design that allows for radial injection of fluids into the annulus while both cylinders are rotating. The ports allow injection of the polyelectrolyte solutions into particle laden flows, to study floc formation and growth in a well defined hydrodynamic field. This work sheds more light on the complexities of polymer flocculation, towards improving dosing and treatment optimization for more efficient water treatment.

Monday 11:15 Audubon B SC4

Soft colloid - polymer mixtures at extreme size ratios: Gelation and confinement effects

Dimitris Vlassopoulos[1], Domenico Truzzolillo[2], and Maria C. Merola[3]
[1]Institute of the Electronic Structure and Laser, Foundation for Research and Technology - FORTH, Heraklion, Crete 70013, Greece; [2]Universirty of Montpellier, Montpellier, France; [3]Chemical Engineering, Stanford University, Stanford, CA 94305, United States

We examine the rheology of mixtures of soft colloids with linear polymers. To this end, we use star polymers as model soft colloids and mix them with linear homopolymers, all polybutadienes, in good solvent squalene. For very small polymer/colloid size ratio (0.05) we find a soft star glass will melt and eventually form a re-entrant gel upon addition of linear polymers. The osmotic force of the additives leading to star shrinkage and depletion is responsible for this behavior that marks a departure from that of respective mixtures with hard spheres. On the other hand, for large size ratios (close to 1) we monitor the relaxation time and modulus of the linear chains in the mixture upon increasing their concentration. Their dependencies on concentration are much weaker compared to the respective ones in the absence of stars, suggesting an effective confinement effect due to the stars. This effect depends sensitively on the concentrations of both stars and linear polymers. We show how to obtain a universal description of the phenomenon with appropriate scaling analysis, and hence to control the chain dynamics. The key concept for rationalizing the observed behavior is, again, the osmotic shrinkage of the (close packed) stars and effective star-linear impenetrability. Work in collaboration with M. Gauthier (Waterloo) and C. N. Likos (Vienna).

Monday 11:40 Audubon B SC5

The effect of dispersion level of CNTs introduced by ultrasonic treatment on linear and nonlinear viscoelastic behaviors of PP/CNT nanocomposites

Avraam I. Isayev[1], Jing Zhong[2], and Tian Liang[2]
[1]Polymer Engineering, University of Akron, Akron, OH, United States; [2]University of Akron, Akron, OH, United States

PP/CNT nanocomposites of various concentrations are prepared using ultrasonic extrusion to achieve different CNT dispersion levels. Accordingly, this study is aimed to investigate the linear and nonlinear rheological behaviors of CNT-filled PP as affected by the dispersion level. Studies are performed using SAOS, LAOS, start-up shear flow and step-strain relaxation. The improved dispersion of CNTs by ultrasonic treatment is found to increase the shear stress level at different shear rates. The relaxation modulus of PP/1wt%CNT composites is found to be lower at low strains, than that at high strains, due to the instability of the filler network. LAOS results of PP and PP/1wt%CNT composites indicate that the elastic and viscous Lissajous curves are ellipses. In contrast, PP/3wt%CNT and PP/5wt%CNT composites at high strain amplitudes the shapes of the Lissajous curves are distorted, as a result of nonlinearity. The intensity of the third harmonic I_(3/1) increases with strain amplitude and CNT concentration. Ultrasonic treatment of PP/CNT nanocomposites, leading an improved CNT dispersion, further enhances the nonlinear

behavior. At low CNT concentrations, both G' and G" decrease with strain amplitude, but at high concentrations, a G" maximum appears. Chebyshev polynomials were used to decompose the elastic and viscous stresses. At higher strain amplitudes, both the elastic and viscous stresses exhibit a nonlinear behavior. All the PP/CNT composites exhibit a strain-stiffening behavior. v_3/v_1shows a peak with increasing of strain amplitude, meaning a firstly intra-cycle shear thickening followed by intra-cycle shear-thinning behavior with the strain amplitude. These intra-cycle nonlinear behaviors are increased with the increase of CNT concentration and enhanced by the ultrasonic treatment.

Symposium BA
Biorheology & Active Fluids

Organizers: David Saintillan and Christian Wagner

Monday 10:00 Audubon DEF BA1

Network formation in an infinite sea of water: Concentration-dependent rheology of hagfish defense gel

Gaurav Chaudhary[1], Douglas S. Fudge[2], and Randy H. Ewoldt[1]
[1]Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Schmid College of Science and Technology, Chapman University, Orange, CA 92866, United States

Hagfish make a unique material with remarkable properties. When provoked or attacked, the animal releases a small volume of biopolymer/biofilament material that unfolds, assembles, and expands in water by a factor of 10,000. The resulting gel is cohesive, forming a clogging network used for defense. The successful use of the defense gel is ever the more remarkable considering that hagfish cannot control the concentration of the resulting gel directly; they simply exude a concentrated material into an "infinite" sea of water. This raises questions about the robustness of gel formation and properties across a range of concentrations. In this work, we study the concentration dependent rheology of hagfish defense gel. We observe that viscoelastic properties are linearly dependent on concentration, over the range explored. Moreover, this ultra-soft material (G~0.02 Pa) has a power-law viscoelastic response in creep (fit by a fractional Kelvin-Voigt model), persistent at all concentrations with nearly constant fractal dimension, indicating a robust self-similarity in its structure. Oscillatory shear experiments are consistent with the creep tests. The linear dependence of elastic modulus on concentration is similar to that of affine stretch-dominated networks with high crosslink density. Notably, this is different from many other biopolymers networks which show a stronger dependence on concentration. Thus, hagfish defense gel seems distinctly suited to assemble in an un-controlled "infinite" sea of water.

Monday 10:25 Audubon DEF BA2

Effect of oleic acid plasticizer and glutaraldehyde crosslinker on zein protein gel formation

Emma A. Barber and Jozef L. Kokini
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Zein is a major byproduct of ethanol production and the most abundant protein in corn. It has film forming capabilities when dissolved in ethanol solvent, but zein alone forms a very brittle film. Research has shown that the properties of these protein films can be changed by incorporating different additives such as plasticizers and crosslinking agents. Both of these chemical groups give desirable characteristics to zein films, but little research has been done on the interactions of both crosslinker and plasticizer together. This study looked at the effect of both glutaraldehyde (GDA) crosslinking agent and oleic acid (OA) plasticizer on zein protein gelation. The concentration of both of these additives was varied from 0-8% GDA (w/w zein) to 0.8-1.2:1 OA (w/w zein). Samples were taken from the solutions every 12 hours until no significant difference was found between the storage modulus (G') over a period of 24 hours. As the protein gelled, the G' increased showing a change from liquid to solid like behavior. The introduction of GDA did increase the final G' values of the protein gels by an order of magnitude, but little change was seen between 4% and 8% GDA samples. An increase in OA content caused a decrease in G' value. The inclusion of GDA decreased the change in G' with OA content, but the 0% GDA gels showed a clear decrease in G' with an increase in OA. Overall the GDA and OA proved to play competing roles within the gelation process of zein protein.

Monday 10:50 Audubon DEF BA3

Using solution shear to test the effects of protein conformational flexibility on dense liquid protein clusters

Michael C. Byington, Mohammad S. Safari, Jacinta C. Conrad, and Peter G. Vekilov
University of Houston, Houston, TX, United States

Shear flow alters the rate at which crystals nucleate from solution, yet the underlying mechanisms remain poorly understood. Here, we explore the response to shear of dense liquid clusters, which may serve as crystal nucleation precursors. Solutions of the protein lysozyme were sheared in a Couette cell at rates from 0.3 to 200 s^{-1} for up to seven hours. The cluster size and total population volume were characterized by dynamic light scattering. We demonstrate that shear rates greater than 10 s^{-1} applied for longer than one hour reduce the volume of the cluster population. The likely mechanism of the observed response involves enhanced partial unfolding of the lysozyme molecules, which exposes hydrophobic surfaces between the constituent domains to the aqueous solution. We show that disruption of the intramolecular S-S bridges does not contribute to the mechanism of response to shear. The decrease of the cluster population with increasing shear rate or shear time suggests that nucleation may be inhibited at relatively high shear rates and that nucleation rate enhancement due to shear may be due to alternative mechanisms.

Monday 11:15 Audubon DEF BA4

Towards modeling biodistribution of nanoparticles in vivo

Rekha R. Rao[1], Jonathan Clausen[1], Jeremy Lechman[1], Justin Wagner[1], Scott Roberts[1], Mark Ferraro[1], Jeffrey Brinker[1], Kim Butler[2], and Zixiang Liu[3]
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It is now recognized in the nanoparticle (NP) therapeutics field that the colloidal stability of NPs in the blood is crucial to avoiding NP clearance via organ filtration or uptake by the macrophage system to achieve delivery to targeted tissue, cells, etc. NP introduced into the blood stream of a living organism experience a complex flow path influenced by many factors dependent both on the particles characteristics and patient specific information. For instance, the size, shape, stiffness, and surface affinity of the NPs determine biodistribution and bioavailability of the therapeutics. Currently, there are no available models that can predict NP biodistribution/dynamics from the generally measured NP physicochemical characteristics. We are developing a multiscale modeling approach to elucidate the underlying mechanisms of NP transport in vivo. Red blood cell level models are used to understand the diffusion of NPs in capillaries and develop appropriate diffusivity tensors to be used at the continuum-scale. A continuum model has been developed for NP transport based on a Casson model with a yield stress for blood rheology and a full diffusivity tensor for the transport equation. Work on imaging vasculature and NP transport in a chicken embryo model to determine blood vessel geometries, particle velocities and sticking coefficients is underway. To perform finite element simulations of transport requires a discrete model that conforms to the CAM geometry. The conformal decomposition finite element method was used to create a 3D finite element mesh of the geometry from 2D surface meshes of the images, which conform to complex interfaces. Preliminary models of blood flow and particle transport in the CAM will be shown and compared to imaging data.

Monday 11:40 Audubon DEF BA5

Mechanical characterization of corneal cells for investigating their conformability with contact lenses

Juho Pokki, Maria C. Merola, Emily C. Hollenbeck, Namita Nabar, and Gerald G. Fuller
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The mechanical properties of cells, which are caused by complex intracellular structures, are modulated by biological processes and extracellular mechanical stimuli. Further, cells' mechanical behavior affects on how cells maintain interactions with their environment during biological strains. These interactions (e.g., adhesion) are crucial for how cells adapt to the presence of artificial material, such as contact lenses or medical implants. A variety of technologies are used to investigate cell mechanics, such as atomic force microscopy (AFM) and microrheological methods, which provide localized information from single cells. To overcome the challenges with the biological variation between individual cells, new technologies are necessary to acquire enhanced statistics on cell mechanics in controlled conditions. We present measurements using a live-cell monolayer rheometer (LCMR) that can characterize averaged cell mechanics or averaged cell adhesion. The LCMR enables the investigation of biologically active layers: controlled amounts of live cells, extracellular components, or artificial material (e.g., contact lenses). In this work, cell mechanics of the ocular cornea are characterized to provide understanding on how these cells mechanically conform onto the artificial surface of a contact lens. To simulate physiological conditions, cell mechanics is quantified in experiments in which cells are sheared tangential to the cell layers. Time-dependent step-strain tests with strain sweeps are used to characterize the mechanical relaxation of the cell layers. The relaxation responses provide quantitative information of the cell interior rearrangements and cell-cell attachments. The quantification of cell mechanics using the LCMR has the potential for multiple biomedical applications, including disease diagnosis and drug-efficacy screening.

Symposium SG
Self-assembled Systems, Gels and Liquid Crystals

Organizers: Kendra Erk and Virginia Davis

Monday 10:00 White Ibis SG1

Rheo-structural characterization of aluminosilicate fluids during the gelation process

Arnaud Poulesquen, Jean-Baptiste Champenois, and Thomas Piallat
DEN, MAR, DTCD, SPDE, LP2C, CEA Marcoule, Bagnols sur Cèze 30207, France

Thanks to their environmental acceptability and their adaptability over a wide range of applications, alkali solutions of aluminosilicates are increasingly used for their important role as inorganic and water based binders (geopolymer applications), notably for the production of mineral based, ecological materials for the building and construction industry. Although such solutions are increasingly used in the industry, there remain outstanding questions regarding their stabilities, and more precisely concerning the gelation process that is driven by the composition of the solution. It is therefore crucial to provide a clear and realistic description of such fluids during the gelation process, which remains quite not well known, and has to be confirmed experimentally and theoretically. The aim of this work is to describe the sol/gel transition according to the chemical composition of the solution (alkali silicates and aluminates content) by combining rheology and time resolved Small Angle X-ray Scattering (SAXS). Rheological results show that the gelling time decreases and the strength of the inorganic network increases when the aluminum content increases. On the other hand, strain sweep experiments demonstrated that the critical strain is the same regardless the sample. This result indicates that the forces responsible for the viscoelastic properties are independent of the aluminum content. These viscoelastic results

are correlated to the results obtained at mesoscale by SAXS where the densification of the percolating network is monitored in situ. The difference in structure of aggregates will be discussed in relation to the rheological results.

Monday 10:25 White Ibis SG2

Processing-dependent gelation of aqueous methylcellulose

Arif Z. Nelson, Yushi Wang, Anthony S. Margotta, and Randy H. Ewoldt
Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

We report experimental measurements of the effect of dynamic flow conditions on aqueous methylcellulose, a material that forms a brittle gel at elevated temperatures. We choose to control the applied stress-rather than the applied deformation-during gelation to systematically explore processing-to-structure-to-property relations. Flow makes gelation more difficult, i.e. increases the apparent gelation temperature, and makes the final gel weaker, i.e. decreases both the hot gel elastic modulus and apparent failure stress. In extreme cases, formation of a fully percolated network is inhibited and a soft granular yield-stress fluid is formed. A design space of material properties is generated as a function of concentration and applied stress during gelation. This reveals the possibility of catastrophic inaccuracy when not designing with processing/application conditions in mind. Additionally, our findings of a stress-dependent gel temperature raise questions for other rheological tests that measure gel temperature at finite stress, such as SAOS. Our systematic approach here should serve as a method for verifying any SAOS gelation measurements, namely, to measure gelation as a function of applied stress, and report the limit that stress goes to zero.

Monday 10:50 White Ibis SG3

Hardening and yielding in colloidal gels

Mehdi Bouzid and Emanuela Del Gado
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Attractive colloidal gel networks are disordered elastic solids that can form even in extremely dilute particle suspensions. With interaction strengths comparable to the thermal energy, their stress-bearing network can locally restructure via breaking and reforming of inter-particle bonds. We use molecular dynamics simulations of a model system to investigate the strain hardening and the yielding process. During shear start up protocol, the system exhibits strong localization of tensile stresses that may be released through the breaking and formation of new bonds. In addition we show that the role of the network connectivity is crucial to understand the emergence of this nonlinear response and helps to rationalize some experimental observations. At large accumulated strains, the strain-induced reorganization of the gel may trigger flow heterogeneities and eventually lead to the yielding of the gel via a quasi brittle damage of its structure.

Monday 11:15 White Ibis SG4

The rheology and microstructure of aging thermoreversible colloidal gels & attractive driven glasses

Melissa B. Gordon, Christopher J. Kloxin, and Norman J. Wagner
Chemical & Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

The properties of colloidal gels and glasses are known to change with age, but the particle-level mechanisms by which aging occurs is are fully understood, which limits our ability to predict macroscopic behavior in these systems. Homogeneous colloidal gels and glasses are disordered systems that are trapped in a dynamically arrested, non-equilibrium state. It is generally accepted that the aging of colloidal gels is governed by their potential energy landscape, where thermodynamic equilibrium is the global minimum; however, many systems cannot reach true equilibrium on an experimental timescale. Instead, the arrested material explores local potential energy minima resulting in aging behavior. Due to their fundamental significance and industrial applicability, we investigate the microstructural basis of aging in a model adhesive hard sphere (AHS) system, consisting of silica nanoparticles grafted with an octadecyl brush dispersed in tetradecane. In this work, we quantitatively relate rheological aging to structural aging by simultaneously measuring the bulk properties and gel microstructure using rheometry and small angle neutron scattering (Rheo-SANS), respectively. Specifically, we develop a quantitative and predictive relationship between the macroscopic properties and the underlying microstructure (i.e., the effective strength of attraction) of an aging colloidal gel and attractive driven glass, and study it as a function of the thermal and shear history. Analysis suggests local particle rearrangements as the mechanism of aging, which strongly supports aging as a trajectory in the free energy landscape dominated by local particle relaxations. The analyses and conclusions of this study may be 1) industrially relevant to products that age on commercial timescales, such as paints and pharmaceuticals, 2) applicable to other dynamically arrested systems, such as metallic glasses, and 3) used in the design of new materials.

Monday 11:40 White Ibis SG5

Isotropic-nematic phase transition in liquid crystal

Chiqun Zhang, Amit Acharya, and Noel Walkington
Carnegie Mellon University, Pittsburgh, PA, United States

The liquid crystal is a distinct phase of matter which is between the crystalline and isotropic liquid states. There are many types of liquid crystal phases, depending upon the amount of order in the material, namely isotropic phase, nematic phase, smectic phase and cholesteric phase. As the temperature decreases, the material transitions from the isotropic phase to the nematic phase. Nematic tactoids will be formed at the beginning of the phase transition, with point defects, cusps, existing. Then, if the temperature keeps decreasing, the nematic tactoids grow and coalesce, possibly causing the formation of disclinations at the domain junctions. Ericksen introduced a variable degree of orientation to indicate different phases. In this work, we adopt Ericksen's work and introduce an augmented Oseen-Frank energy, with non-convexity in both the interface energy and the

phase state. We derive the governing equations for the phase transition dynamics. With our model, we study and predict tactoid nucleation, expansion and coalescence during the process of the phase transition. And we try to reproduce observed behaviors in experiments and make predictions that can be tested in experiments.

Symposium EF
Emulsions, Foams & Interfacial Rheology

Organizers: Cécile Monteux and Sachin Velankar

Monday 10:00 Sandhill Crane EF1

The effect of a yield stress on the drainage of the thin film between two colliding Newtonian drops

Sachin Goel and Arun Ramachandran

Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada

Coalescence of drops immersed in fluids possessing a yield stress has been of interest to many industries such as the oil extraction, cosmetics, and food industries. Unfortunately, a theoretical understanding of the drainage of the thin film of Bingham fluid (a model yield stress fluid) that develops between two drops undergoing a collision is still lacking, with the exception of two prior studies (Can. J. Chem. Eng., vol. 65, pp. 384-390, 1987, and J. Phys. Chem., vol. 90, pp. 6054-6059, 1986.) that make ad-hoc assumptions about the film shape. In this work, we examine this problem via a combination of scaling analysis and numerical simulations based on the lubrication analysis. There are four key features of the film drainage process of Bingham fluids. First, the introduction of a yield stress in the suspending fluid retards the drainage process relative to Newtonian fluid of the same viscosity. This effect becomes stronger for low capillary numbers in the spherical configuration of the film, and for large capillary numbers in the dimpled configuration. Second, the drainage time shows a minimum with respect to the capillary number. Third, the effect of yield stress on the drainage process becomes more pronounced at lower Hamaker constant. Lastly, as a critical height is approached, drainage can be arrested completely due to the yield stress. This critical height scales as $\tau_0^2R^3/\gamma^2$, where τ_0 is the yield stress, R is the drop radius and γ is the interfacial tension, and is, surprisingly, independent of the force colliding the drops. Therefore, the yield stress can be employed as an independent tuning parameter that sets an upper limit on the drop size beyond which coalescence is suppressed in sheared emulsions. This and other distinguishing characteristics of the drainage process will be elucidated in the presentation.

Monday 10:25 Sandhill Crane EF2

A new mechanism for the wetting of a surface by the droplets of an emulsion

Suraj Ganesh Borkar and Arun Ramachandran

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Classical hole nucleation theory for dewetting of a film requires the formation of a hole of sufficiently large diameter to grow and cause film rupture. In our experiments of film drainage of silicone oil between a deformable glycerol droplet and a rigid mica surface, an immobilized flat film was formed, by virtue of polymer confinement. At long time scales (~50 hours), nucleation and growth of glycerol islands were observed underneath the droplet at the silicone oil/mica interface. These islands grow, coalesce and eventually lead to film rupture. To the best of our knowledge, such a wetting mechanism has been reported for the first time. We studied the buoyancy-driven film drainage between a deformable droplet and a rigid mica surface. The film drainage profiles were reconstructed using Reflection Interference Contrast Microscopy (RICM) by application of a ray tracing algorithm. Optical measurements and scaling analyses showed three distinct temporal regimes during the settling period. Agreements with Newtonian film drainage dynamics were established for film thicknesses greater than ~ 10 nm. For silicone oil films, formation of a flat immobilized layer was eventually attained. The origin of this repulsive force is attributed to layering and pinning of silicone oil chains leading to entropic repulsion. The effective viscosity of the confined polymer film was estimated to be six orders of magnitude higher than that of the bulk, with a yield stress value of 0.1 Pa s. Upon waiting for sufficiently long time, nucleation and growth of glycerol islands were observed on the mica surface. The process is similar to the phenomena of Ostwald ripening wherein glycerol is transported via diffusion from the glycerol droplet to the silicone oil/mica interface. TOF-SIMS and cryo-SEM/FIB were used to confirm the new mechanism that we observe.

Monday 10:50 Sandhill Crane EF3

The role of elasticity in bubble breaking

Daniele Tammaro, Rossana Pasquino, Massimiliano M. Villone, Gaetano D'Avino, Ernesto Di Maio, Nino Grizzuti, and Pier Luca Maffettone

Università di Napoli Federico II, Napoli, Italy

The breaking dynamics of the thin film separating a bubble from bulk air has been studied since several centuries. When a hole is induced in a bubble made by a Newtonian fluid, a creep due to the surface tension works provoking the hole opening. The kinematics of the hole opening is tricky, but easily understandable, with viscous forces and inertia involved in the process. However, when the liquid entrapping air is of viscoelastic origin, unusual behavior in rupture is displayed. Elasticity is indeed an important parameter, both during the bubble floating and in the hole opening: viscoelastic fluids can, in fact, store elastic energy (which can be released during rupture) that, in turn, strongly affect the breaking dynamics. The mechanism of viscoelastic bubble breaking is unknown and only very few experimental observations have been recently reported in the literature. In this contribution, the retraction of a circular viscoelastic sheet with a hole in the middle is studied by finite element simulations.

The interplay between inertial, viscous, surface and elastic forces on the hole evolution is investigated. The simulation results are compared with experiments where the breaking dynamics of a viscoelastic bubble is thoroughly tracked through a fast camera.

Monday 11:15 Sandhill Crane EF4

Direct numerical simulation of a bubble suspension in small amplitude oscillatory shear flow

Patrick Anderson, Christos Mitrias, Martien Hulsen, and Nick Jaensson
Eindhoven University of Technology, Eindhoven, The Netherlands

In this work we present 3D direct numerical simulations of bubbles suspended in a Newtonian fluid subject to oscillatory strain. The influence on the rheology of the sus- pension due to the increase of the volume fraction is investigated for the cases of a single bubble and a random distribution of bubbles in a fully periodic domain. The resulting stress, as an output of our simulation, is used to calculate the viscosity of the bubbly fluid. Using the linearized Frankel and Acrivos model we validated our results. The analytical model shows good agreement with the numerical results even for volume fraction well above the dilute limit. Comparing the analytical results, where only linear terms of volume fraction are included, with our simulations we are able to study the effect of higher-order terms. This effect seems to be minimal for the high and low frequency regimes, but significantly increases when the scaled frequency ?? is close to 1. The increase in volume fraction has the opposite effect on viscosity in the high and low frequency regimes. When the frequency is small, the bubbles act as rigid fillers, thus increasing the viscosity. In contrast, in the high frequency regime the bubble deformation rate compared to the bulk strain rate is much larger, hence, most of the strain is taken by the inviscid phase leading to a decrease in viscosity. Results of the single bubble problem show surprisingly good match with the ones obtained from the multiple bubbles simulations.

Monday 11:40 Sandhill Crane EF5

Modeling microstructural inertia effects in dilute emulsions

Paul M. Mwasame, Norman J. Wagner, and Antony N. Beris
Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Existing conformation tensor models for the rheology of emulsions in the limit of zero particle Reynolds number predict a positive first normal stress differences (N_1) and negative second normal stress differences (N_2), in agreement with simulations. On the contrary, emulsions of ellipsoidal droplets at finite particle Reynolds numbers display an interesting rheology where N_1 is negative and N_2 is positive. This rheological behavior is also accompanied by a reversed orientation of emulsion droplets towards the velocity gradient direction [1]. At the moment, there are no macroscopic theories that describe such behaviors. This work extends upon our previous model, rigorously developed for small Capillary and zero particle Reynolds numbers [2]. Here we outline a new application of non-equilibrium thermodynamics to allow for the incorporation of microstructural inertia effects into a conformation tensor model for emulsions. The resultant contravariant tensor model for such emulsions is rigorously validated through a comparison to known asymptotic theory in the limit of small but finite Reynolds numbers [3]. Among the findings is the emergence of a new extended co-deformational time to characterize microstructural inertia effects through an additional term weighted by a parameter ζ. ζ is inversely related to the Ohnesorge number ($Oh \equiv \mu/(\rho a T)^{1/2}$) as $\zeta \propto Oh^{-2} \propto Re/Ca$ and reflects the competition between Capillary and Reynolds number effects. The resultant model, with all parameters obtained from independent asymptotic theory, compares well with independent rheological data on emulsions at finite Reynolds numbers [1].

[1] X. Li and K. Sarkar, J. Rheol. 49, 1377 (2005). [2] P. M. Mwasame, N. J. Wagner, A. N. Beris "A Thermodynamically Consistent Macroscopic Model for Dilute Emulsion Behavior" (abstract submitted for SOR 2016 annual meeting) [3] R. V. Raja, G. Subramanian, and D. L. Koch, J. Fluid Mech. 646, 255 (2010).

Symposium SM
Polymer Solutions & Melts

Organizers: Carlos R. López-Barrón and Nicolas Alvarez

Monday 10:00 Snowy Egret SM1

Solution rheology of dry native cellulose in ionic liquids

Ralph H. Colby and Behzad Nazari
Materials Science and Engineering, Penn State University, University Park, PA 16802, United States

Cellulose is the most abundant renewable polymeric natural resource on our planet. Native cellulose can dissolve in certain ionic liquids and the fibers spun from those solutions have higher modulus than fibers from spun from solutions of chemically modified cellulose, since native cellulose has maximal hydrogen bonding. We report solution rheology of five native cellulose samples of different molecular weight in three different ionic liquids. 1-ethyl-3-methylimidazolium methylphosphonate ([EMIm] [P(OCH3)(H)O2]) is a good solvent for cellulose, while 1-butyl-3-methyl imidazolium chloride ([BMIm] [Cl]) and 1-ethyl-3-methylimidazolium acetate ([EMIm] [Ac]) are ?-solvents for cellulose, based on the concentration dependences of viscosity and longest relaxation time. Failure of the Cox-Merz rule for cellulose solutions in ionic liquids suggests that cellulose is not a simple flexible polymer in solution. Trace amounts of water compete for hydrogen bonds and can impart a yield stress to the solution rheology, which grows in magnitude as more water is incorporated. However, simply heating the solution to 80 C drives off the water and reverts the solutions to viscoelastic liquids with no yield stress.

Monday 10:25 Snowy Egret SM2

A multi-fluid model of phase-inversion membrane formation

Douglas R. Tree and Glenn Fredrickson
University of California Santa Barbara, Santa Barbara, CA, United States

Industrial processes for producing polymer-based materials operate away from equilibrium, making the final microstructure - and thus the properties of the material - dependent on process history. Describing such processes by traditional simulation methods has proven difficult because of the confluence of complex thermodynamics and non-trivial fluid mechanics. We have recently developed a "multi-fluid" simulation framework for examining the dynamics of multiphase polymer solutions that combines a field-theoretic approach to thermodynamics with continuum fluid mechanics. In this framework, we use a ternary polymer solution model to investigate the phase inversion process for making polymer membranes. After characterizing the model and methods, we investigate a number of important phenomena that occur across several length and time scales including (i) mass-transfer between the polymer film and the non-solvent bath, (ii) phase separation between polymer lean and polymer rich regions and (iii) long-time coarsening behavior. We will discuss the implications of these results on the formation mechanisms of various microstructures found in polymer membranes.

Monday 10:50 Snowy Egret SM3

Dynamics of polymer-grafted nanoparticles in solutions of linear polymer investigated using neutron and x-ray scattering techniques

Ryan Poling-Skutvik, Jacinta C. Conrad, and Ramanan Krishnamoorti
University of Houston, Houston, TX, United States

Grafting particles with polymers enhances particle dispersion in high molecular weight polymer solutions and melts and thereby increases the storage modulus of composite materials. To disperse the particles in these materials requires an understanding of the dynamics of polymer-grafted nanoparticles. When the grafted polymer is small compared to the particle, the dynamics of a grafted particle are similar to those of a bare particle. In the opposite limit, when the grafted polymer is much larger than the particle, the grafted particle dynamics are similar to those of a star polymer. Between these two limits, the dynamics of grafted nanoparticles are poorly understood. We dispersed silica particles grafted with high molecular weight polystyrene in solutions of linear polymer of various molecular weight and concentration. The molecular weights span the entanglement molecular weight Me in solution. Exploiting the difference in scattering contrast between neutrons and x-rays, we measured the relaxations of both grafted polymer chains and of the silica cores. Over length scales less than 20 nm and time scales less than 100 ns, the relaxations of grafted chains were markedly different than those of free polymer. The grafted chains relaxed diffusively but were confined by neighboring chains. The confining length scale decreased with matrix concentration and was independent of matrix molecular weight. On length scales larger than 50 nm and time scales longer than 1 ms, the grafted nanoparticles moved diffusively at low matrix molecular weights and subdiffusively at high matrix molecular weights, due to polymer entanglements. Our results indicate that the matrix polymer in a semidilute solution confines the grafted polymer and slows particle relaxations, especially at high matrix molecular weights. When the grafted polymer is similarly sized to the particle core, the particle dynamics depend on the relaxations of the grafted polymer, with implications for targeted drug delivery and rheology on composite materials.

Monday 11:15 Snowy Egret SM4

Microscopic origin of elastic instability in flow of polymer solutions through porous media: Using microfluidics and DNA imaging

Pouyan E. Boukany, Durgesh Kawale, and Shaurya Sachdev
Chemical Engineering, Delft University of Technology, Delft 2629 HZ, The Netherlands

Polymeric flows at high Weissenberg number (Wi >1), typically exhibit a number of intriguing flow phenomena such as wall slip, shear banding, vortex formation, and necking during extensional, shear and mixed flow. However, the origin and molecular picture behind many of these complex flow responses is not understood yet. This work focuses on extending the single molecule experiments to flow of polymer in porous media. We experimentally investigate the flow of HPAM solution in model porous media at high Wi. First, we explore the effect of pore shapes on flow pattern and pressure drop using periodic arrays of micro-pillars. In the apparent shear thinning regime, stationary dead zone has been formed around obstacles with fast flow-zones between them. At higher Wi, these dead-zones become unstable with strong temporal fluctuations in both pressure drop and flow field. To understand the microscopic origin of this flow instability, we directly visualised the conformational dynamics of individual polymers during flow in porous media. We observed that this dead zone formation is directly related to coil-strech transition of the polymers with flow around the obstacle. The presence of the stretched polymers modifies the flow in the vicinity of the obstacle giving rise to formation of low and high shear flow, and large molecular elongations with broad distribution. The mechanism of elastic instability in porous media is explicitly described based on single molecule measurements.

Monday 11:40 Snowy Egret SM5

Stress-gradient-induced polymer migration in solutions flowing between rotating concentric and eccentric cylinders

Elnaz Hajizadeh and Ronald G. Larson

Chemical Engineering, University of Michigan, Ann Arbor, MI 48105, United States

We extend our recent continuum theory for the stress-gradient-induced migration of polymers in solution (Zhu et al., J. Rheology, 60, 327-343, 2016) to concentric (the so-called Taylor-Couette flow) and eccentric cylinders by incorporating the effect of solid boundaries on concentration variations. We obtain theoretical results for the steady-state distribution of dilute solutions of polymer dumbbells using a systematic perturbation analysis in Weissenberg number, Wi and Peclet number, Pe. We establish the range of validity of our theory by comparing the theoretical results with the Brownian dynamics (BD) simulations; excellent agreement is achieved for relatively small molecules, while the theory breaks down when the gradient number Gd, which quantifies the ratio of polymer size to the length scale over which, steep changes in velocity gradients exist, is greater than 0.5. We find that the presence of a thin wall depletion zone changes the lowest order solution from second to first in Wi and drastically changes the concentration field far from the depletion layer, due both to a coupling of the second derivative of the velocity field to the concentration gradient, and to convection of the polymer-depleted fluid in this layer to the bulk of the fluid. In general, we demonstrate that the polymer concentrates at different domains in the flow, depending on Pe and Wi.

Monday Afternoon

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Monday 1:30 Audubon B SC6

Anomalous stress buildup under constant strain in an aging soft glassy material: A critical evaluation

Asheesh Shukla and Yogesh M. Joshi
Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India

Soft glassy materials (SGMs), owing limited mobility of its constituents, are thermodynamically out of equilibrium. Consequently, in search of equilibrium, their microstructure and the physical properties evolve as a function of time, a phenomenon known as physical aging. Interestingly, some of relaxation modes of SGMs are so slow that they have been observed to show residual stresses when subjected to constant strain. In this work we report a peculiar phenomenon observed for aqueous suspension of Laponite, a strongly aging model SGM. An aqueous suspension of Laponite, studied in this work has been observed to be in the hyper-aging state, wherein its mean relaxation time scales stronger than linear with respect to time. The studied Laponite suspension also demonstrates time dependent evolution of modulus. We observe that, this system, when subjected to constant strain immediately after shear melting, shows stress response in two steps. Immediately after imposition of step strain, as expected, stress indeed decreases. However, after a certain finite time stress shows a minimum and starts increasing as a function of time. These experiments have been carried out on an Anton Paar MCR 501 rheometer, and it has been ensured that strain remains constant with corresponding strain rate being in the range $\pm 10^{-5}$/s. The behavior has also been observed to remain identical within experimental uncertainty upon change in the direction of applied strain. In this talk we will discuss the experimental results, the thermodynamic implications of the same, and possible microscopic origin of the observed behavior.

Monday 1:55 Audubon B SC7

Aging in soft solids: Elastically driven, intermittent relaxation

Emanuela Del Gado[1], Mehdi Bouzid[1], Jader Colombo[2], and Lucas Vieira Barbosa[3]
[1]Physics and Institute for Soft Matter Synthesis and Metrolog, Georgetown University, Washington, DC, United States; [2]Physics, Georgetown University, Washington, DC, United States; [3]CAPES, Ministry of Education of Brazil, Brasilia, Brazil

Soft solids with tunable mechanical response are at the core of new material technologies. A crucial point for applications is the progressive aging such materials undergo over time, which can have a dramatic impact on their functionalities. It is generally understood that the aging emerges from thermally activated microscopic processes, detectable via quasi-elastic scattering and akin to slower than exponential dynamics in super-cooled liquids or glasses. Nevertheless, time- and space-resolved measurements reveal dynamics faster than exponential, intermittency and abrupt microstructural changes in a wide range of materials, challenging the fundamental understanding and the control of their long-term performance. Our numerical study of a model soft solid shows that the relaxation dynamics underlying the aging of these materials change dramatically if enthalpic stresses, frozen-in upon solidification when the material is deeply jammed, are significantly larger than Brownian stresses. The timescales governing stress relaxation respectively through thermal fluctuations and elastic recovery are key. When thermal fluctuations are weak with respect to enthalpic stress heterogeneities, the stress can partially relax through elastically driven fluctuations. Such fluctuations are intermittent, because of strong spatio- temporal correlations that persist over the timescale of experiments or simulations. Hence the elasticity built into the solid structure controls microscopic displacements, and the time correlations of density fluctuations have a faster than exponential decay, as reported in experiments. Brownian motion, instead, disrupts the spatial distribution of local stresses and their persistence in time, favoring a gradual loss of correlations and a slow evolution of the material properties.

Monday 2:20 Audubon B SC8

Relaxation of colloidal glasses after flow interruption

Alan R. Jacob and George Petekidis
Dept. Mat. Sci.Tech. and IESL, Univeristy of Crete and FORTH, Heraklion 70013, Greece

Colloidal glasses of nearly hard spheres, are formed at high volume fraction (>0.59) due to entropic caging of spheres by its neighbors where Brownian motion within the cages is permitted but out-of-cage motion is largely suppressed or inhibited. These well-defined colloidal glasses are ideal for studying intriguing open problems in out of equilibrium systems under flow and after flow arrest. Experiments in sheared colloidal glasses corroborated with theory and computer simulations have helped to promote the understanding of the underlying mechanisms involved in non-linear flows such as steady shear[1], transient start-up shear tests [2] and large amplitude oscillatory shear [3]. Moreover, residual stresses persisting in colloidal glasses after cessation of steady shear flow have been recently examined [4]. Here we investigate experimentally the effects of flow interruption at various times after steady shear and during transient start up shear. Finally, insights into the microstructural rearrangements after flow cessation are gained with the help of Brownian Dynamics simulations.

[1] Convective Cage Release in model Colloidal glasses, A. R. Jacob et. al., Phys. Rev. Lett. 115, 218301 (2015). [2] Yielding of hard-sphere glasses during start-up shear, N. Koumakis et. al., Phys. Rev. Lett. 108, 098303 (2012). [3] Complex oscillatory yielding of model hard-sphere glasses, N. Koumakis et. al., Phys. Rev. Lett. 110, 178301 (2013). [4] Residual stresses in glasses, M. Ballauff et. al., Phys. Rev. Lett. 110, 215701 (2013).

Monday 2:45 Audubon B SC9

Yielding of attractive colloidal glasses during start-up shear

Esmaeel Moghimi and George Petekidis
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By a combination of experimental rheology and Brownian Dynamics simulations we investigate the transient response of attractive glasses in start up shear flow providing a link between microstructure, dynamics, and stresses. Both experiments and Brownian Dynamics (BD) simulations reveal two stress peaks indicative of two step yielding process. BD simulations give insight into microscopic origins of these two peaks. The average number of bonds per particle exhibits the maximum where the first peak takes place. The maximum of the pair distribution function, g(r), in the extension axis shows a minimum at the second peak similar to HS glasses [1, 2]. Decomposition of the stress into a hard-sphere (HS) and an attractive (depletion) contribution reveals that there are strong contributions of both stresses into the first stress peak. In contrast, the second peak is mainly linked with HS contributions. Similar with HS glasses, shear-induced cage deformation induces local constriction, reducing in-cage diffusion. A super-diffusive behavior of particles is detected near the first stress peak. Finally, attractive glasses behave dynamically as HS glass above the 1st yield stress peak indicating that the contribution of the attractions diminishes beyond the 1st yield stress peak.

[1] Koumakis, N., Laurati, M., Egelhaaf, S.U., Brady, J.F. and Petekidis, G., 2012. Physical review letters,108(9), p.098303. [2] Koumakis, N., Laurati, M., Jacob, A.R., Mutch, K.J., Abdellali, A., Schofield, A.B., Egelhaaf, S.U., Brady, J.F. and Petekidis, G., 2016. Journal of Rheology (1978-present), 60(4), pp.603-623.

Monday 3:35 Audubon B SC10

Rheology and hydrodynamic diffusion in suspensions of flow-aligning ring-shaped particles in a low Reynolds number simple shear flow

Neeraj S. Borker[1], Donald L. Koch[2], and Abraham D. Stroock[2]
[1]Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14850, United States; [2]Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States

A class of finite aspect ratio rigid particles that do not tumble in an unbounded simple shear flow at low Reynolds number were recently discovered. These flow-aligning particles have the topology of a ring of radius R with a non-circular cross-section which has a sharp outer edge and a blunt inner edge. The rheology and hydrodynamic diffusivity in a dilute (nR^3<&lt1) suspension of flow aligning rings is obtained from an analysis of pairwise interactions. The hydrodynamic interactions between interacting particles are obtained using a slender-body theory (SBT) developed for the case where the ring radius R is large compared with the characteristic radius a of the cross-section. A method of reflections expansion that can be truncated based on the weak hydrodynamic disturbances of slender rings along with force and torque free conditions lead to analytical expressions for the ring velocities and rotation rates. The asymmetric shape of the ring cross-section leads to a force per unit circumference caused by the local shear flow, a term that does not arise in previous applications of SBT. It is found that pairwise interactions do not cause flow-aligning particles to undergo a full flipping motion through a Jeffery half-orbit. Instead their orientation makes a small amplitude wobble around the stable orientation during the interaction. As a result, the viscosity remains small compared with that of slender rotating particles even in the presence of hydrodynamic interactions. While hydrodynamic particle diffusion in the gradient and vorticity directions arises from pairwise interactions, this diffusion is likewise small compared with that of rotating particles. These results show that a modification of particle shape can yield materials with strongly anisotropic structure even in the absence of external fields, suggesting a route to producing highly anisotropic reinforced polymers using simple processing flows such as injection molding.

Monday 4:00 Audubon B SC11

Structure and rheology in sheared suspensions of fibers

Jason E. Butler
Chemical Engineering, University of Florida, Gainesville, FL 32611, United States

Examples of the influence of boundaries on the dynamics, microstructure and rheology of sheared suspensions of rigid fibers are described. In the first example, fiber alignment is controlled by applying an oscillatory shear flow to the confined suspension. With the correct choice of shear amplitude and wall-spacing, the fibers can be strongly aligned perpendicular to the flow-gradient plane, whereas fibers in shearing flows typically align with the flow direction. In the second example, the rheological characterization of fiber suspensions is shown to depend on confinement. Specifically, normal stress differences as measured using free surface flows are compared with measurements from standard rheological devices. The bounding walls, which strongly confine the suspensions in the rheometers, are shown to alter the microstructure, and consequently the measured rheology, of the suspensions. In both examples, direct comparison of simulations with experiments demonstrates that a simple model, which considers only excluded volume and self-mobilities, can accurately predict the fiber dynamics and orientation distributions for these concentrated suspensions.

Monday 4:25 Audubon B SC12

A three-fluid model for predicting the behavior of concentration heterogeneities in concentrated lignocellulosic biomass

Joshua C. Duncan[1], Daniel J. Klingenberg[1], Michael D. Graham[1], and Charles T. Scott[2]
[1]Chemical and BIological Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States; [2]Forest Products Laboratory, United States Department of Agriculture, Madison, WI 53726-2398, United States

Concentrated lignocellulosic biomass is a fibrous yield stress material that is compressible because of gas voids between and within individual fibers. When a flow rate is imposed, in Poiseuille flow, this material will exhibit a nonlinear pressure profile in the flow direction with a positive curvature. This behavior can be predicted by modeling biomass as a single compressible viscoplastic material with a density-dependent yield stress. Other experimental observations cannot be captured by a single-fluid model. In extrusion experiments concentrated biomass does not always maintain a uniform composition of solid, liquid, and gas components. We also observed transient pressure fluctuations that may be related to compositional heterogeneities. We have developed a three-fluid continuum model, which includes concentration profiles for each of the components, to understand the development of concentration heterogeneities and their impact on flow behavior. We will discuss the ability of a three-fluid model to predict the formation and behavior of dry regions in flow, and their relationship with measured transient pressure fluctuations.

Monday 4:50 Audubon B SC13

Effect of temperature on rheology of fiber suspensions in water as suspending liquid

Shalaka Burlawar[1], Daniel J. Klingenberg[1], Thatcher W. Root[1], and Charles T. Scott[2]
[1]Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, United States; [2]Forest Products Laboratory, United States Department of Agriculture, Madison, WI 53726-2398, United States

Preliminary tests in our group have revealed that the apparent viscosity of the concentrated suspensions of biomass fibers (solids concentration >15 wt.%, aspect ratio <50) decreases significantly and reversibly with increasing temperature (for temperatures less than approximately 150 °C). In this work, we confirmed that the reversible rheological changes with temperature is not unique to biomass fiber suspensions, but is a characteristic of monodisperse synthetic fiber suspensions as well. The quantitative variation of the rheological behavior depends on the fiber type, fiber volume fraction, and fiber aspect ratio. The steady-state behavior of such suspensions is well-described by the Bingham fluid model. The yield stress is a strong decreasing function of temperature, in agreement with the 20 wt.% biomass suspensions. The synthetic fiber suspensions are high yield stress fluids with negative plastic viscosity at low temperatures. As the temperature was increased, the plastic viscosity became less negative, similar to that observed for the biomass suspensions. The yield stress of the fiber suspensions followed an Arrhenius dependence where the activation energy is 5-80 kJ/mol depending on the conditions. The fiber suspensions form the heterogeneous fiber networks where the state of aggregation depends on the experimental conditions. The fiber networks and their change with temperature and fiber properties are proposed to be the cause of the variation in rheological behavior, as well as the negative plastic viscosity of the synthetic fiber suspension.

Monday 5:15 Audubon B SC14

Shear thickening and mechanical gelation of flexible non-Brownian fiber suspensions

Antonio Perazzo[1], Janine K. Nunes[1], Stefano Guido[2], and Howard A. Stone[1]
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Suspensions of flexible microfibers are commonly encountered in paper pulp processing and have been broadly studied in the dilute and concentrated regimes where they commonly flocculate under flow conditions even for low concentrations (<1% wt). These systems have been reported to show shear thinning behavior and the presence of large first normal stress differences. Here, we show that microfluidic methods allow creation of polymeric fibers with tailored geometrical and mechanical features achieving high aspect ratio, flexible, concentrated non-Brownian fiber suspensions. We exploit the fibers high aspect ratio and concentration to impart a novel shear thickening behavior that eventually leads to the gelation of the suspension. Such gelation is purely flow-induced and triggered by fibers mechanical interlocking. We report rheological behavior of the suspension over time as a function of concentration, applied shear rate and fiber confinement. The viscoelasticity of the obtained gels is characterized under small amplitude oscillatory shear.

Symposium BA
Biorheology & Active Fluids

Organizers: David Saintillan and Christian Wagner

Monday 1:30 Audubon DEF BA6

Shear thinning of blood and the clustering of red blood cells in microcapillary flow

Christian Wagner
Univ. Saarland, Dep. of Physics, Saarbrücken, Germany

The shear thinning of blood results mostly from an aggregation and dissagregation process of the red blood cells (RBC). The plasma protein fibrinogene is responsible for this reversible process but also the addition of specific macromolecules to a physiological solution containing RBCs

leads to the formation of aggregates, also called rouleaux. Recently, we used single cell force spectroscopy to characterize typical adhesion energies, both for dextran and fibrinogen. We used confocal microscopy and numerical simulations to study the topology of these aggregates as a function of the adhesion energy. Our in vitro (Fig. 1), in vivo and numerical studies show that despite large shear rates, the presence of either fibrinogen or the synthetic polymer dextran leads to an enhanced formation of robust clusters of RBC in microcapillaries under flow conditions. However, the contribution of hydrodynamic interactions and interactions induced by the presence of macromolecules in the cluster formation has not been established. In order to elucidate this mechanism, we used microchannels under flow conditions in order to compare pure hydrodynamical cluster formation of RBC and cluster formation of RBC in the presence of macromolecules inducing aggregation. The results reveal strong differences in the cluster morphology. In the case of clusters formed by two cells, the surface-to-surface distance between cells in the different solutions shows a bimodal distribution that can be reproduced with our numerical simulations by varying the bending rigidity of the cell membrane within the tabulated range reported in healthy physiological conditions.

Monday 1:55 Audubon DEF BA7

Regulating fibrin formation, structure, and mechanical strength

Uranbileg Daalkhaijav[1], Joanna L. Sylman[2], Owen J. McCarty[2], and Travis W. Walker[1]
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Blood coagulation proceeds through a number of pathways within the coagulation cascade. These pathways can be initiated via exposure to negatively charged surfaces (intrinsic contact pathway) or through interaction with tissue factor (extrinsic pathway). However, the series of plasma protein reactions that occur to subsequently produce thrombin and fibrin can be drastically affected by a deficiency in zymogen factor XI (FXI), an integral protein in the coagulation cascade, which is activated by FXIIa and thrombin, or in zymogen factor XII, which is the starting point of the intrinsic pathway. Deficiencies in FXI result in prolonged bleeding times, suggesting that FXI plays a crucial role in regulating hemostatic plug formation. The structure of fibrin is integral to the kinetics and stability of thrombus formation, controlling clot strength and susceptibility to lysis. Thus, we used a suite of FXI inhibitors to measure the role of FXI on fibrin by analyzing the kinetics of fibrin formation, quantifying the extent of fibrin gel structure, and measuring the rheological properties of the transient coagulation. We show that FXI plays a key role in regulating the kinetics of fibrin formation and overall fibrin gel structure.

Monday 2:20 Audubon DEF BA8

Sub-cellular modeling of platelet transport and adhesion in micro-channels with constrictions

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Platelet transport and its adhesive function are the major contributing factors to the formation of thrombi in the circulation. We perform high-fidelity mesoscopic simulations of blood flow in micro-channels with or without constriction, where the wall shear rates within the constrictions reach levels as high as 8, 000 s-1 , similar to those encountered in moderate atherosclerotic plaques. Both red blood cells and platelets are modelled at the sub-cellular with Dissipative Particle Dynamics (DPD) which integrates the key components of blood rheology: cell mechanics and platelet adhesive dynamics. Platelet adhesion inside the constrictions is thought to be mediated through GPIba receptors on the platelet's surface and by von Willebrand Factor multimers; here it is simulated by a stochastic bond formation/dissociation model triggered by thrombin evolving at the site of injury. Thrombin emerges as the product of the coagulation cascade of enzymatic reactions simulated by transport DPD. We find that higher levels of constriction and wall shear rates lead to significantly enhanced margination of platelets, consistent with experimental observations of enhanced post-stenosis platelet aggregation. We also study the mechanics of adhesion under different wall-shear rate and flow conditions.

Monday 2:45 Audubon DEF BA9

Investigation of the human blood rheology in transient flows

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Blood is a complex suspension composed of erythrocytes, leukocytes, platelets, and a variety of proteins in plasma. As a result of the aggregation and subsequent breakup of erythrocytes under shear flow, blood has been shown to exhibit a non-Newtonian behavior characterized by a yield stress, shear thinning, and thixotropy. Understanding the complex nature of blood rheology is critical in detecting and understanding causes of various arterial diseases. To properly model blood flow throughout the circulatory system, not only the steady state, but also the transient behavior must be considered. Previous modeling efforts by our group have led to a parametric Casson representation for the steady state blood rheology based on literature data [1]. More recently, a structural-based model of the thixotropic behavior has been provided that semi-quantitatively describes the limited data available in the literature [2]. In this work, experimental results are presented on healthy human blood rheology with a focus on the response to transient shear experiments. By carefully preconditioning the sample, we have obtained some of the first reliable data for various transient experiments. Critical for the interpretation of these results was a full physiological characterization of the blood samples, which many previous works on blood rheology failed to provide. Based on the physiological data available, the previous model [1] predictions for the yield stress and infinite shear viscosity compared well with the steady state data. By fitting the additional model parameters to a hysteresis ramp experiment, we compare the predictions of the transient model [2] to large amplitude oscillatory shear experimental data. Our analysis shows a suitable fit at low and high shear rates. However, a breakdown from Casson behavior is detected at moderate shear rates suggesting the need to incorporate modifications to our model.

[1] Apostolidis and Beris, J. Rheol., 58, 607, (2014). [2] Apostolidis et al., J. Rheol., 59, 275, (2015).

Monday 3:35 Audubon DEF BA10

Squeezing of vesicles through narrow tubes

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Squeezing of vesicles through narrow constrictions increases membrane tension and enhances membrane permeability to molecular diffusants - e.g. pharmaceutical drugs - through the formation of transient pores. This process of "mechanoporation" shows promise for targeted drug delivery applications. The aim of the present work is to provide a theoretical model for vesicle squeezing that relates vesicular shape deformation in a highly confined, channel flow to the enhancement of hydrodynamic drag and membrane tension. The vesicle is modeled as an inextensible elastic sheet with a Helfrich bending stiffness and placed inside a circular tube of near-minimal diameter. Using a combination of semi-analytical theory and direct numerical simulation, the drag and tension are calculated as functions of the reduced volume, radius ratio, and bending capillary number. Significantly, corrections to "leading-order" calculations previously reported in the literature are reported here for the first time for vesicles. These findings show that the shape deformation near the vesicle "end-caps" lead to significant drag enhancement and strong variation in the membrane tension. As vesicles shorten in length, this end-cap effect changes quantitatively. Bending elasticity plays a comparatively weaker role relative to the effect of confinement. However, calculations performed at low bending capillary numbers reveal lobe-swelling and drag enhancement via occlusion of the small-gap flow. The theoretical results presented in this work show excellent agreement with prior and our present full numerical simulations performed for vesicles in confined flows as well as mobility measurements of confined red blood cells.

Monday 4:00 Audubon DEF BA11

The drift volume in viscous flows

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"Drift" refers to the deformation of material surfaces in a fluid induced by the movement of an immersed body. Quantifying drift is important in pool boiling, vortex motion, flow in fluidized beds, and mixing by self-propelled (active) swimmers. The "drift volume" is the volume of fluid that is displaced due to a translating body after it has traveled an infinite distance; it is formally defined as the volume between the initial and final positions of an unbounded marked plane of fluid that is initially infinitely far ahead of the body and perpendicular to its path of motion. Darwin's classic result for inviscid flow is that the drift volume (multiplied by the fluid density) is equal to the added mass of the body. Here, we reinterpret the drift volume as the time-integrated flux of fluid between streamlines via a conservation-of-mass argument, thereby generalizing the concept to finite dimensions and viscous flows. Our interpretation allows for the expedient computation of the drift volume without the need to explicitly resolve the motion of the marked fluid elements. Using asymptotic and numerical calculations, we demonstrate that the drift volume diverges with time if the fluid is viscous and the body translates under an external force; moreover, the drift volume may be many times larger than that of the body itself. In Stokes flow, this divergence is logarithmic. For finite Reynolds numbers, the long-time behavior is still logarithmic due to a viscous wake containing a mass deficit; the contribution to the drift volume from outside of the wake is comparatively small. For a steady self-propelled swimmer, the viscous wake contains no mass deficit, which has profound consequences for the drift volume.

Monday 4:25 Audubon DEF BA12

Nanorheology with nanopropellers in biological fluids

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Nanopropellers that can be magnetically and wirelessly actuated are used to probe the rheology of biological fluids. The nanopropellers are grown by a fabrication scheme we term nano-glancing angle deposition (nano-GLAD) [1]. The nanopropellers are multifunctional in that they can be optically active (chiral and plasmonic) and ferromagnetic. The former allows for observation in opaque solutions (optical density OD>3) and the latter permits for their remote actuation. We demonstrate a spectroscopic measurement of the local shear which allows for the determination of the viscosity of blood plasma in whole blood [2]. The spectroscopic observation is background-free as the probes are chiral whereas the biological fluid shows no significant optical activity at the probe wavelength. We also report the propulsion of the nanopropellers in biological fluids, such as the gastric mucus [3] and the vitreous humor. With nano-GLAD, we fabricate nanopropellers with a ?lament diameter of ~70 nm, which are smaller than previously reported nanopropellers [4]. In viscoelastic hyaluronan gels, the nanopropellers show a signi?cant advantage than micropropellers, as they are similar to the size of the gel's mesh. In gastric mucus, we present the reactive propellers that mimic the bacterium Helicobacter pylori to move through gastric mucin gels by changing the local rheology. The propellers that are functionalized with urease raise the pH and consequently liquefy the mucus, which enables the controlled propulsion through the gel.

References: [1] A.G. Mark, J.G. Gibbs, T.C. Lee, P. Fischer, Nature Materials 12, 802-7, 2013. [2] H.-H. Jeong, A.G. Mark, T.-C. Lee, M. Alarcón-Correa, S. Eslami, T. Qiu, J.G. Gibbs, P. Fischer, Nano Lett. 16, 4887-94, 2016. [3] D. Walker, B.T. Käsdorf, H.-H. Jeong, O. Lieleg, P. Fischer, Science Advances 1, e1500501, 2015. [4] D. Schamel, A.G. Mark, J.G. Gibbs, C. Miksch, K.I. Morozov, A.M. Leshansky, P. Fischer, ACS Nano 8, 8794-801, 2014.

Monday 5:15 Audubon DEF BA14

Rheology of active colloidal suspensions

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The rheological properties of a colloidal suspension are a function of the concentration of the colloids and the interaction between colloids and the fluid. While passive solutions have been studied in the literature, the properties of an "active" suspension have only recently garnered much interest. Pioneering studies of the rheology of non-equilibrium bacterial fluids and actin-motor-protein suspensions have, respectively, revealed superfluid-like and gel-like states in the active suspensions [1,2,3]. The rheology of these biological systems changes dramatically when their activity is switched off. Here, we ask if similar effects can be realized in a fully inanimate synthetic active suspension. Inanimate active colloids have been observed to give rise to dynamic clustering and microscale turbulence [4,5,6]. We use a general fabrication scheme to asymmetrically coat passive SiO2 colloids with an active component that can be externally triggered [7]. We study the rheological properties of the resulting dense aqueous active colloidal suspensions as a function of the activity of the colloidal particles. Reversible tuning (10-fold change) of the effective viscosity is demonstrated using a magnetic micro-rheometer. We discuss scaling to larger fluid volumes and possible practical applications.

References : [1] A.Sokolov, I.Aranson, Phys.Rev.Lett., 103,148101(2009). [2] D.Mizuno, C.Tardin, C.F.Schmidt, F.C.MacKintosh, Science, 315, 5810,370-373(2007). [3] T.Sanchez, D.T.N.Chen, S.J.DeCamp, M.Heymann ,Z. Dogic, Nature, 491, 431-434(2012). [4] I.Buttinoni, J.Bialké, F.Kümmel, H.Löwen, C.Bechinger, T.Speck, Phys.Rev.Lett.,110, 238301(2013) [5] J. Palacci, S. Sacanna, A. P. Steinberg, D. J. Pine, P. M. Chaikin, Science 339, 936(2013). [6] J.Yan, M.Han, J.Zhang, C. Xu, E.Luijten, S.Granick, Nature Materials, 15, 1095-1099(2016). [7] A. G. Mark, J.G. Gibbs, T.C. Lee, P. Fischer, Nature Materials, 12, 802-807(2013).

Symposium SG
Self-assembled Systems, Gels and Liquid Crystals

Organizers: Kendra Erk and Virginia Davis

Monday 1:30 White Ibis SG6

Microstructure, rheology and suspension stability of surfactant micelle-acrylate copolymer compositions

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This presentation focuses on a newly introduced acrylates copolymer, SurfaThix-N, a multi-functional rheology modifier used in surfactant-rich compositions. The key functionality of suspension stability in formulations depends on rheological profile including value of yield stress, zero shear viscosity. These properties are dependent on surfactant chassis, target pH, surfactant mix ratio, co-additives and most importantly, copolymer selection. The space filling efficiency of polymeric chains is governed by 'hydrodynamic volume expansion';extent of swelling through charge repulsion during neutralization. This presentation will address challenges in polymer choice for achieving optimum yield, shear thinning, clarity, stability, pumpability from typical packaging components used for dispensing.

Monday 1:55 White Ibis SG7

Mesoscopic modelling for rheology of branched micellar solutions

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We extend our recently developed mesoscopic model for entangled wormlike micelles to quantitatively describe the effect of branching on the rheology of surfactant solutions. Because in a branched micelle the surfactant molecules can diffuse rapidly through branch points causing micelle branch to grow, and shrink, the presence of these branches provide extra paths allowing micelles to slide quickly from their entanglements. Therefore, a "constrained" diffusion model (in which constraint forces are imposed to balance the flux of micellar materials at each branch point) as well as a mechanism to create new branches (i.e. budding of a tiny branch along a micelle strand randomly at a constant rate) are developed, and these mechanisms are now incorporating into the evolution of "pointers" (which tracks the ends of un-relaxed regions along each micelle) for characterization of branched micelles and prediction of their flow behaviors. Our simulation results remarkably agree with the experimental observations showing a pronounced decrease of zero shear viscosity with an increase of micellar branches, which would allow, for the first time, modeling of the flow behaviors of micelle solutions across the whole range of salt concentrations, including conditions where branched micelles are present.

Monday 2:20 White Ibis SG8

Static and dynamic signatures of branching in wormlike micelles (WLMs)

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Altering the topology of self-assembled surfactant solutions and chemical polymers provides a route for tailoring key properties, such as the rheology. Here, we develop an empirical understanding of the role of branching on the linear and nonlinear shear properties of worm-like micelles (WLMs). A model series of WLMs with controlled levels of branching is studied via the combination of linear and nonlinear rheology, dynamic light scattering (DLS), and advanced neutron techniques to distinguish features of branching. The degree of branching in the mixed cationic/anionic surfactant (CTAT/SDBS) system is controlled via the addition of the hydrotropic salt sodium tosylate, and is confirmed by cryo-TEM [1,2]. The linear viscoelastic rheology (LVE) shows deviations from Maxwellian behavior with branching, and the spectra are connected to two distinct relaxation modes identified by DLS and neutron spin echo (NSE). Orthogonal superposition rheology (OSP) is used to quantify the changes in the LVE spectra under shear, which are distinct for different branching levels. The normalized orthogonal plateau modulus, G0, and crossover frequency as a function of Wi decrease more rapidly with branching, indicating a breakdown of network-like structures. Shear startup measurements indicate that branching inhibits shear banding, as well as the stress overshoot, which has been observed in polymeric systems of different topologies [3]. The disappearance of shear banding with branching is confirmed with time- and spatially-resolved flow-small angle neutron scattering (flow-SANS) measurements in two shear planes. This research employs advanced rheological and neutron techniques to determine characteristic differences in linear versus branched WLMs, and is part of a broader effort to characterize branching in chemical polymers and self-assembled systems.

[1] Schubert, B., N.J. Wagner, and E.W. Kaler, Langmuir 19(10): 2003. [2] Calabrese, M.A., et al., J Rheol 59(5): 2015. [3] Snijkers, F., et al., J Rheol 57(4): 2013.

Monday 2:45 White Ibis SG9

Reinterpreting viscoelasticity in terms of Laun’s elastic strain and an equilibrium shift: Application to worm-like micelles

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The strain- and stress-controlled viscoelastic response of a linear worm-like micellar is interpreted in terms of Laun's elastic strain [Laun, J. Rheol. 30, 459 (1986)] and a moving equilibrium position. Within this framework, the modulus and viscosity are shown to be constant in the linear regime, and all dynamics are accounted for by the moving equilibrium position. Notably, we measure a constant modulus (the plateau modulus) by mapping the elastic strain, and a constant viscosity (the zero-shear viscosity) by following the transience of the equilibrium position. Even in small-amplitude oscillatory shearing (SAOS), these measurements are independent of frequency over a wide range of frequencies. Having identified and measured the elastic strain, modulus, and viscosity, we are able to calculate the instantaneous energy stored and dissipated, and show that the averages of our measured values scale with the dynamic moduli. We show that the micellar rheology can be described by a single equation that accounts for responses to step strains, step rates, step stresses, and oscillatory stresses and strains. The successful explanation of the micellar rheology suggests that a coupling of Laun's elastic strain concept and a moving equilibrium has significant utility in understanding other nonlinear protocols, notably large amplitude oscillatory shear (LAOS).

Monday 3:35 White Ibis SG10

Rheology of lyotropic nanomaterial dispersions

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Processing of lyotropic nanomaterial dispersions is increasingly recognized as a scalable route for producing large ordered assemblies of anisotropic nanomaterials. However, achieving this assembly requires understanding the dispersions' rheological properties. It is well established that lyotropic dispersions of rod-like polymers typically have the following rheological signatures: a maximum in the viscosity versus concentration curve, long oscillatory transients, three region viscosity versus shear rate behavior, and a first normal stress difference that goes from positive to negative and back to positive with increasing shear rate. Since rheological properties are largely governed by shape, lyotropic dispersions of rod-like nanomaterials can also be expected to have some of these features. On the other hand, the range of possible nanomaterials sizes, polydispersities, attractive interactions, and densities suggests a broader possible variation in rheological properties between systems. This work reports the rheological commonalities and distinctions between lyotropic dispersions of carbon nanotubes, low aspect ratio silica nanorods, high aspect ratio silver nanowires, and cellulose nanocrystals. For example, the high surface charge on the cellulose nanocrystals causes the absence of a maximum in the viscosity versus concentration curve. However, all systems studied to date have shown a small plateau in the viscosity versus shear rate curve which is suggestive of three region behavior. Increased understanding of the reasons for the similarities and differences between systems is not only scientifically important, it will also aide in developing a framework for lyotropic nanomaterial rheology that can help guide the development of effective processing schemes.

Monday 4:00 White Ibis SG11

Using μ^2rheology to characterize repeatable phase transitions of a rod-like colloidal gel

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Rheological modifiers are common ingredients in home care goods that undergo phase changes during manufacturing and regular use. It is important to know how the material and rheological properties are altered by repeatable phase transitions, and the extent to which these structural changes affect the performance of the product. This work characterizes the phase change of one rheological modifier, hydrogenated castor oil (HCO), a rod-like colloid (aspect ratio 50-2500) that forms a stable aqueous suspension with the addition of a surfactant. μ^2rheology combines microfluidics and microrheology as a novel method of observing gelation-degradation cycles on a single sample. A new microfluidic device design enables the exchange of reactants without adding excess shear to the sample. Multiple particle tracking (MPT) microrheology is used to measure phase transitions. Fluorescent probe particles are embedded in the sample and the Brownian motion of the probes is related to rheological properties using the Generalized Stokes-Einstein Relation. The microfluidic design allows measurement of multiple phase changes, and to date a maximum of 4 complete cycles has been observed. MPT and bulk rheology data are compared to phases previously defined in the literature. The phases of rod-like systems are network, bundles of rods, and a transitional phase where the colloidal particles lose some scaffold structure and form bundles. The MPT results show that a 4wt% HCO gel undergoes a repeatable phase transition between the network and transitional phases, but never reaches the bundled phase. A 0.125wt% solution of colloidal rods undergoes repeatable phase transitions but does not form the network structure measured in the 4wt% gel due to the initial shearing of the material permanently breaking the network structure. Therefore, equilibrium structures depend on the shear history of the starting material, which can have important implications in end use products made with rheological modifiers.

Monday 4:25 White Ibis SG12

Rheo-SANS of lyotropic cellulose nanocrystal dispersions

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The effects of shear on cellulose nanocrystal (CNC) dispersions were quantified using rheo-SANS. The 2.5 to 8.5 vol % concentration range included isotropic, biphasic, cholesteric liquid crystal and gel dispersions. The CNC were extracted via sulfuric acid hydrolysis of woody biomass, purchased from the US Forest Service's Cellulose Nanomaterials Pilot Plant, and dispersed in D_2O. The rheology and phase behavior of CNC in D_2O was very similar to that previously obtained for aqueous dispersions. Analysis of the scattering patterns enabled evaluation of the order parameter as a function of concentration and shear rate. In contrast to polymer liquid crystals, a viscosity plateau was observed at intermediate shear rates for biphasic dispersions, but not for liquid crystalline dispersions. This three region behavior was confirmed by a similar region II plateau in the order parameter. However, based on order parameter, the region II plateau occurred at slightly higher shear rates than the viscosity plateau. Investigation of microstructural relaxation showed that the 3.8 vol % biphasic dispersion became globally isotropic approximately 10 minutes after the cessation of shear while the 8.5 vol % dispersion showed no appreciable changes in scattering pattern even 1 hour after shear cessation. These results are important for understanding the potential three region behavior observed in other rod-like nanomaterial dispersions and for determining the processing conditions required to produce flow-aligned CNC films.

Monday 4:50 White Ibis SG13

Morphology of carbon nanotube liquid crystal solutions

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Solutions of carbon nanotubes (CNTs) in chlorosulfonic acid (CSA) form liquid crystals at high concentrations. These liquid crystal solutions are of special interest for the fluid-phase self-assembly approach for processing CNT-based macroscopic materials. We used techniques including polarized optical microscopy and small angle x-ray scattering to have a better understanding of the ordering inside the liquid crystal phase and how it is affected by the CNT properties and the concentration. Polarized optical micrographs of the semi-dilute solutions of short CNTs show the formation of spindle-shaped nematic droplets emerging out of the isotropic phase, while long CNTs show bi-continuous phases. We studied the shape of the nematic droplets to measure the elastic and the interfacial properties of the nematic phase. We also show that the nematic liquid crystals of CNTs coexisting with the isotropic phase, partially wets the solid glass surface by forming flattened spindle-shaped sessile droplets with an anisotropic contact angle. By comparing these experimental observations with our theoretical predictions we were able to measure the line tension for the first time for the lyotropic liquid crystal droplets. Additionally, our studies on solutions of CNTs at higher concentrations show that long CNTs present scattering patterns indicative of the transition to higher ordered phases while short CNTs present characteristics of the nematic phase.

Monday 5:15 White Ibis SG14

Adhesive hard rods: A thermoreversible model system to quantify the effects of particle shape anisotropy and short-range attractions on dynamic arrest transitions

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Suspensions containing anisotropic colloids such as clays, proteins, and various organic and inorganic crystals are common in many particle-based technologies. Particle shape anisotropy is known to affect the thermodynamic and rheological properties of colloidal suspensions, for example, by influencing the random close packing, shear thinning or thickening behavior, liquid crystal phase behavior, and elasticity at low particle volume fractions. However, we lack a comprehensive understanding of how the coupled effects of particle shape anisotropy and interparticle attractions influence dynamic arrest transitions, or gel and glass formation. An experimental model system of adhesive hard rods (AHR) was developed to quantify these effects for rod-like systems with tunable aspect ratios and short-range, thermoreversible attractions. The AHR system is composed of octadecyl-coated silica rods suspended in tetradecane, serving as a chemically consistent, one-dimensional extension of the well-studied adhesive hard sphere system. Various experimental techniques characterized the dynamic arrest transitions of AHR suspensions as a function of the particle aspect ratio (3 to 7), a wide range of volume fractions (0.1 to 0.5), and moderate temperatures (15 to 40 C). SAOS measurements revealed thermoreversible transitions from fluid-like to gel-like states. Quasi-elastic light scattering methods probed the particle dynamics and further quantified the critical transition temperatures for dynamical arrest. Neutron and X-ray scattering methods also showed unique microstructural transitions between the fluid-like and gel-like states. Further quantification, simulation, and modeling of the AHR system will help link the coupled effects of particle shape and attraction strength with the macroscopic rheology. We propose that the tunable AHR system enables quantitative mapping of the gel, glass, and phase boundaries onto a universal state diagram for anisotropic colloids with short-range attractions.

Symposium EF
Emulsions, Foams & Interfacial Rheology

Organizers: Cécile Monteux and Sachin Velankar

Monday 1:30 Sandhill Crane EF6

A thermodynamically consistent macroscopic model for dilute emulsion behavior

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Conformation tensor models are important to describe the rheology of complex fluids including polymers, suspensions and emulsions at the macroscopic level of description [1,2,3]. However, only for viscoelastic systems is the foundation available, through microscopic kinetic theory, to make the use of these models widely acceptable. Existing conformation tensor models for emulsions have empirical parameters and are not always consistent with known limiting rheological behaviors. Here we describe how a contravariant tensor model for deformable ellipsoidal droplets, derived consistently within a non-equilibrium thermodynamics framework, is rigorously validated through a comparison against asymptotic theories in the limit of zero particle Reynolds numbers and for small Capillary numbers [4]. An additional benefit is that, through this asymptotic matching, all the parameters can be obtained from previous independent theoretical work. At the heart of this modeling success is the use of a more accurate expression for the surface area of the ellipsoid, needed to describe the surface energy of the emulsion. In addition, a simpler and more natural form for the relaxation that involves a lower order dependence on the conformation tensor than previous models [5,6] is adopted. The resultant a-priori predictions compare well against classic experiments [7].

[1] G. Batchelor, J. Fluid Mech. 41, 545-570 (1970). [2] M. Doi and T. Ohta, J. Chem. Phys. 95, 1242-1248 (1991). [3]A. N. Beris and B. J. Edwards, Thermodynamics of flowing systems (Oxford University Press, New York, 1994). [4] W. R. Schowalter, C. E. Chaffey and H. Brenner, J. Colloid Interf. Sci. 26, 152-160 (1968). [5]P. Maffetone and M. Minale, J. Non-Newton. Fluid. 78 227-241 (1998). [6] M. Grmela, A. Ammar, F. Chinesta and G. Maitrejean, J. Non-Newton. Fluid. 212, 1-12 (2014). [7] S. Torza, R. Cox and S. G. Mason, J. Colloid Interf. Sci. 38.2, 395-411 (1972).

Monday 1:55 Sandhill Crane EF7

Effects of hydrodynamic interactions on interfacial particle microstructure deformation under shear and aggregation kinetics using a Stokesian approach

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Experimental studies of particle laden interfaces have increased significantly in recent years due to the prevalence of Pickering emulsions in commercial applications and industrial processes. Studies have focused on pair-interactions, aggregation, microstructure deformation, and interfacial rheology. However, it is often difficult to extrapolate connections between individual studies. To begin such a process, we previously developed a Stokesian dynamics simulation to explore the connection between microstructure dynamics and pair-interactions of monodisperse particle laden interfaces. In the model, viscous forces were balanced by capillarity due to contact line undulation and induced dipole repulsion. Initial results showed promising agreement with experimental results.

However, hydrodynamic interactions between particles and Brownian motion were initially neglected due to the large interparticle spacing used and the dominance of applied shear in study systems. In order to deduce the relevance of these mechanisms, the simulation has been updated to incorporate hydrodynamic interactions and Brownian motion. We outline how interfacial hydrodynamics and Brownian motion are modeled in our simulations, and then compare results between simulations with and without these effects. First, the microstructural deformation of hexagonal packed interfacial particles under steady surface Couette flow is investigated. The addition of hydrodynamic interactions appear to reinforce particle motion off streamlines when interparticle forces create rotation perpendicular to applied Couette flow. Furthermore, the transitions between the two observed deformation regimes are shifted when hydrodynamic forces are included. In studies of aggregation, hydrodynamic interactions and Brownian motion appear to speed up aggregation kinetics and create more chainlike open structures in comparison to compact structures seen when these forces are ignored.

Monday 2:20 Sandhill Crane EF8

Coalescence inhibition through asphaltene adsorption

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Asphaltenes are complex polar components of heavy oils and are only marginally stable in organic solvents. Because of this marginal solubility, they have a propensity to adsorb onto oil/water interfaces to form viscoelastic layers. This can result in a strong stabilization of water-in-oil emulsions that cause difficulties in refining operations. In this work we examine the coalescence process of both water and oil droplets against an oil/water interface in the presence of asphaltenes using a newly developed instrument where the thickness of thin, draining films can be measured in space and time. Using this device, thin film thickness, internal droplet pressure and coalescence times can be measured. These results are further compared against measurements of the interfacial shear and dilatational viscoelasticity of asphaltene-laden interfaces. In addition to asphaltene concentration in an aromatic hydrocarbon (toluene), the aging time of the interfaces was varied. Both asphaltene concentration and aging time were found to strongly affect the coalescence dynamics for water droplets. On the contrary, for oil droplets, the asphaltene concentration and the aging time had a weaker effect on the coalescence dynamics. In addition, we found that the contact of water against asphaltene/toluene solutions induced the production of a remarkable emulsification where micron-sized water droplets, stabilized by asphaltenes, spontaneously appeared.

Monday 2:45 Sandhill Crane EF9

Fluid to solid phase transition of asphaltenes laden interfaces

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Asphaltenes are crude oil constituents stabilizing water-oil emulsions. This is often ascribed to the gelation of the interface between phases. Recent work contrarily suggested that asphaltenes laden interfaces undergo a fluid to solid transition due to steric effects: pendant droplets depart from a Laplace shape upon compression and not upon expansion [1], compressed droplets wrinkle after short aging provided compression is large enough [1], shear rheology exhibits soft glass features [2]. Fractional coverage causing a steep departure from Laplace shapes was evaluated around 0.83 with the Langmuir model [1]. This analysis is refined with Lattice Gas models known to exhibit phase transitions well below maximum packing. Relevant models are selected from the evaluation of asphaltenes molecular area by the Langmuir model (0.3 nm2 i.e. 3-4 times that of a water molecule) and from the compact molecular structure of asphaltenes. By comparison with experimental dilatational rheology, the best match is found to be a hexagonal adsorbate covering three sites on a triangular lattice. This model predicts a transition from fluid to solid interface between 0.65 and 0.83 coverage, corresponding to 23 and 32 mN/m surface pressure in agreement with observed deviation from Laplace shape [1]. Converted into mass coverage, a 0.83 coverage corresponding to a fully solid interface yields to a value of 3.5 mg/m2 consistent with the critical value reported to cause emulsion stability [3].

[1] Pauchard, V., Rane, J. P., & Banerjee, S. (2014). Asphaltene-laden interfaces form soft glassy layers in contraction experiments: a mechanism for coalescence blocking. Langmuir. [2] Samaniuk, J. R., Hermans, E., Verwijlen, T., Pauchard, V., & Vermant, J. (2015). Soft-glassy rheology of asphaltenes at liquid interfaces. J. Dispersion Sci. Technol. [3] Pauchard, V., & Roy, T. (2014). Blockage of coalescence of water droplets in asphaltenes solutions: A jamming perspective. Colloids Surf., A

Monday 3:35 Sandhill Crane EF10

Deposition behavior of asphaltene-stabilized water-in-oil emulsions with its interfacial rheology at oil-brine interface

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Asphaltenes are polyaromatic molecules in crude oil that are known to precipitate and deposit in pipelines, leading to significant flow assurance problems. Asphaltenes are surface-active and stabilize water-in-oil emulsions by flocculating and coagulating at interfaces. Stability of these emulsions is widely studied, but their role on the deposition behavior in the multiphase flow system is unclear. In this study, we elucidate the deposition behavior of asphaltene-stabilized water/brine-in-oil emulsions in microfluidics and further use the double-wall ring (DWR) rheometer to characterize the rheological responses of the asphaltene interface. The interface formed with 1mM to 1M of NaCl and CaCl2 showed different rheological responses at oil-brine interface as well as the deposition rate in microfluidic devices. Higher salinity lowered the elasticity of the

interface resulting in larger emulsions and eventually altered the blockage of the microchannel. Also, various oil-to-water ratios (water concentration: 0 wt% to 20 wt%) are studied. Lower the ratio gives rise to higher deposition rate. Finally, this multiphase deposition in microchannel is characterized by confocal laser scanning to determine the composition of the deposit. This combined imaging in microfluidics and interfacial rheology platform provides an effective method to understand deposition rate of the emulsions to the interfacial rheological properties.

Monday 4:00 Sandhill Crane EF11

Interfacial viscoelasticity of therapeutic protein solutions

Aadithya Kannan[1], Ian C. Shieh[2], Danielle L. Leiske[3], Gigi Lin[1], and Gerald G. Fuller[1]

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Monoclonal antibodies (mAbs) are proteins that uniquely identify targets within the body, making them well-suited for therapeutic applications. However, these amphiphilic molecules readily adsorb onto air-solution interfaces where they tend to aggregate, and aggregation can negatively impact the potency and immunogenicity of the therapeutic. We investigated two mAbs from Genentech with a high (mAb1) and low (mAb2) propensity to aggregate at air-solution interfaces. The understanding of the interfacial rheological behavior of the two mAbs is crucial in determining their aggregation tendency. To study this, we performed stress relaxation studies under compressive step strain on an air bubble in solution using a custom-built dilatational rheometer. Bubbles were created, aged, and compressed while the bubble image and pressure were recorded. The dilatational relaxation modulus (the change in stress over the strain) was quantified. These viscoelastic interfaces had a relaxation behavior. The initial value (defined as the initial dilatational modulus) and the equilibrated value (the static dilatational modulus) increased as the interface aged and was larger in magnitude for mAb1 compared to mAb2. Next, to study the influence of surfactants in mAb formulations, polyethylene glycol (PEG) was chosen as a model surfactant. In the mixed PEG/mAb system, mAb1 is known to coadsorb with PEG and form domains at the interface. In contrast, PEG entirely covers the interface when mixed with mAb2. This was reflected in the relaxation behavior of the mixed systems. In conclusion, this study shows that mAb aggregation and competitive co-adsorption can be correlated to single bubble studies.

Monday 4:25 Sandhill Crane EF12

Can pendant drop instruments measure rheology?

Mathias Nagel and Jan Vermant

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The analysis of the shape of pendant drops (or sessile bubbles), has developed into an important and standard technique in the interfacial science of fluid-fluid interfaces. The interfacial properties are derived from the shape of drops or bubbles. Provided that robust numerical schemes are used, Axisymmetric Drop Shape Analysis (ADSA) is an accurate method for determine the surface tension of simple interfaces by fitting the drop shape with YL [1]. However, when going to interfaces which become "complex", due to the presence of an interfacial structure and the corresponding mechanical response a scalar value of the surface tension no longer suffices to describe the properties of the interface as two principal interfacial stresses are not necessarily equal to one another [2]. Knoche et al. [3] extended the analysis of the elastic interface to membranes under compression. Danov et al. [4] clarified that the analysis of material properties relies on the knowledge of the unstrained reference state. In the present paper we present a novel algorithm to solve the Young-Laplace equation and it's (visco-)elastic generalization. The algorithm is based on the spectral method which yields exponential convergence and allows to decouple the numerical error from other sources of error. In addition we solve the inverse problem to determine the material parameters with an implicit approach that converts the solution of a non-linear differential equation into the iterative solution of a non-linear equation system. With a combination of computing theoretical drop shapes and converting those in to images and fitting these shapes and images we obtain a theoretical error estimation. We furthermore analyze the impact of different constitutive models.

[1] M. Hoorfar, Adv. colL. Int . SCi. 121 (2006) 25-49. [2] Carvajal, E. J. et al. Soft Matter 7 (2011) 10508-12. [3] S. Knoche et al. , Langmuir 29 (2013) 12463-12471. [4] K. D. Danov, R et al. J. Coll. Int. Sci 440(2015) 168-178.

Monday 4:50 Sandhill Crane EF13

Effect of non-ionic and ionic surfactant on interfacial rheology of particle laden interfaces

Syed Ehsanur Rahman and Gordon F. Christopher

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The use of Pickering emulsions in commercial products and energy applications has led to increasing study of particles laden interfaces. These interfaces create various interfacial viscoelasticity which increases emulsion stability. However, often there are additional surface active materials, in particular surfactants, that may interact with interfacial particles and create mixed systems. The effect of surfactants on interfacial aggregation has indicated a pronounced difference between particle only interfaces, non-ionic surfactant and particle interfaces, and ionic surfactant and particle interfaces. How these observations relate to shear interfacial rheology has not been studied.

Using a non-ionic surfactant, Tween80, and an anionic surfactant, SDS, at bulk concentrations up to the CMC, surfactant effect on the interfacial rheology of particle laden interfaces composed of polystyrene particles has been examined. Using a modified double wall ring interfacial rheometer, both microstructure and rheology are characterized. For Tween80, both loss modulus and storage modulus decrease with the increasing surfactant. The interfaces are still clearly viscoelastic, and the decrease is attributed solely to the change in surface tension and contact angle caused by the non-ionic surfactant. However, addition of SDS at concentration 100 times less than the CMC, creates interface that no longer appear to have any viscoelasticity within measurement resolution. By examining how SDS affects both surface tension and contact angle, we conclude that the SDS must be changing the magnitude of contact line undulation, creating interfaces that have negligible shear resistance.

Monday 5:15 Sandhill Crane EF14

Stability and interfacial rheology of nanoemulsion-based antimicrobial delivery systems stabilized by lecithin or Tween 20

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Nanoemulsion-based delivery systems containing lipophilic antimicrobial compounds are routinely employed in food processing to eliminate harmful foodborne pathogens such as E. coli from our food supply. The rheology of oil-in-water (O/W) droplet interfaces stabilized by commonly utilized food-grade surfactants (soy lecithin or Tween 20) was investigated to elucidate its contribution in the kinetic stabilization of nanoemulsion oil droplets containing carvacrol, a naturally derived antimicrobial compound. Nanoemulsions were formulated from mixtures of carvacrol and medium-chain triglyceride (MCT) oil dispersed in water (pH 7) using ultrasonication. The dynamic adsorption of surfactant molecules, as well as the dilational viscoelasticity of the surfactant-adsorbed interfacial layer were quantified via axisymmetric drop shape analysis. Zwitterionic lecithin molecules adsorbed to the O/W interface for 24 hours formed a notably viscoelastic layer compared to nonionic Tween 20 molecules, presumably due to the formation of a strongly hydrogen-bonded network between lecithin and surrounding molecules. Correspondingly, nanoemulsions containing lecithin encapsulated higher concentrations of carvacrol within the dispersed oil droplets without phase separating. Furthermore, nanoemulsions stabilized by lecithin displayed notably better kinetic stability compared to nanoemulsions stabilized by Tween 20, indicated by relatively small increases in the size distribution of dispersed oil droplets over 30 days. Adjusting the aqueous phase pH from neutral (pH 7) to acidic (pH 3) led to an increase in initial Z-Ave diameter for lecithin-stabilized nanoemulsion droplets, but led to no discernable change in initial diameter for Tween 20-stabilized droplets. The positive association between high viscoelasticity of the O/W interface and nanoemulsion stability may potentially be very useful for food industries interested in optimizing the encapsulation and delivery of lipophilic antimicrobial molecules using food grade emulsifiers.

Symposium SM
Polymer Solutions & Melts

Organizers: Carlos R. López-Barrón and Nicolas Alvarez

Monday 1:30 Snowy Egret SM6

Weld formation in polymer extrusion additive manufacturing processes

Jonathan E. Seppala[1], Seung Hoon Han[2], Kaitlyn E. Hillgartner[3], Chelsea S. Davis[1], and Kalman B. Migler[1]
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In polymer extrusion additive manufacturing, thermoplastic filament is extruded though a rastering nozzle onto previously deposited layers. However, parts are often weaker compared to traditional manufacturing methods. The strength of the part is limited by the strength of the weld between each layer. To overcome the weak weld strength a fundamental understanding the polymer physics of weld formation is needed, beginning with the relationship between welding strength and welding time. Welding time and strength are determined with by a combination of in situ infrared thermography, offline rheology, and mode III fracture. Since the processing conditions are known a prioi this approach provides the data needed to estimate the final build strength at time of design. The resulting agreement between weld time and weld strength for a range of printing conditions are discussed.

Monday 1:55 Snowy Egret SM7

Understanding the fused deposition modeling (3D printing) process

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The flow of polymer melt in the extruder of a fused deposition modeling instrument is poorly understood. The process has a filament approximately 3 mm in diameter which is forced into a heated circular die that tapers to a smaller orifice with a diameter 10 times smaller. The filament is melted as it enters the die and the filament induced drag flow forces melt out of the orifice. However, a back flow must occur due to the entry pressure into the orifice. Yet, just like a plasticating extruder the drag flow is greater than the back flow and material exists the orifice. We determined the force at the fastest possible feed velocity, when the filament begins slipping on the wheels of the feed mechanism, and found the maximum pressure in the orifice is approximately 20 MPa or 3000 psi in older units. This allowed us to model the flow process and through a mathematical model we were also able to develop a master curve for three different polymers and two different orifice diameters for dimensionless feed velocity versus dimensionless temperature. This correlation will allow researchers and designers the ability to optimize the process for a given polymer and hopefully allow faster print speeds.

Monday 2:20 Snowy Egret SM8

Disentanglement in polymer melts during additive manufacturing

Peter D. Olmsted and Claire McIlroy
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Additive manufacturing (3D printing) is rapidly transforming manufacturing in all areas. One of the most common methods of 3D printing is "fused filament fabrication (FFF)", in which a solid filament is melted and deposited on demand. The mechanical performance of FFF parts is often compromised by the weak bond at the interface between filaments. To study this, we have modeled the extrusion and deposition process, using the Rolie-Poly model modified to incorporate convected constraint release, applied to amorphous glass-forming polymers. We use this to study the degree of distanglement during extrusion and deposition, and the subsequent welding behaviour at the interface as the material cools.

Monday 2:45 Snowy Egret SM9

Pinch-off dynamics, dripping-onto-substrate (DoS) rheometry and printability of dilute and semi-dilute polymer solutions

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

Free surface flows and drop formation processes present in printing, jetting, spraying, and coating involve the development of columnar necks that undergo spontaneous surface-tension driven instability, thinning, and pinch-off. Stream-wise velocity gradients that arise within the thinning neck create and extensional flow field, which induces micro-structural changes within complex fluids that contribute elastic stresses, changing the thinning and pinch-off dynamics. We show that visualization and analysis of capillary-driven thinning and pinch-off dynamics of the columnar neck in an asymmetric liquid bridge created by dripping-onto-substrate can be used for characterizing the extensional rheology of complex fluids. Using a particular example of dilute and semi-dilute aqueous PEO solutions, we show the measurement of both the extensional relaxation time and extensional viscosity of weakly elastic, polymeric complex fluids with low shear viscosity (< 20 mPa.s) and relatively short relaxation time (< 1 ms). Characterization of elastic effects and extensional relaxation times in these dilute and many semi-dilute solutions is beyond the range measurable in the standard geometries used in commercially available shear and extensional rheometers (including CaBER, capillary breakup extensional rheometer). Furthermore, we use dripping-onto-substrate (DoS) extensional rheometry technique for examining the influence of extensibility, flexibility and concentration on pinch-off dynamics and extensional rheology response of aqueous polyethylene oxide (PEO) solutions, aqueous polyacrylamide (PAM) solutions and aqueous 2-Hydroxyethyl cellulose (HEC) solutions. Both extensional relaxation time and the transient extensional viscosity display concentration-dependent behavior that is strikingly different from the response observed in typical shear rheology measurements.

Monday 3:35 Snowy Egret SM10

Modulus increase and crystallization evolution during gel spinning and post drawing of UHMWPE fibers

Christopher K. Henry, Giuseppe R. Palmese, and Nicolas J. Alvarez
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We revisit the old problem of high modulus and high strength UHMWPE fibers from gel spinning and post drawing. The goal of this work as opposed to previous investigations is to understand the structure and modulus evolution as a function of strain and stress during the evolution of the fiber during processing. Two unique apparati have been built to monitor the stress and strain evolution in the gel spinning and post drawing unit operations. The gel spinning apparatus monitors the deformation of the polymer solution as a function of time and position during extrusion from the nozzle as a function of different temperatures, strain rates, and crystallization time. The stress and strain during post drawing is monitored using a filament stretching rheometer with novel sample plates to monitor the evolution of modulus and crystallization as a function of draw ratio. SAXS and Raman measurements are used ot determing crystallization. SEM and AFM images of the fiber crystalline morphology are monitored as a function of traditional processing variables.

Monday 4:00 Snowy Egret SM11

Model-guided experimental design of flow-induced crystallization of poly(1-butene) under uniaxial extensional flow as measured by small-angle x-ray scattering

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A key assumption in most current flow-induced crystallization models is that flow-induced molecular orientation/stretching leads to enhanced nucleation rate, which in turn leads to accelerated crystallization kinetics. This underlying hypothesis was directly tested by subjecting poly(1-butene) to various extension rates and Hencky strains that resulted in similar number density of flow-induced nuclei. The number density of flow-induced nuclei was calculated from the degree of stretch during extensional flow and relaxation, as predicted by a simplified Rolie-Poly model. Uniaxial extensional flow was produced using an SER housed in a custom-built oven designed to facilitate *in situ* synchrotron x-ray experiments. Samples were first heated well into the melt, and then cooled to a crystallization temperature selected such that negligible quiescent crystallization would occur on reasonable time scales. A short burst of uniaxial extensional flow was then applied, and crystallization as well as the degree of crystallite orientation was monitored using small-angle x-ray scattering (SAXS). For experimental conditions that are expected to result in similar degree and kinetics of crystallization, SAXS invariants generally do not show agreement, while the degrees of orientation are in general agreement.

Monday 4:25 Snowy Egret SM12

Flow-induced crystallization

Ralph H. Colby[1], Behzad Nazari[1], Jiho Seo[1], Alicyn M. Rhoades[2], and Richard Schaake[3]
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A brief interval of shear is applied to various semicrystalline polymer melts just above their melting temperature and at high enough shear rate this creates flow-induced precursors that accelerate isothermal crystallization on quenching. The precursors are found to be remarkably stable so that the sheared sample can be 1) studied in the DSC to observe crystallization on cooling at 5 K/min that is typically at a temperature 15 K higher than the crystallization of the same polymer that has not been sheared and 2) studied in an optical microscope hot stage to observe isothermal rates of nucleation and growth and final morphology. The precursors can also be annealed at various elevated temperatures to study their stability. We compare results on isotactic polypropylenes, poly(ethylene terephthalate)s, poly(ether ether ketone)s and Nylon 6,6 to learn which aspects of flow-induced crystallization are universal to all semicrystalline polymers and which are polymer-specific.

Monday 4:50 Snowy Egret SM13

Flow-induced crystallization of polycaprolactone as probed by simultaneous Raman spectroscopy, rheology, and optical microscopy

Anthony Kotula and Kalman B. Migler
Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD, United States

Polycaprolactone is a semicrystalline polymer that is widely employed in biomaterials applications and is often used in additive manufacturing processes to generate custom-made parts. Methods for the additive manufacturing of polycaprolactone often extrude the polymer at high (> 1000 s^{-1}) shear rates prior to cooling and crystallization. Although the effects of shear on polymer crystallization are well known, they are not well understood. An understanding of the relationship between the flow properties, microstructure, and molecular ordering during flow-induced crystallization would provide critical insight into the additive manufacturing process. To this end, we use a rheo-Raman microscope to simultaneously measure the rheology, Raman spectroscopy, and polarized optical microscopy of polycaprolactones during crystallization. Shear flow (~1 s^{-1}) applied at temperatures just below the equilibrium melting point enhances isothermal crystallization kinetics at lower temperatures as indicated by all three measurements. Birefringent structures are shown to appear prior to significant changes in the Raman spectra or rheology during crystallization. In addition, the effect of shear on the generation of ordered polycaprolactone chain conformers in the melt state is discussed. Suspension-based models are used to explain the correlation between the complex modulus and the crystallinity as measured by Raman spectroscopy.

Monday 5:15 Snowy Egret SM14

Viscoelastic and orientational relaxation of linear and ring Rouse chains undergoing reversible end-association and dissociation

Hiroshi Watanabe[1], Yumi Matsumiya[1], and Youngdon Kwon[2]
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For dilute telechelic linear and ring Rouse chains undergoing reversible end-association and dissociation, the time (t) evolution equation was analytically formulated for the subchain bond vector, $\mathbf{u}(n,t;\mathrm{c})$ with n being the subchain index and the index c specifying the chain (c = L and R for the linear and ring chains). The end-association of the linear chain (*i.e.*, ring formation) occurs only when the ends of the linear chain come into close proximity. Because of this constraint for the ring formation, the time evolution equation for $\mathbf{u}(n,t;\mathrm{L})$ of the linear chain was formulated with a conceptually new, two-step expansion method: $\mathbf{u}(n,t;\mathrm{L})$ was firstly expanded with respect to its sinusoidal Rouse eigenfunction, $\sin(p\pi n/N)$ with p = integer and N being the number of subchains per chain, and then the series of odd sine modes is re-expanded with respect to cosine eigenfunctions of the ring chain, $\cos(2q\pi n/N)$ with q = integer, so as to account for that constraint. This formulation allowed analytical calculation of the viscoelastic relaxation functions (integral of subchain orientational anisotropy) of the linear and ring chains. It turned out that the terminal relaxation of the ring and linear chains is retarded and accelerated, respectively, due to the motional coupling of those chains occurring through the reaction. This coupling breaks the ring symmetry (equivalence of all subchains of the ring chain), thereby leading to oscillation of the orientational anisotropy of the ring chain at long t with the subchain index n.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Audubon DEF PL2

Frictional rheology of very dense suspensions

Mike Cates

University of Cambridge, Cambridge, United Kingdom

The phenomenon of discontinuous shear-thickening (DST) in very dense suspensions comprises a viscosity jump of several orders of magnitude upon a very small increase in strain rate. After eluding explanation for many years, this is now understood in outline. Suspended particles form a network of mechanical contacts at which solid-solid friction is absent at low stresses but becomes activated at high stresses. This causes a crossover from sliding to rolling contacts, which is smooth as a function of stress, but results in S-shaped flow curves that broadly explain the discontinuities, hysteresis and flow instabilities associated with DST. I will review these developments and point to the difficulties in converting this theory of steady-state flow curves into a full rheological theory for time-dependent flows.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Tuesday 10:00 Audubon B SC15

A hierarchy of granular continuum models: From flow fields to traction applications

Ken Kamrin

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Granular materials, when treated at the continuum level, are a historically complex material to model accurately. Modeling efforts span the spectrum of complexity, from simple rate-independent frictional yielding models, to nonlocal and rate-dependent approaches which account for size-effects due to finite grain size. This talk will show the utility of different modeling approaches from across this spectrum. The overarching theme is that, with granular media, depending on the question one wishes to have answered, the level of modeling needed to obtain a useful prediction varies dramatically. For example, if one desires a complete flow and stress field beyond qualitative accuracy, one typically must resort to a grain-size dependent nonlocal continuum model. On the other hand, if the question is reduced, oftentimes, the modeling complexity can be reduced significantly. In fact, we will show that to answer the specific question of "what are the intrusion forces of a rigid object moving in a granular bed?" many of the experimentally observed results emerge from the simplest frictional plasticity models. In fact, the empirical Resistive Force Theory of granular intrusion can be derived, essentially, from the most basic Coulomb plasticity models. From this realization, we have identified a set of scaling laws inherent to the problem of granular locomotion. We have validated these forms experimentally by comparing the dynamics of different sized wheels under different loads and rotation speeds in a sand bed. The results suggest a new down-scaled design approach to granular locomotion.

Tuesday 10:25 Audubon B SC16

Granular physics in yield-stress fluids: Carbopol suspensions versus wet concrete

Jeremy A. Koch[1], Daniel I. Castaneda[2], David A. Lange[3], and Randy H. Ewoldt[1]

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Wet concrete is often cited as an example of a yield-stress fluid, and modeled as a Bingham or Herschel-Bulkley material. We show this is an incomplete understanding to rationalize simple but important flow phenomena in wet concrete. Specifically, we will describe how granular physics must be considered. As a motivating phenomenon, we consider the practice of vibrating wet concrete during placement to induce flow and remove air voids. A simple yield-stress fluid (an aqueous polymer microgel particle suspension, Carbopol) cannot recreate the phenomenon, falsifying the hypothesis that traditional yield-stress fluid models embody the key physics. Instead, we show that a granular hard-particle suspension (millimetric glass beads in silicone oil) succeeds in recreating the phenomenon. We use vibration-dependent and depth-dependent shear rheology to further show that concrete and mortar display noticeable granular physics, as indicated by (i) vibration-induced loss of the yield stress, consistent with the granular suspension model of Hanotin et al. (2015), and (ii) depth-dependent flow resistance. These are also recreated by the glass beads in oil, but not the Carbopol suspension. A dimensionless group rationalizes why Carbopol suspensions (whose microstructure is indeed 'granular') do not have the granular signatures of depth- and vibration-dependent rheology. These results have implications for understanding the unseen phenomenon of air bubbles rising in concrete, but moreover, the depth- and vibration-dependent rheological signatures add a new dimension to categorizing the vast realm of yield-stress fluids more generally.

Reference: Hanotin, C., S. Kiesgen de Richter, L. J. Michot, and Ph. Marchal, "Viscoelasticity of vibrated granular suspensions," Journal of Rheology (2015).

Tuesday 10:50 Audubon B SC17

Powder flowability study to optimize mixing and predict final product properties: A study on PVC formulations

Sara Reynaud

Analytical & System Research, Arkema, King of Prussia, PA, United States

The rheology of granular flow has recently been a topic of interest for additive manufacturing, 3D printing and laser sintering applications where the polymer is directly processed in a powder form. In this work, we study the effect of impact modifier, filler type and level on the rheology of PVC compounds. In particular, the aggregation and demixing of CaCO3 particles from the PVC matrix has been observed at certain CaCO3 concentrations leading to reduced impact performance. Dynamic powder testing was performed on 25 different PVC compounds with a concentration of CaCO3 in the range of 5 to 50%wt. The data showed a good correlation between powder flow properties (BFE, SI and FRI) and formulation ingredients (IM, CaCO3, and TiO2). Finally, the correlation between properties-structure and performance will be investigated.

Tuesday 11:15 Audubon B SC18

Elongational flows of some non-colloidal suspensions

Roger I. Tanner and Shaocong Dai

School of Aerospace, Mechanical and Mechatronic Engineering, University of Sydney, Sydney, New South Wales 2006, Australia

It is a general principle that the rheology of a system must be explored not only in viscometric flows, but also in other flow classes. Because there are relatively few results for suspensions in extensional flows, we present some results for the axisymmetric elongational flow of non-colloidal suspensions of spheres and compare them with results in shear. We have experimented with non-colloidal suspensions of 40µm diameter polystyrene spheres with volume fractions (?) varying from 0.3-0.5. Two matrix fluids were used-one was a near-Newtonian polydimethyl siloxane (silicone oil) of 12Pa-s viscosity and the other was a more viscous variant of the M1 Boger fluid sample of Sridhar which we called M1*. We did not find that the Trouton ratio for either of these fluids was 3; generally the ratio was much larger, around 6. We note that for more dilute suspensions (? < 0.2) it was shown by Batchelor and Green that,up to second order in ?,the elongational relative viscosity exceeded the shear relative viscosity by a multiple of ?2. We investigated the role of sphere roughness using spheres roughened to 5.3% of the radius in a 50% suspension in silicone oil and found an increase of elongational viscosity of about 65% above the result with smooth spheres; this is comparable with the 60% increase in shear viscosity with roughness noted previously (Tanner and Dai- J. of Rheology 2016). However, we note that some simulations predict a decrease of viscosity with increasing roughness, which disagrees with our experimental findings. For the silicone oil matrix, we found no rate effect, and there was very little strain-hardening. By contrast, the M1-type matrix suspensions showed strain-hardening and an increase of elongational viscosity with elongation rate.

Tuesday 11:40 Audubon B SC19

Calculating effective viscosity using boundary integral equations

Lukas Bystricky, Sachin Shanbhag, and Bryan Quaife

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Boundary integral equations (BIE) are an efficient tool to model the motion of rigid body particles in a Stokesian fluid. They require discretization only along the boundary, thus reducing a two dimensional problem into a one dimensional line integral. To begin, we will first review some of the important concepts of BIE relating to Stokes flow, including the completed double layer potential. We will then use this formulation to calculate the effective viscosity of a particle suspension in a Couette apparatus with various shear rates and suspension densities.

Symposium BA
Biorheology & Active Fluids

Organizers: David Saintillan and Christian Wagner

Tuesday 10:00 Audubon DEF BA15

Shear rheology of active Brownian suspensions

Sho Takatori and John F. Brady

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We investigate the non-Newtonian shear rheology of active matter systems by considering a new contribution to the suspension shear stress generated by self-propelled micro-swimmers. Current understanding is that changes in the effective shear viscosity of active systems are governed

by fluid-mediated hydrodynamic interactions associated with self-propulsion. Here we identify an additional contribution to the suspension shear stress that predicts both thickening and thinning behavior, even for spherical micro-swimmers where the hydrodynamic stress contribution is zero. A simple micromechanical model of active Brownian particles in simple shear flow reveals the existence of off-diagonal shear components in the swim stress tensor, which are independent of hydrodynamic interactions and fluid disturbances. Theoretical predictions from our model are consistent with existing experimental measurements of the effective shear viscosity for both pusher and puller-type micro-swimmer suspensions, but also suggest new behavior not predicted by conventional models.

Tuesday 10:25 Audubon DEF BA16

Linear viscoelasticity of a dilute active suspension

Toni M. Bechtel and Aditya S. Khair

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The linear viscoelasticity of a dilute suspension of active (self-propelled) rigid spheroidal particles is calculated under a small-amplitude oscillatory shear (SAOS) deformation. The imposed shear acts to drive the microstructure of the suspension, as parameterized by the orientational probability distribution function, out of equilibrium. The microstructure relaxes via two independent mechanisms: rotational Brownian motion and correlated tumbling; the combination of which results in an increased rate of stress relaxation, relative to a suspension that relaxes solely by either mechanism. We explicitly calculate the non-equilibrium orientational microstructure due to the SAOS deformation, rotational diffusion, and tumbling. From this, we determine the linear viscoelasticity of the suspension from the orientationally averaged stresslet, which arises from the imposed flow, rotational diffusion, and particle activity (self-propulsion). Next, we demonstrate that a modified Cox-Merz rule is applicable to a dilute, active suspension via a comparison of our linear viscoelasticity results to a theoretical prediction of the steady shear viscosity of active, slender rods (Saintillan, (2010)). Finally, through a comparison of our results to experiments on *E. coli* (Gachelin *et al.*, (2013)), we show that the linear viscoelasticity of an active suspension can be utilized to determine the mechanism of self-propulsion (i.e. pusher or puller), and estimate the strength of self-propulsion and correlation between tumbling events.

Tuesday 10:50 Audubon DEF BA17

Microscopic dynamics of bacterial “superfluids” under planar oscillatory shear

Shuo Guo[1], Devranjan Samanta[1], Yi Peng[1], Xinliang Xu[2], and Xiang Cheng[1]

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Bacterial suspensions show interesting rheological behaviors including a remarkable "superfluid" flows with vanishing apparent viscosity. To reveal the microscopic dynamics of bacterial "superfluids", we systematically studied the shear profiles of *E-coli* suspensions using ultra-fast confocal microscopy. The flow fields of bacterial suspensions under planar oscillatory shears of different shear rates are measured along both the flow-vorticity and the flow-gradient planes. We found that concentrated bacterial suspensions exhibit strong non-homogeneous flow profiles at low shear rates, where shear rates vanish away from the moving shear plate. We characterized the shape of the nonlinear shear profiles at different applied shear rates and bacterial concentrations and activities. The shear profiles follow a simple scaling relation with the applied shear rates and the enstrophy of suspensions. We demonstrated that this scaling relation can be quantitatively understood by considering the ensemble average of the unusual shear banding predicted by the theory of active liquid crystals. Our experiments reveal a profound influence of shear flows on the locomotion of bacteria and provide new insights into the dynamics of active fluids.

Tuesday 11:15 Audubon DEF BA18

Effective rheology and transition to spontaneous flows in confined active suspensions

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We analyze the effective rheology of a dilute suspension of self-propelled slender particles between two infinite parallel plates in a pressure-driven flow. We use a continuum kinetic model to study the dynamics and transport of particles, where hydrodynamic interactions induced by the swimmers are taken into account. Using finite volume simulations we study how the activity of the swimmer and the external flow modify the rheological properties of the system. Results indicate that at low flow rates, activity decreases the value of the viscosity for pushers and increases its value for pullers. Both effects become weaker with increasing the flow strength due to the alignment of the particles with the flow. In the case of puller particles, shear thinning is observed over the entire range of flow rates, where a Newtonian plateau is reached at very high flow rates. Pusher particles exhibit shear thickening at intermediate flow rates, where passive stresses start dominating over active stresses and the viscosity reaches a maximum that is greater than that of the Newtonian fluid. Finally shear thinning is observed at high flow rates, where the same Newtonian plateau is achieved. In the case of pushers, an increase in concentration is shown to lead to a decrease of the low-shear viscosity towards zero, suggesting a transition to apparent superfluidity in agreement with experimental observations. The consequences of this transition for the emergence of spontaneous flows are discussed and analyzed using numerical simulations.

Tuesday 11:40 Audubon DEF BA19

Geometry-dependent viscosity reduction and mixing in active fluids

Jorn Dunkel and Jonasz Slomka
Massachusetts Institute of Technology, Cambridge, MA, United States

We investigate flow pattern formation and viscosity reduction mechanisms in active fluids by studying a generalized Navier-Stokes model that captures the experimentally observed bulk vortex dynamics in microbial suspensions. We present exact analytical solutions including stress-free vortex lattices and introduce a computational framework that allows the efficient treatment of previously intractable higher-order shear boundary conditions. Large-scale parameter scans identify the conditions for spontaneous flow symmetry breaking, geometry-dependent viscosity reduction and negative-viscosity states amenable to energy harvesting in confined suspensions. The theory uses only generic assumptions about the symmetries and long-wavelength structure of active stress tensors, suggesting that inviscid phases may be achievable in a broad class of non-equilibrium fluids by tuning confinement geometry and pattern scale selection.

Symposium SG
Self-assembled Systems, Gels and Liquid Crystals

Organizers: Kendra Erk and Virginia Davis

Tuesday 10:00 White Ibis SG15

Quasi-properties and fractional constitutive equations for protein gels: Connecting gel microstructure to power-law linear rheology

Thibaut Divoux[1], Bavand Keshavarz[2], Mathieu Leocmach[3], Thomas Gibaud[4], Sébastien Manneville[4], and Gareth H. McKinley[2]
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In the present work we investigate the physical origin of the power-law rheology of model acid-induced protein gels. Viscoelastic soft solids are prepared by mixing sodium caseinate and glucono-delta-lactone (GDL) in water at different concentrations. Once mature, these gels show a robust power-law response in the time/frequency domain to the traditional linear viscoelasticity tests consisting of frequency sweeps, stress relaxation and early creep. A one-element fractional (Scott Blair) model captures this striking behavior and requires only two parameters to describe the linear gel rheology, which are a 'quasi-property' or 'gel strength' and a dimensionless exponent. To provide a physical interpretation of the latter parameters, we perform two sets of experiments. First, using space- and time-resolved measurements during the gelation we show that such power-law behavior emerges at the gelation point, and that the corresponding fractional exponent decreases towards a terminal value reached when the gel is fully mature. Time lapse images recorded by confocal microscopy reveal that the fractal dimension of the network evolves likewise, which allows us to link quantitatively the fractal properties of the network to the fractional exponents. Second, a thorough characterization of mature gels prepared with different amount of proteins and GDL allow us to directly link the two parameters of the fractional constitutive model to the sample microstructure. Gels prepared with the same GDL/protein ratio show a constant power-law exponent and similar microstructures which allow us to confirm quantitatively the link between the gel fractal dimension and the power-law exponent. Moreover, the gel strength increases with the protein content, which can be interpreted by simple scaling arguments to lead to a fractal dimension consistent with the one determined from the power-law exponent. Our results provide, for the first time, a direct link between a gel microstructure and its resulting power-law rheology.

Tuesday 10:25 White Ibis SG16

Rheology-structure relationships in “ductile” and “brittle” fats

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Food Science, University of Guelph, Guelph, ON N1G 2W1, Canada

The rheological behavior of fat crystal networks has been studied to understand its role in material performance. Here, we compare commercial fats with heterogeneous molecular composition, which lie at the two opposite sides of the functionality spectrum, and share mechanical features similar to solids displaying ductile (roll-in) and brittle (all-purpose) failure modes. Using FT-Chebyshev stress decomposition (1), we obtained elastic and viscous nonlinear rheological "fingerprints" relevant to bulk material properties. We found that "ductile" fats experienced dramatically less intracycle shear thinning at both instantaneous- and large- rates-of-strain than "brittle" fats, suggesting increased plastic deformation in "ductile" fats. Structural characterization using Ultra-Small Angle X-ray Scattering and Scanning Electron Microscopy revealed the presence of three hierarchy levels and layered microstructures in "ductile" fats in contrast to only two hierarchies and random microstructures in "brittle" fats. We suggest that these structural features provide resistance to flow and plastic deformation, contributing to "ductile-like" behavior. Furthermore, we argue that in achieving "ductile-like" behavior, the exact molecular composition is not as important as long as the unique nonlinear rheological fingerprint is matched.

References (1) R. H. Ewoldt, a. E. Hosoi and G. H. McKinley, J. Rheol. (N. Y. N. Y)., 2008, 52, 1427-1458.

Tuesday 10:50 White Ibis SG17

From non-linear rheology to the onset of macroscopic failure: An integral constitutive model for biopolymer gels

Bavand Keshavarz[1], Thibaut Divoux[2], Sébastien Manneville[3], and Gareth H. McKinley[1]
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We explore the nonlinear rheology of a class of biopolymer gels (namely acid-induced protein gels), which display a multiscale microstructure that is responsible for their solid-like properties. These soft viscoelastic materials exhibit a generic nonlinear mechanical response characterized by pronounced stress- or strain-stiffening prior to irreversible damage and failure, most often through macroscopic fractures. Using a series of acid-induced casein gels we show that the nonlinear viscoelastic properties of these hydrogels can be described in terms of a "damping function" which describes the gel mechanical response quantitatively up to the onset of macroscopic failure. Using a nonlinear integral constitutive equation built upon the experimentally-measured damping function, in conjunction with a power-law linear viscoelastic response, we derive the form of the stress growth in the gel following the start up of steady shear. We further couple the shear stress response with Bailey's durability criteria for brittle solids in order to predict the critical values of the stress σ_c and strain γ_c for failure of the gel, and how they scale with the applied shear rate. This provides a generalized failure criterion for biopolymer gels over a range of different deformation histories. Finally, we apply this framework to fatigue tests and provide qualitative predictions for the fracture parameters associated with these oscillatory tests.

Tuesday 11:15 White Ibis SG18

Strain-stiffening and negative normal stress in alginate hydrogels

Seyedmeysam Hashemnejad and Santanu Kundu
Dave C Swalm School of Chemical Engineering, Mississippi State University, MS State, MS 39762, United States

Polysaccharide networks are widely used in biomedical and food applications. Polysaccharides are semiflexible polymers and the networks consisting of these molecules can display interesting mechanical properties. In this presentation, results on alginate hydrogels, a model polysaccharide network, will be presented. Effect of two different types of crosslinking, ionic and covalent, on the mechanical properties will be considered. Calcium salts have been used to obtain ionically crosslinked gels and these gels consist of junction zones with finite dimensions. Diamines have been used for synthesizing covalently crosslinked gels. Shear rheology techniques were utilized to investigate the mechanical properties of these gels. The large amplitude oscillatory shear (LAOS) rheology captures the strain-stiffening behavior for these gels. In addition, negative normal stress has been captured in LAOS experiments, which has not been reported earlier for any polysaccharide networks. The magnitude of negative normal stress increases with the applied strain amplitude and can exceed that of the shear stress at large-strain. Deformation mechanism of alginate gels involves stretching and bending of the alginate chains. The results presented here provide new understanding of the deformation behavior of alginate hydrogels.

Tuesday 11:40 White Ibis SG19

Rheology of pluronic-hyaluronic acid thermoreversible gelling systems

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Pluronic F-127 is a triblock copolymer that exhibits thermoreversibe sol-gel transition contributed by the formation of micelles that self assemble and subsequently form a close packed cubic structure. Systems of pluronic with polysaccharides are generally considered to enhance gel stability and mechanical strength for controlled drug delivery applications. This study aims at elucidating the gelation behavior and structure-property relationship of pluronic (Pl) in the presence of Hyaluronic acid (HA) using rheology. HA increased the width of gel transition in Pl-HA systems as opposed to the sharp transition in case of Pl. Small amplitude oscillatory shear indicated weak frequency dependence of G' and G''. Strain rate frequency superposition (SRFS) was performed to probe their low frequency structural relaxation. Large deformation response indicated shear induced yielding with both the moduli following power law decay beyond the critical strain amplitude. G'' exhibited a well-defined peak just before the decay, a typical characteristic of soft glassy materials/soft solids. For the same yield strain, yield stress increased with HA content. Quantitative measures, in terms of higher harmonics and intracycle measures, obtained from Fourier and Chebyshev decomposition indicated similar features, though interestingly, there is a non-monotonic increase in G' with HA content. An Elasto-visco-plastic model is shown to simulate linear as well as nonlinear response of the systems.

Symposium EF
Emulsions, Foams & Interfacial Rheology

Organizers: Cécile Monteux and Sachin Velankar

Tuesday 10:00 Sandhill Crane EF15

Rheology of emulsions stabilized by solid particles: The role of nanoparticles at the liquid-liquid interface

Maziar Derakhshandeh, Milana Trifkovic, and Steven Bryant
The University of Calgary, Calgary, AB, Canada

We present the combined study of spatially resolved structure and shear rheology for a model emulsion system comprised of silica nanoparticles, dodecane and water. Combining conventional rheometry, cryo-scanning electron microscopy, and laser scanning confocal microscopy, completely characterizes the system and enables quantifying contribution of the particle arrangement at the interface on the rheological properties and stability of the emulsions. Calculated and determined interfacial coverage as a function of the initial volume fraction of nanoparticles match well and allow us to connect the microstructure to the macroscopic rheology. These results represent a direct experimental demonstration of the association between interfacial coverage and rheological enhancement for particle stabilized emulsions.

Tuesday 10:25 Sandhill Crane EF16

Localizing graphene on the interface of cocontinuous polymer blends

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Interfacial localization of graphene in cocontinuous polymer blends is known to be effective in stabilizing morphology and increasing conductivity with a lower electrical percolation threshold. However, little is known regarding the origin of graphene localization and the structure-properties relationship during annealing. Here, we fabricated polylactic acid (PLA) and polystyrene (PS) cocontinuous blends filled with thermally reduced graphene oxide (r-GO) at the interface. The resulting conductive composites show dramatically improved conductivity at low filler loadings and an ultralow percolation threshold of 0.028 vol%. We systematically studied the changes of conductivity and rheology of the PLA-PS composites during annealing. We found that r-GO transfers from PLA phase to the interface during melt compounding and annealing and forms a spanning 3D network, which effective suppresses the coarsening of the cocontinuous structure. Our study further showed that the 3D r-GO network significantly increases the conductivity and the storage modulus of the melt blends. Finally, we quantitatively interpreted the observed correlation between electrical and rheological properties of conductive composites via a simple model.

Tuesday 10:50 Sandhill Crane EF17

Microstructure and rheology of particulate suspensions in a binary fluid

Domenech E. Trystan and Sachin Velankar
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When particles are suspended in a binary fluid (i.e. a physical mixture of two immiscible fluids), the resulting microstructure arises from a coupling between three factors: (1) capillarity, i.e. the tendency to minimize interfacial area between the immiscible fluids, (2) wettability, i.e. the relative preference of the particles for each fluid, and (3) viscous forces required for mixing. We examine the morphology and the rheological properties of ternary mixtures of particles (30 vol%) and two immiscible polymeric liquids of low molecular weight. The particles are fully-wetted by one of the immiscible liquid phases, and the fraction of the fully-wetting liquid ranges from very small to large values.

Morphological characterization reveals a sequence of morphological changes as the composition is varied: meniscus-bound particle aggregates at low wetting fluid fraction, cocontinuous morphologies when the two fluids have comparable fraction, and a "drops-in-suspension" microstructure at high wetting fluid fraction. Rheological characterization by small and large amplitude oscillatory shear, and by stress ramp experiments reveals that many of these mixtures have solid-like rheology with yielding at high strain. The solid-like behavior (quantified by the low-amplitude storage modulus or the yield stress in a stress ramp experiment) is highest for meniscus-bound aggregates; this is in contrast to particle-free mixtures in which cocontinuous morphologies tend to show the greatest solid-like behavior. Surprisingly, the frequency dependence of the moduli in linear viscoelastic experiments agrees well with the Mason and Weitz model for hard spheres near the glass transition even though the particle loading is relatively low (30 vol%) and the particles experience attractive forces due to capillarity. We construct a microstructural map for such ternary blends in which the various morphologies and the phase inversion composition are mapped on a triangular composition diagram.

Tuesday 11:15 Sandhill Crane EF18

Tuning the phase separated morphology in carbon nanotube filled blends with a random or block copolymer: Part 1. Effects on the electrical conductivity

Ruth Cardinaels[1], Avanish Bharati[2], and Paula Moldenaers[2]
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The need for conducting polymeric materials in applications such as flexible electronics and soft robotics is on the rise. Immiscible blends containing conducting particles offer a generic route to tune the electrical functionality by means of tailoring their morphology combined with selective localization of the particles. The conductivity of biphasic blends consisting of PaMSAN and PMMA containing multiwall carbon nanotubes (MWNTs) was enhanced by tailoring the blend morphology with a polystyrene-polymethylmethacrylate copolymer. The PaMSAN/PMMA blends undergo phase separation by spinodal decomposition during which the MWNTs preferentially localize in the PaMSAN phase. The effects of the architecture (block or random) and molecular weights of the copolymers on the morphology, linear viscoelastic moduli and the resulting blend conductivity were systematically investigated at various copolymer concentrations. Effective compatibilization is achieved with block copolymers independent of their molecular weight. Short random copolymers are not effective, whereas long random copolymers are as effective as the long block copolymers. An effective compatibilizer led to interfacial tension mediated suppression of coarsening of the PaMSAN domains, resulting in increased connectivity and refinement of the PaMSAN phase containing the MWNTs, as confirmed by optical microscopy and the linear viscoelastic response of the blends. A pronounced increase by 3 decades in magnitude of the low frequency electrical conductivity was achieved upon addition of only 0.25 wt% long random copolymer to blends with 0.5 wt% MWNTs. Furthermore, the copolymer concentration required to develop a percolating network of MWNT-MWNT and PaMSAN-MWNT are approximately the same, independent of the type and molecular weight of the copolymer, suggesting that the electrical and rheological percolations are comparable. In conclusion, the ability of the copolymer to refine and stabilize the PaMSAN domains governs the blends electrical conductivity.

Tuesday 11:40 Sandhill Crane EF19

Tuning the phase separated morphology in carbon nanotube filled blends with a random or block copolymer: Part 2. Effects on the microcapacitor network

Avanish Bharati[1], Ruth Cardinaels[2], Michael Wübbenhorst[3], and Paula Moldenaers[1]
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There is a tremendous demand for flexible dielectric materials in applications such as EMI shielding and supercapacitors. From this viewpoint, immiscible blends containing conducting particles offer possibilities to tune the electrical functionality by tailoring their morphology and selective particle localization. The dielectric properties of bi-phasic blends of PaMSAN and PMMA containing multiwall carbon nanotubes (MWNTs) selectively localized in the PaMSAN phase were tuned by stabilization of the blend morphology with PS-PMMA copolymers. The dielectric loss spectra reveal an interfacial peak from the entrapped charges of the MWNTs with enclosed PaMSAN. Having elucidated the effects of the molecular weight, architecture (block or random) and concentration of the compatibilizer on the percolating network of the MWNTs, we unravel here the effects of the physical characteristics of the compatibilizer on the network of the MWNTs with enclosed PaMSAN. At low molecular weight a block copolymer has a more prominent effect, whereas at high molecular weight the random copolymer is as effective as the block copolymer. An increase by 4 decades in magnitude of the interfacial capacitance was achieved for compatibilized blends containing only 0.5 wt% MWNTs. The increase in the interfacial capacitance was attributed to the network of adjacent MWNTs entrapping a thin dielectric layer of PaMSAN resulting in an increased amount of parallel RC elements. The physical characteristics of the microcapacitor namely the gap spacing between the MWNTs and the volume fraction of entrapped PaMSAN contributing to the microcapacitor network were estimated using the fluctuation induced tunneling model and the interlayer model respectively. The gap spacing was unaltered for the various systems, whereas the volume fraction showed a similar trend as that of the interfacial capacitance. Combining the aforementioned parameters allowed the prediction of the total interfacial capacitance of the microcapacitor network for various systems.

Symposium SM
Polymer Solutions & Melts

Organizers: Carlos R. López-Barrón and Nicolas Alvarez

Tuesday 10:00 Snowy Egret SM15

Modeling extensional viscosity of linear and LCB polymers by dynamic dilution and interchain tube pressure

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A novel Hierarchical Multi-mode Molecular Stress Function (HMMSF) model for linear and LCB polymer melts is presented, which implements the basic ideas of (i) hierarchical relaxation, (ii) dynamic dilution, and (iii) interchain tube pressure. The modelling is solely based on the linear-viscoelastic relaxation modulus with only one non-linear material parameter, the dilution modulus. The model is assuming that chain stretch results from a tube diameter which decreases with increasing deformation. A decreasing tube diameter in turn leads to an increasing interchain tube pressure, which limits stretch. Through hierarchical relaxation, dynamic dilution results in larger tube diameters of chain segments with longer relaxation times, which increases the potential of these modes for larger stretches. The onset of dynamic dilution occurs when the relaxation process has reached the dilution modulus. The relaxation times in combination with the dilution modulus determine the magnitude of strain hardening, which is enhanced by long relaxation times and narrow molecular weight distribution. This is exemplified by metallocene catalysed polymers with star molecules featuring only one branch point: Due to their narrow molecular weight distribution, there is less dilution by oligomers, and the dilution modulus is larger, leading to enhanced strain hardening. The HMMSF model demonstrates excellent qualitative and quantitative agreements with the uniaxial extensional viscosity data of polydisperse linear as well as long-chain branched polymer melts for a wide range of strain rates based solely on the linear-viscoelastic relaxation modulus with only one free non-linear parameter, the dilution modulus.

Tuesday 10:25 Snowy Egret SM16

Resuscitating the dual slip link model: Linears, stars, and blends

Sachin Shanbhag
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Tube models, despite their sophistication, are unable to consistently predict the linear rheology of linear-linear and star-linear blends with a uniform set of parameters. In contrast, slip-link models with different degrees of resolution and computational complexity have been remarkably successful on the same datasets. One key difference between the tube and slip link models is the treatment of the process of constraint release. Unlike tube models, which represent entanglement between chains using a mean-field approach, slip-link models explicitly model entanglements using real-space or virtual-space coupling between chains in an ensemble. In this work, motivated by the success of other slip-link models, we resuscitate the dual slip link model (DSLM) of Shanbhag et al (2001), which is unarguably the least sophisticated slip link model. Despite, or perhaps because of, its simplicity, it has been useful in understanding the mechanism of dynamic dilution in symmetric stars. We show its recent success in predicting the linear rheology of star and linear polymers, almost quantitatively with a single set of parameters. Preliminary results on star-linear blends are reported and discussed.

(*) S Shanbhag; RG Larson, JI Takimoto, M Doi, Phys. Rev. Lett., 2001, 85, 195502.

Tuesday 10:50 Snowy Egret SM17

Brownian dynamics simulations of single comb DNA molecules

Amir Saadat[1], Danielle J. Mai[2], Bamin Khomami[1], and Charles M. Schroeder[3]
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A bead-spring model for semi-flexible macromolecules is developed to overcome the deficiencies of current coarse-grained bead-spring models. Specifically, model improvements are achieved through incorporation of a bending potential which is parametrized using the properties of the real WLC model. The new model is designed to accurately describe the correlation along the backbone of the chain, segmental length, and force-extension behavior of the macromolecule even at the limit of 1 Kuhn step per spring. The relaxation time of different normal modes is used to demonstrate the capabilities of the new model in predicting chain dynamics.

The new model, denoted by WLC-SK, is then utilized in Brownian dynamics (BD) simulation of DNA molecules. The relaxation and stretching dynamics of linear and comb DNA molecules are evaluated and compared against experimental data. Both transient and steady state fractional extension obtained using BD simulations for linear and comb-shaped chains with different degree of branching (low branching with up to 4 branches per backbone and high branching with 5 to 9 branches) are in good agreement with experimental results. Moreover, an unusual slow-down of unfolding event which is observed in the experiment is confirmed using simulations.

It is also found that relatively long branches have a profound influence on the relaxation dynamics of comb molecules. In particular, the transient fractional extension in stretch-relaxation tests revealed a slower relaxation of the backbone when the branches are placed near the ends of the molecule. This effect was found to be entropic, hence, suggesting the essence of additional relaxation modes for the chain backbone with grafted arms. Moreover, the presence of side branches was found to diversify the molecular individualism.

Tuesday 11:15 Snowy Egret SM18

Nonlinear rheology and dynamics of dendritically branched macromolecules in shear and uniaxial extension

Qian Huang[1], Salvatore Costanzo[2], Chinmay Das[3], and Dimitris Vlassopoulos[2]
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The nonlinear rheological properties of model polymers with well-defined architectures provide profound implications in finessing molecular models. While rheology of polymer melts is highly sensitive to branching, the exact role of number, size and distribution of branches is not fully understood. In this work, we present nonlinear rheological measurements and model predictions of well-defined symmetric Cayley-tree poly(methyl methacrylates) with 3 and 4 generations in both shear and uniaxial extension. These dendritically branched macromolecules were synthesized anionically by Hirao and co-workers [1]. Each tree polymer consists of equal segments between generations. The number average molar mass of each segment is 11,000 g/mol (i.e., 2.4 entanglements) and the polydispersity index is 1.02. The linear viscoelastic properties and stress growth in uniaxial extension of the two polymers have been previously discussed by van Ruymbeke et al. [2]. Here we extend the work to nonlinear shear and stress relaxation following both shear and uniaxial extension by using state-of-the-art instrumentation, i.e., cone-partitioned plate (CPP) shear rheometry and filament stretching rheometry (FSR). The data shows that nonlinear shear is characterized by transient stress overshoots and the validity of the Cox-Merz rule. Nonlinear stress relaxation is much broader and slower in extension compared to shear. It is also slower at higher generation, and rate-independent for rates below the Rouse rate of the outer segment. It is suggested that coupling of stretch between generations is responsible for the observed effect in extension. The experimental results can be semi-quantitatively described by state-of-the-art modeling predictions using the Branch-on-Branch (BoB) algorithm [3][4].

[1] A. Hirao et al., Macromolecules 38, 8701-8711 (2005; [2] E. van Ruymbeke et al., J. Rheol. 54, 643 (2010); [3] C. Das et al., J. Rheol. 50, 207 (2006); [4] Q. Huang et al., J. Rheol. accepted (2016)

Tuesday 11:40 Snowy Egret SM19

High temperature extensional rheology of linear, branched and hyper-branched polycarbonates

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Predicting and controlling the rheology of polymeric fluids as a function of molecular chemistry has been of great interest in both academia and industry. While extensional rheology measurements of polymer melts have been performed in the past, those experiments were performed under nitrogen and at temperatures chosen to avoid polymer degradation and reaction. In this presentation we will explore the effect that oxygen at high temperatures can have on both the shear and extensional rheology of a series of polymer melts. We will demonstrate the high temperature evolution of extensional viscosity of three selected commercially available polycarbonates - one linear, one branched and one hyper-branched. The measurements were performed using a custom built high temperature capillary extensional break up rheometer (CABER). The experiments were performed in the temperature range of T = 250ºC and 370ºC both in air and nitrogen. In the present work we will show the effect on polycarbonate extensional viscosity due to degradation at high temperatures and how differences in the molecular structure and end groups affects the evolution of extensional viscosity as a function of strain and time at temperature. In this study, we will show that the measurements of extensional rheology are orders of magnitude more sensitive to polymer degradation as compared to shear rheology. We will also present stark difference in the extensional behavior of the three grades of polycarbonate and demonstrate an obvious differentiation between random chain scission which is the first phase of polymer degradation and repolymerization or crosslinking which takes place at higher temperatures.

Tuesday Afternoon

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Tuesday 1:30 Audubon B SC20

Dynamics and rheology of colloidal dispersion near to the glass transition concentration

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We prepared and investigated two colloidal dispersions, i.e., a soft thermosensitive PS-PNIPAM latex with core-shell structure dispersed in water and a hard-sphere silica dispersed in a mixture of ethylene glycol and water. Rheological behavior of the dynamic and creep tests of these colloidal dispersions were measured at equilibrium in the vicinity of the glass transition concentration. Mastercurves show that both time-aging time and time-concentration superposition principles are valid for the colloidal dispersion and the validity of time-concentration superposition principle is also demonstrated by van Gurp-Palmen plot, i.e., phase angle d vs G* or tan d vs ?. The shift factors and relaxation times follow super-Arrhenius behaviors as the glass transition concentration is approached. Time-concentration superposition requires vertical shift of the data by a factor bfeff which varies as bfeff 8 feffn, where n=4.88 for the soft colloidal dispersion and n=12.16 for the silica dispersion. The conventional softness parameters n (Gp 8 feffn) are found to be frequency dependent, i.e., Gp at fixed frequency or Gp at G"(?) min, for both soft and hard colloidal dispersions. The conventional softness parameter n is not consistent the concentration dependence of the vertical shift factors n suggesting that prior evaluations of colloidal softness should be reconsidered.

Tuesday 1:55 Audubon B SC21

Testing the paradigms of the glass transition in colloids

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In this work we develop a computational framework for studying the glass transition in colloids from a micromechanical perspective, with a view toward shedding light on the molecular glass transition. Upon cooling, molecular glass-formers undergo a glass transition during which viscosity appears to diverge, and the material transitions from a liquid to an amorphous solid. However, the new "state" is path-dependent, and is not an equilibrium phase: material properties such as enthalpy continue to evolve in time. Rather, the material relaxes toward an "intransient" state, as measured by the Kovacs signature experiments, i.e. the intrinsic isotherms, the asymmetry of approach and the memory effect. But molecular relaxation is so fast that the transition is conflated with the subsequent aging process, which makes it difficult to capture structural changes during the transition. Colloidal glass formers provide a natural way to model such behavior, owing to the disparity in colloidal versus solvent time scales that allows tracking of particle dynamics and structure, and how these evolve with liquid-to-glassy macroscopic behavior. We interrogate these ideas via large-scale dynamic simulation of a hard-sphere colloidal glassy state, which we induce by jumps in volume fraction. During and following each jump, the positions, velocities, and particle-phase stress are tracked and utilized to characterize relaxation time scales and structural changes. The impact of both quench depth and quench rate on arrested dynamics and "state" variables is explored. Analogs for the Kovacs signatures are developed. The results provide insight into the existence of an "ideal" glass transition.

Tuesday 2:20 Audubon B SC22

A reinterpretation of the rheological behavior of hard-sphere colloidal glass under shear start-up

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The rheology and dynamics of a hard-sphere colloidal glass under shear start-up are investigated with Brownian dynamic simulations. Under shear start-up, colloidal glasses show yielding behavior which is manifested by a stress overshoot. In this work, the stress overshoot behaviors are reinterpreted in terms of Laun's elastic strain and an equilibrium position shift. This is a departure from the dominant rheological approach that assumes a fixed equilibrium position. Upon initiation of shearing, the elastic strain, which is the difference between the applied strain and the equilibrium position, is determined by a series of hybrid step rate (rate-controlled) and recovery (stress-controlled) tests. The elastic strain change facilitates a reasonable and quantitative explanation of the stress overshoot behavior of our colloidal glass, demonstrating a close relationship to the stress response. Additional analysis of the particle dynamics and microstructural changes is correlated to the change in elastic strain. The

successful explanation of the stress overshoot of the colloidal glass suggests that Laun's elastic strain concept has significant utility in understanding other nonlinear protocols, notably large amplitude oscillatory shear (LAOS).

Tuesday 2:45 Audubon B SC23

Shear transformation avalanches determine the Herschel-Bulkley exponent in soft glassy solids

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Many soft glassy solids such as: foams, emulsions, and suspensions of soft particles (e.g. hydrogel particles), exhibit bursty stress relaxations in steady shear at low rate. We argue that these bursts, or avalanches, determine the Herschel-Bulkley (HB) exponent, b, of these materials. We perform simulations using two different variants of Durian's bubble model with different modles for the form of the drag force on the bubbles. We show that the resulting b can be understood using a scaling theory which relates b to two other exponents; one, n, which governs the characteristic length of the largest avalanches at a given stress scale, the other, z, which governs the relationship between the size and duration of a given avalanche. We show that both variants of the Durian model exhibit a common value of n, but give different values for b and, correspondingly, z. These results suggest that diverse soft glassy solids may exhibit different HB exponents depending on the form of the viscous forces acting on particles despite similar elastic interactions between particles and help explain previous experimental results on the flow curves of bubble rafts sheared at an air-water interface.

Tuesday 3:35 Audubon B SC24

Why not friction and hydrodynamics? A generalized model of the dynamics and structure of dense colloidal suspensions

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We perform mesoscopic DPD simulations incorporating both hydrodynamic and frictional interparticle interactions to study the effect of interaction potential on the rheology and structure of dense frictional colloidal suspensions. In particular, we performed a series of viscosity and normal stress measurements in suspensions with different volume fractions and obtained, for the first time, a complete picture of the dynamic state and of the microstructure. We confirmed that N1 for semi-dense suspensions stays negative and grows with shear rate, which is consistent with hydrocluster-induced shear-thickening. We show that continuous shear-thickening, CST, in colloidal suspensions can be explained solely via hydrodynamics, frictional bonds being transient and negligible to the rheological response. In dense suspensions and close to the jamming transition however, friction is required to obtain DST and replicate the recently experimental findings of a transition from negative to positive N1. We prove that hydroclusters form first at low stresses; this brings the particles together, thus allowing frictional contacts to develop, eventually leading to discontinuous shear-thickening, DST. In addition, when each particle is subject to an average of one frictional contact, N1 reverses its increase but remains negative; at approximately two frictional contacts, a percolating network forms and N1 becomes positive.

Tuesday 4:00 Audubon B SC25

Active microrheology of dense colloidal suspensions

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We investigate the constant-force microrheology of a probe particle in dense colloidal (Brownian) suspensions using particle-scale simulations. These particle simulations allow transition from a lubricated hydrodynamic interaction to an unlubricated frictional contact and have been successful in quantitatively reproducing the non-Newtonian shear behavior of thickening suspensions including discontinuous shear thickening. In this study, we focus on the structural anisotropies induced by the probe motion depending on the non-dimensional force strength characterized by a Peclet number and the probe to bath particle size ratio. As external force strength increases, we observe the development of a particle accumulation zone in front and a depleted wake zone behind the probe particle, in agreement with the observations from previous studies. However, in this study the nature of the accumulation zone in front of the probe particle becomes distinctly different for large external force strength. For high enough external force the nature of contacts switch from a lubricated to a frictional one, thus a contact network is generated emanating from the probe particle. We characterize this contact network and the velocity of the probe as a function of the applied external force.

Tuesday 4:25 Audubon B SC26

Flow of non-equilibrium states of attractive colloids: Insights from experiments and computer simulations

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The rheology of non-ergodic states of attractive colloids has been the subject of intense investigation both experimentally and by computer simulations [1,2], while theoretical models aim in describing the dependence of their viscoelastic properties on key parameters such as volume fraction and attraction strength. Here we examine fundamental aspects of the linear and non-linear rheology of systems ranging from low and

intermediate volume fraction gels to highly concentrated attractive glasses and compare experimental findings with results from Brownian Dynamics simulations. We mainly focus on the way such systems yield under the application of steady or oscillatory shear via start-up shear tests and large amplitude oscillatory shear, as well as on the mechanisms of gel reformation and accompanied stress relaxation after shear cessation. We discuss the phenomenology of two step yielding, widely observed experimentally, and the underlying mechanisms and relevant length- and time-scales that cause such behavior and contrast it with findings from computer simulations with and without hydrodynamic interactions. We further report on the types of rejuvenation protocols, either by shear (steady or oscillatory) or by a temperature quench, as a tool to provide reproducible initial states or, more interestingly, to tune the final properties of such non-equilibrium states.

References: [1] N. Koumakis and G. Petekidis, Soft Matter, 7, 2456-2470, (2011). [2] N. Koumakis, E. Moghimi, R. Besseling, W. C. K. Poon, J.F. Brady and G. Petekidis Soft Matter 11, 4640-4648, (2015). Work in collaboration with E. Moghimi, N. Koumakis and J. Brady,

Tuesday 4:50 Audubon B SC27

Gravitational collapse of colloidal gels and connections to kinetic "arrest"

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We investigate the phenomenon of gravitational collapse in colloidal gels via dynamic simulation. In moderately concentrated gels formed via arrested phase separation, rupture and re-formation of bonds of strength O(kT) permit ongoing structural rearrangements that lead to temporal evolution - aging - of gel structure and rheology. The reversible nature of the bonds also allows the gel to transition from solid-like behavior to liquid-like behavior under external forcing, and back to solid-like behavior when forcing is removed. But such gels have also been shown to be susceptible to sudden and catastrophic collapse of the entire structural network, after which the gel sediments into a dense layer, eliminating any intended functionality of the network scaffold. Although the phenomenon is well studied in the experimental literature, the microscopic mechanism underlying the collapse is not understood. To study this behavior, we conduct large-scale dynamic simulation to model structural and rheological evolution in colloidal gels subjected to gravitational stress, examining the detailed micro-mechanics in three temporal regimes: slow, pre-collapse evolution; collapse and rapid sedimentation; and long-time compaction. A range of attraction strengths and gel ages, and their effect on the critical force that triggers collapse, are studied. The influence of the interplay between Brownian motion, attractive forces, and gravitational forces on collapse and subsequent restructuring is elucidated, and a connection to phase behavior is made.

Tuesday 5:15 Audubon B SC28

Elasto-kinetic transition for sheared granular flows: From soft to hard particles

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Granular materials belong to the class of amorphous athermal systems, like foams, emulsion or suspension they can resist shear like a solid, but flow like a liquid under a sufficiently large applied shear stress. While the mechanical behavior of soft particles is usually thought of in terms of localized elastoplastic events, the shear motion of rigid particles is rather analyzed in terms of coherent non-affine displacements along floppy modes. We investigate numerically the transition from soft to rigid particles, varying their softness compared to the confining pressure, and the normalized shear rate I (inertial number). The cross-over condition is identified using three criteria: the isostatic condition, the ratio of potential to kinetic energy and the presence of localized elasto-plastic events. We find that the rheological constitutive relation is marginally affected by the transition from soft to hard particles but depends essentially on inter-particle friction. Accordingly, we show that the distribution of local shear rate mostly depends on the inertial number I, allowing us to propose an interpretation of the robustness of the rheology across the elasto-kinetic and the isostatic transitions.

Symposium BA
Biorheology & Active Fluids

Organizers: David Saintillan and Christian Wagner

Tuesday 1:55 Audubon DEF BA21

Active-to-passive transitions in microtubule based biopolymer gels

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We will present a rheological characterization of the viscoelastic properties of active biopolymer fluids and gels. Passive in-vitro biopolymer networks have been intensively characterized using bulk- and micro-rheology. However, active networks remain largely unexplored. We use a unique class of biologically derived extensile active materials, based on stabilized microtubules, kinesin motor proteins, and adenosine triphosphate (ATP), to explore the viscoelastic transition from active to passive states. Using our coupled confocal-microscopy rheometer (con-rheo) platform we directly determine the bulk network response while simultaneously quantifying the microscopic dynamics based on the activity magnitude as driven-force. Our preliminary results indicate that these materials are purely viscous in the active state despite the existence of long-lived spanning filaments. Moreover, we observe a clear transition to elastic behavior that occurs as the magnitude of the activity is gradually reduced in time.

Tuesday 2:20 Audubon DEF BA22

Bacteria and transport of colloids at fluid interfaces

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The study of motion in suspensions of bacteria has provided valuable insights into how small self-propelled objects interact. We study bacteria near fluid-fluid interfaces. We track the movement of passive polystyrene spheres at hexadecane-water interfaces laden with *Pseudomonas aeruginosa* PA14 *?pelA* bacteria. Such systems are commonly studied by calculating the ensemble average statistics of particle trajectories to determine interface dynamical and microrheological properties. Here, we argue that such averages can mask important information. We note signature trajectory shapes and rates of displacement of passive particle that are not consistent with hydrodynamic interactions via lubrication-type interactions, and suggest other, as yet unappreciated interactions. These results have implications in understanding the ability of bacteria to transport passive species.

Tuesday 2:45 Audubon DEF BA23

Effects of bacteria mobility on the formation of P. Aeruginosa pellicles

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Biofilms are communities of microorganisms surrounded by extracellular polymer matrix of self-secreted, biomolecules that enable survival in hostile environments. Biofilms create persistent infections, affect oil processing, and are utilized in water treatment. At solid surfaces, biofilms are soft viscoelastic solids affected by temperature, flow, pH, bacteria motility and other factors. Biofilms at air/water interfaces, known as pellicles, are relevant to many applications. However, pellicle mechanical properties are still being discovered, and even the effects of bacteria motility on the pellicle growth are not well characterized. A better understanding of pellicle formation may provide strategies to regulate their growth.

In this study, the interfacial shear rheology and microstructure of pellicles composed of multiple strains of P. aeruginosa are characterized to understand how motility affects strength and development. In particular, the role of flagella, which provide run and reverse motion, type IV pili, which provide twitching behavior, and swarming on pellicle development are characterized. What is clear from current results is that any change to bacteria motility results in slower growing and ultimately weaker pellicles. In particular, non- swarming and non- flagellated mutants exhibit dramatic reduction in mechanical strength of pellicle, and increase in formation times. Changes to twitching motility seem to have a smaller effect in comparison. These results are compared to what is known for the behavior of these systems at solid surfaces.

Symposium NF
Non-Newtonian Fluid Mechanics & Instabilities

Organizers: Sandra Lerouge and Becca Thomases

Tuesday 3:35 Audubon DEF NF1

Thermal Marangoni migration of droplets in an Oldroyd-B fluid under creeping flow conditions

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In this work we investigate the impact of elasticity on the thermocapillary motion of droplets for the case of vanishing Reynolds and Marangoni numbers, i.e. when inertial terms in the momentum equation and convective-transport contribution in the energy equation are negligible. The study has been carried out employing a coupled Level-Set-Volume of Fluid approach and an adaptive mesh refinement strategy implemented in the framework of the CFD toolbox OpenFOAM. The interfacial stresses induced by a non-uniform temperature distribution at the fluid-fluid interface have been accounted for by adding to the momentum equation an "extra" source term based on the so-called "Continuum Surface Force" approach. The calculation of such contribution requires the knowledge of the temperature field, which makes the momentum and energy equations fully coupled. Here, we consider the case of an initially quiescent droplet placed in a box-shaped domain where a constant temperature gradient is applied under reduced gravity conditions. The imbalance of the interfacial stresses generated by the non-uniform temperature distribution causes the liquid in the proximity of the drop to migrate from the hot to the cold region. This mechanism results in the drop moving in the opposite direction due to the thrust generated by the counter motion of the surrounding phase. For the specific case of a droplet of Newtonian fluid in a viscoelastic surrounding matrix, we use an Oldroyd-B constitutive equation to capture the viscoelasticity of the matrix in the absence of shear-thinning effects. We have investigated the effect of the Deborah number and found the droplet shape and its asymptotic migration velocity deviate significantly from those observed for a Newtonian system. This departure of the observed dynamics from Newtonian behaviour can be ascribed to the complex interplay between different effects, including droplet morphological evolution and related distribution of surface-tension-driven and elastic stresses at the interface.

Tuesday 4:00 Audubon DEF NF2

Dynamics of dimples on bubbles approaching free interfaces in wormlike micellar solutions

Vineeth Chandran Suja[1], Aadithya Kannan[1], Andrew Kubicka[2], and Gerald G. Fuller[1]
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Bubbles approaching free interfaces from the bulk of a liquid, often deform and entrain liquid to have a local maxima in the film thickness at the centre of the bubble called as a dimple. The dynamics of these dimples are known to play an important role in bubble stability, with dimple washouts initiating complex Marangoni instabilities in the presence of surfactants. However no literature exists on the dynamics of dimples in worm-like micellar solutions where the effects of bulk rheology play a significant role. We report experimental data from single bubble drainage experiments focused on the drainage dynamics of the dimples at different Capillary (**Ca**) and Deborah numbers (**De**). In wormlike micellar solutions [cetyltrimethylammonium bromide (CTAB) + Sodium Salicylate (NaSyl)], the washout dynamics of dimples is seen to be influenced by the micellar structures. At low surfactant concentrations (spherical micelles), the dimples are seen to become unstable at low **Ca** and have larger washout velocities (compared to higher surfactant concentrations) for a given **Ca**. However, at higher concentrations, the entangled polymer structure of the micelles stabilizes the dimples against washout at low **Ca**. Further at these concentrations, depending on the reptation times (characterized by **De**), complex washout dynamics involving rapid dimple deceleration, recoil and oscillatory washouts are observed at different **Ca**.

Tuesday 4:25 Audubon DEF NF3

Forced spreading of films and droplets of colloidal suspensions

Leonardo Espin and Satish Kumar
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When a thin film of a colloidal suspension flows over a substrate, uneven distribution of the suspended particles can lead to an uneven coating. Motivated by this phenomenon, we analyze the flow of perfectly wetting films and droplets of colloidal suspensions down an inclined plane. Lubrication theory and the rapid-vertical-diffusion approximation are used to derive a coupled pair of one-dimensional partial differential equations describing the evolution of the interface height and particle concentration. Precursor films are assumed to be present, the colloidal particles are taken to be hard spheres, and particle and liquid dynamics are coupled through a concentration-dependent viscosity and diffusivity. We find that for sufficiently high Péclet numbers, even small initial concentration inhomogeneities produce viscosity gradients that cause the film or droplet front to evolve continuously in time instead of travelling without changing shape as happens in the absence of colloidal particles. At high enough particle concentrations, particle diffusion can lead to the formation of long-lived secondary flow fronts in films. Our results suggest that particle concentration gradients can have a dramatic influence on interface evolution in flowing films and droplets, a finding which may be relevant for understanding the onset of patterns that are observed experimentally. The influence of solvent evaporation is also considered, revealing that the interaction between evaporation and non-Newtonian suspension rheology gives rise to several distinct regimes of droplet shapes and particle concentration distributions. The results provide insight into how evaporation and suspension rheology can be tuned to minimize sagging as well as the well-known coffee-ring effect.

Tuesday 4:50 Audubon DEF NF4

Influence of the yield stress on the evolution of a bubble population in a viscoplastic fluid, consequences on the macroscopic swelling of bitumen drums

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The goal of this study is to predict the swelling of bitumen barrels in which radioactive salts are mixed (60% wt of bitumen and 40% wt of salts). Radioactivity generates uniform volume production of hydrogen by radiolysis of bitumen chains. Since the production of gas occurs on very large time scales (more than a hundred years), one needs to set up models to predict the material swelling. It has been shown that bitumen is a yield stress fluid. The present work therefore proposes to study the influence of the yield stress and the production rate of gas on the evolution kinetics of a bubble population. Usually, in a non-yield stress fluid and without gas creation, a supersaturation of gas leads to a scenario of germination, bubble growth and Ostwald ripening (growth of large bubbles at the expense of the small ones). Over long times, a self-similar distribution of large bubbles is selected, independent of the initial distribution of nuclei. In this work, a new model for bubble growth in an infinite viscoplastic material is introduced. Then it is shown that there exist conditions for which the production rate of gas competes with the kinetics of ripening and where the yield stress induces hysteresis and pulsing phenomena on the evolution of bubbles distribution. The effect of the yield stress and the initial distribution of nuclei on the final population is discussed.

Tuesday 5:15 Audubon DEF NF5

Color interferometry applied to yield-stress fluid drop impacts on heated surfaces

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Yield-stress fluids, including gels and pastes, are effectively fluid at high stress and solid at low stress. In liquid-solid impacts, these fluids can stick and accumulate where they impact, motivating several applications of these rheologically-complex materials. Here we use high-speed imaging and color interferometry to experimentally study liquid-solid impact of yield-stress fluids on heated surfaces. Aqueous materials tend to adhere at to a surface low temperature and release at high temperature; our prior work showed that increasing the yield stress decreases the temperature required to prevent material from sticking. Here we present videos captured using interferometry to observe the thickness of the vapor layer between the drop and the surface during both stick and non-stick events. We use these data to gain insight into the physics behind the phenomenon of the yield stress reducing sticking to hot surfaces.

Symposium SG
Self-assembled Systems, Gels and Liquid Crystals

Organizers: Kendra Erk and Virginia Davis

Tuesday 1:55 White Ibis SG21

Modeling of fluids with transient mesoscale structures

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Transiently networked fluids are often studied through macroscopic modeling. To avoid the need for a closure approximation to integrate a mesoscopic model to the macroscopic level, we simulate and present results of a stochastic mesoscale model of a transiently connected system of coupled bead spring elements. This work is based on the earlier work of van den Brule and Hoogerbrugge, 1997, in which the topology of the network and its composite chains was tracked spatio-temporally. This topological tracking allows the quantification of the distribution of chain lengths and allows for the breakage and recombination of the bead-spring chains to be determined by local, as opposed to globally averaged, quantities. Several breakage/recombination energy dependences are considered including an attractive bead energy represented by a parabolic potential well. Both linear, Hookean, and nonlinear, FENE, springs are considered in the modeling and simulations. Simulation predictions in equilibrium and in transient and steady shearing are presented including mesoscale properties (chain lengths and Q distributions) and macroscale properties (shear stress, viscosity, normal stresses).

Tuesday 2:20 White Ibis SG22

Influence of thermal and deformation history on the viscoelastic properties of well-defined entangled segmented copolymers

Guilhem P. Baeza[1], Ashwinikumar Sharma[2], Ameur Louhichi[1], Carel Fitié[3], Hadi Goldansaz[2], Dimitris Vlassopoulos[1], and Evelyne Van Ruymbeke[2]

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We explore the role of chain rigidity in thermoplastic elastomers (TPE) consisting of segmented copolymers [1] based on soft poly-tetrahydrofuran (pTHF) blocs and more rigid crystallizable T4T units [2] (called "hard-segments" HS). By means of X-rays scattering techniques (SAXS and WAXS) as well as differential calorimetry (DSC), we first evidence that the ribbon-like crystallites made of HS become thicker (1 to 5 nm) and tend to spontaneously align at a 10-50 nm lengthscale when the HS content passes from 5 to 20%w in the material. Based on these results and statistical calculations, we discuss the impact of the chain rigidity on the rheology of the TPEs in a systematic way. First, small amplitude oscillation shear (SAOS) shows a strong increase of both the plateau modulus (from 1 to 30 MPa) and the melting point Tm (from 90 to 160°C) respectively for 5 and 20%HS. Then, cyclic strain amplitude sweeps performed around Tm evidence the crucial role of the chain segments mobility on the HS network building. While at T>Tm, the chains seem to associate under shear making the material stiffer, the crystallite network is irreversibly destroyed after one cycle at T<Tm and its modulus keeps on decreasing with further solicitations. More interestingly, at intermediate temperature (slightly below Tm), our experiments reveal that a structure can raise in the first few cycles before to collapse after a long solicitation. All the authors acknowledge the financial support of the European Initial Training Network "SUPOLEN".

References: [1] Gaymans, R.J., Segmented copolymers with monodisperse crystallizable hard segments: Novel semi-crystalline materials. Progress in Polymer Science, 2011. 36(6): p. 713-748. [2] Vanhutten, P.F., R.M. Mangnus, and R.J. Gaymans, Segmented Copolymers with Polyesteramide Units of Uniform Length - Structure-Analysis. Polymer, 1993. 34(20): p. 4193-4202.

Tuesday 2:45 White Ibis SG23

Viscoelasticity and its temperature-dependence in thermosensitive copolymer-laponite nanocomposite systems in the limiting ranges of low and high nanoparticle impact

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Nanocomposites of polymer-clay nanoparticles are attracting a large interest primarily because property enhancements could be achieved at either very low polymer or nanoparticle volume fractions. However, the understanding of the rheology and structure of these materials, particularly in the intermediate concentration regime, is still challenging. The purpose of this presentation is to provide an insight into the role of each component in influencing the fluid-solid transition induced by temperature. The system consists of a thermosensitive copolymer micellar solution, a pluronic triblock copolymer in solution to which we add synthetic clay laponite nanoparticles. We will describe the thermo-rheological proprieties of the nanocomposites in the relatively concentrated nanoparticle range. The viscoelastic behavior, and its temperature-dependence, will be discussed. We will show that in this domain, the data are strongly reminiscent of those found in coated-laponite colloidal dispersions, i.e. where the copolymer is fully adsorbed on the surface of the laponite nanoparticles. The rheological properties will be compared with the data obtained on nanocomposite systems where the viscoelastic properties are solely dictated by the presence of copolymer micelles. The results will also be discussed in the light of additional information obtained from structural studies performed on these systems.

Symposium MF
Micro/Nano Fluidics and Probe Rheology

Organizers: Monica Oliveira and Gordon Christopher

Tuesday 3:35 White Ibis MF1

Particle migration in electro-hydrodynamic bidirectional flows of a viscoelastic fluid

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We present in this work an interesting electrophoresis-tuned particle migration phenomenon in pressure-driven flow of a viscoelastic polymer solution. We find that particles leading and lagging behind the fluid flow due to electrophoresis migrate towards the wall and center of a straight rectangular microchannel, respectively. These observations are exactly opposite to those reported in the literature on particle migration in Newtonian fluids. They are, however, consistent with recent studies of transverse migration of colloidal particles and DNA molecules in electro-hydrodynamic bi-directional flows of a viscoelastic solution. We attribute this phenomenon to the competing result of the electrophoretic slip-induced inertial Saffman lift, polymer-induced elastic lift and wall-induced electrical lift.

Tuesday 4:00 White Ibis MF2

Mean squared displacement: Uncertainty estimation

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A time-dependent modulus can be estimated from the mean squared displacement, obtained from particle trajectories, through the generalized Stokes-Einstein equation. Traditionally, in order to estimate the errors in these values from molecular simulations, multiple replicates are run. Recently, Shanbhag proposed a method to estimate the error in diffusion coefficients by bootstrap sampling the particle trajectories from a single simulation in order to cheaply generate multiple estimates of the diffusion coefficient. Since the proposed method works on mean squared displacement, a similar procedure should be applicable to calculating a viscoelastic modulus from probe data. However, the method was originally tested on a simple system with non-interacting particles: as bootstrapping assumes the items under study to be independent, this work examines how well bootstrap sampling performs on interacting systems of particles. The distribution of diffusion coefficents from multiple simulations of a Lennard-Jones fluid was compared with the distributions obtained by performing bootstrap sampling. At lower densities, the distributions of the independent and bootstrap samples were fairly comparable. However, at higher densities the bootstrapped samples underestimated the amount of error: in some cases, the error was half that of the independent simulations. Since particles interact more at higher densities, this suggests that the interactions between the particles can lead to false confidence when using the bootstrap. While bootstrapping may still be useful, care will have to be taken to quantify the relationship between particle interactions and error underestimation.

Tuesday 4:25 White Ibis MF3

Sticky-probe microrheology

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We conduct a theoretical study of the impact of attractive forces on the microviscosity of colloidal dispersions. Prior theoretical work has largely focused on the influence of Brownian and hydrodynamic forces on rheology of purely repulsive hard spheres. However, attractive interactions between a probe and surrounding structure are suspected to underlie anomalous motion in e.g. biological suspensions. In active microrheology, the externally-forced probe distorts surrounding microstructure from its equilibrium configuration; the degree of this distortion is set by the strength of external forcing relative to entropic restoring forces; attractive forces further influence this evolution. To examine the influence of this interplay on rheology, we formulate a Smoluchowski equation governing pair configuration as it evolves with flow strength and interparticle attractions. We determine its solution and, from it, compute the microviscosity via statistical mechanics. At equilibrium, attractions produce an accumulation of bath particles near the probe surface. A dipolar disturbance arises under weak forcing, but attractions weaken or reverse this dipole within the attraction range. We find that, as probe forcing grows strong, the familiar boundary-layer and wake structure forms; but attractions shift the detachment angle of the boundary layer downstream around the probe. These structural changes induced by attractions affect rheology: we find that attractive forces quantitatively increase the low-Pe Newtonian viscosity, because external forcing is too weak to detach bath particles from the probe, effectively increasing its size. As forcing grows stronger, the suspension force-thins and the high-Pe Newtonian plateau for freely-draining hard-sphere suspensions is recovered; however, the plateau is delayed owing to increased energy required to separate particle pairs.

Tuesday 4:50 White Ibis MF4

No tracking necessary: Probe microrheology by differential dynamic microscopy

Alexandra V. Bayles, Todd M. Squires, and Matthew E. Helgeson
Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106-5080, United States

Multiple particle tracking (MPT) has become a ubiquitous tool for probe microrheology, in which the mean squared displacement (MSD) of Brownian particles can be used to extract viscoelastic information from complex fluids including colloids, polymers, gels and glasses. However, MPT is not without its drawbacks - it is limited to optically dilute suspensions, to probe particles with known intensity profiles, and by subjective user inputs that must be chosen in an ad hoc manner, resulting in significant information loss. In this work, we report an alternative method for extracting MSDs and linear viscoelastic material functions from passive probe video microscopy using differential dynamic microscopy (DDM). By correlating the intensity fluctuations of a video micrograph in Fourier space, DDM can be used to extract the self-intermediate scattering function (SISF) in systems that would otherwise be difficult to measure using traditional photocorrelation spectroscopy or probe microrheology. We use a simple theoretical framework to show that the SISF obtained by DDM on dilute suspensions can be inverted to obtain the real-space MSD over length and time scales comparable to MPT. As demonstrative examples, we apply DDM to passive microrheology videos of dilute probes in Newtonian fluids, viscoelastic wormlike micelles, and crosslinking polymer gels. Ultimately, we use our results to discuss the relative strengths and weaknesses of DDM compared to MPT. In all cases, however, the MSD data obtained by DDM is nearly indistinguishable from that obtained by MPT, and compares well with bulk rheological data vis-à-vis the generalized Stokes-Einstein relation. Our results show that DDM is a potentially powerful tool to perform probe microrheology experiments in a wider range of fluids than MPT, while circumventing many of its drawbacks.

Tuesday 5:15 White Ibis MF5

Characterization of gelling suspensions by differential dynamic microscopy

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In this work, we study the gelation dynamics of aqueous dispersions of silica nanoparticles. In the presence of salt, these colloidal dispersions form a reversible gel network at equilibrium and can be rejuvenated under shear deformation. We first, characterize the rheology of these materials on the macroscale. Through time-resolved bulk rheometry, we show that these systems are excellent model fluids for evaluation of thixotropic constitutive equations, as their thixotropic time scales can be tuned over a wide dynamic range by adjusting the ionic strength of the matrix fluid., We then use differential dynamic microscopy, which was originally developed by Cerbino and Trappe (2008) for investigating the Brownian dynamics of suspensions at equilibrium to investigate the miscrostructural characteristics of the gelling dispersions. We present the results in terms of the wave vector-dependent characteristic diffusive time scales as the dispersions progressively transitions from a liquid phase to a gel phase. We show that for these gelling fluids, unlike non-gelling suspensions at equilibrium, the dynamics of the aggregates can be dominated by advective motions rather than classical diffusive processes.

Symposium EF
Emulsions, Foams & Interfacial Rheology

Organizers: Cécile Monteux and Sachin Velankar

Tuesday 1:30 Sandhill Crane EF20

Dynamics and mechanics of nanoparticle-surfactant complex coated fluid-fluid interfaces

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Oppositely charged particles and surfactants dispersed in solvents associate strongly to form stable complexes. The interfacial behavior of these complexes is influenced by the adsorbed surfactant and allow the complexes to adsorb to fluid-fluid interfaces. Material remains adsorbed to the interfaces after removal of the bulk dispersion. The dilatational modulus, probed during adsorption and after rinsing of interfaces, is low suggesting a low surface coverage. However, compression of the interface leads to an increase in surface pressure. The critical surface area for the increase in surface pressure is not a function of compression for interfaces in contact with clean water, but is a function of number of compressions for a system in contact with a bulk solution. This suggests that compression/expansion of the interface allows for enhanced transport from the bulk and a mechanism to load the interfaces through processing.

Tuesday 1:55 Sandhill Crane EF21

Nanoparticle-surfactant films: Coalescence and interfacial rheology

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Nanoparticles Surfactants ('NPSs') are fascinating systems consisting of nanoparticles dispersed in one liquid phase, and functionalized surface-active polymers, known as 'ligands' dispersed in a second, immiscible fluid phase. NPSs are ideal candidates to generate fluid bi-continuous structures, also termed 'bijels". Such systems can be achieved by using emulsification processes, mechanical shearing or 3D printing. Subsequent external stimuli can also be used to dynamically reconfigure the spatial distribution of the fluids. Particles and ligands interact at a liquid-liquid (in our case, water-oil) interface to form the NPSs and the assembly of the NPSs results in the formation of a viscoelastic monolayer of NPSs.

In this work, we combine Pendant Drop Tensiometry, Interfacial Shear Rheology and Coalescence measurements to investigate the rheology and stability of the NPSs films, with a goal to understand the macroscopic structures that they stabilize.

We present results demonstrating that the formation of NPSs significantly reduces water-oil interfacial tension. Moreover, interfacial shear rheology indicates that the NPSs rapidly form strongly elastic interfaces. These interfaces were found to be very robust and able to quickly recover their interfacial moduli following large-amplitude shearing. Aging time independence of the film stability and structure upon coalescence are reported, and the films were found to be moderately stable against coalescence.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05-CH11231 within the Adaptive Interfacial Assemblies Towards Structuring Liquids program (KCTR16).

Tuesday 2:20 Sandhill Crane EF22

Interfacial stability and bubble formation with amphiphile – metal oxide particle complexes

Charles Sharkey and Shelley L. Anna
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The fluid-fluid interface of an air bubble or oil droplet can be stabilized through the adsorption of surface active particles. If unconfined, the bubbles and droplets assume spherical shapes to reduce their surface area and thus the interfacial energy. In our previous work we demonstrated that non-spherical stabilized bubbles can be generated by using a confined geometry to direct the adsorption of colloidal silica coated with cetyltrimethylammonium bromide (CTAB) to the interface of a bubble. A variety of capsules were produced with shapes ranging from spherical to nearly cylindrical. To further probe the mechanisms for interfacial adsorption, mechanics, and stability, we investigate the behavior of a variety of surface active particles composed of metal oxide nanoparticles coated with surface modifying amphiphiles. The metal oxide particles include silica, alumina, and magnetite, and amphiphiles include short acids and charged surfactants. Surface modifications of the metal oxide particles by amphiphilic molecules adjust particle wettability and adsorption to the interface. We examine the interfacial mechanics as well as bulk suspension characteristics for several amphiphile and metal oxide pairs, as a function of nanoparticle and amphiphile concentrations, pH, and method of formation of the interface. Bubble stability is assessed by dispensing air bubbles in a concentric co-flow micro-capillary apparatus through a suspension of the amphipile-metal oxide complex particles. These results enable the identification of mechanisms underlying the observed interfacial adsorption and stability.

Tuesday 2:45 Sandhill Crane EF23

Modeling of geopolymer foam swelling to determine optimum rheological properties of a geopolymer paste

Antoine Marchal, Svetlana Petlitckaia, and Arnaud Poulesquen
DEN, MAR, DTCD, SPDE, LP2C, CEA Marcoule, Bagnols sur Cèze 30207, France

In the context of liquid radioactive waste management, the French atomic energy commission develops hierarchical inorganic porous materials used as filters. Geopolymers (aluminosilicate binders) are promising materials to reach this goal since intrinsically, they are mesoporous with high specific surface area allowing to graft specific molecules on the pore wall and it is possible to create connected macroporous network by adding blowing agent into the mixture. This macroporous network has to be optimized for the transport of the contaminated liquid. The creation of the macroporous network consists in mixing hydrogen peroxide in a geopolymer paste composed of sodium hydroxide, metakaolin and surfactant. The dissociation of the hydrogen peroxide in the basic medium is used to generate oxygen. This generation of gas leads to the creation of bubbles and these bubbles are stabilized by the presence of surfactant. The growth of these bubbles results in a swelling of the material until a foamed state. Therefore, the aim of this study is to determine the rheological behavior of the initial geopolymer paste according to the chemical formulation parameters (surfactant nature and content, setting time, amount of blowing agent...) in order to control and optimize the bubble size distribution of the macroporous network. By taking into account all the physical phenomena namely, source term, gas diffusion, Ostwald ripening, nucleation and growth, a model is proposed in order to determine the optimum rheological properties of the starting geopolymer paste. The results show that the bubble size distribution of the macroporous network is highly impacted by the rheology of the initial geopolymer paste.

Tuesday 3:35 Sandhill Crane EF24

Domain and nanoridge growth kinetics in stratifying, micellar foam films

Yiran Zhang and Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, United States

Foam films are freestanding thin liquid films that typically consist of two surfactant-laden surfaces that are ~ 5 nm -- 10 micron apart. Sandwiched between these interfacial layers is a fluid that drains primarily under the influence of viscous and interfacial forces, including disjoining pressure. Interestingly, a layered ordering of micelles inside the foam films (thickness < 100 nm) leads to a stepwise thinning phenomena called stratification, which results in a thickness-dependent variation in reflected light intensity, visualized as progressively darker shades of gray. Thinner, darker domains spontaneously nucleate and grow within foam films. During the initial expansion, a nanoridge forms near the moving front between the expanding thinner domain and the surrounding region, which influences the dynamics of domain growth as well as stratification. Using interferometry digitial imaging optical microscopy (IDIOM) technique we developed recently, we capture, for the first time, the nanoridge shape evolution dynamics in freestanding films with unprecedented high spatial (thickness <1nm) and temporal (<1ms) resolution. Finally we show that the nano ridge evolution, domain growth and stratification dynamics can be described quantitatively using the nonlinear thin film equation amended with supramolecular oscillatory structural forces contributed by the layering of micelles.

Tuesday 4:00 Sandhill Crane EF25

Visualizing the smart foam rheology in crude oil displacement on a pore scale micromodel

Yongchao Zeng, Siyang Xiao, Eric D. Vavra, Maura C. Puerto, George J. Hirasaki, and Sibani Lisa Biswal
Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States

Foam flooding is a process of increasing interest for subsurface applications such as enhanced oil recovery, aquifer remediation, and hydraulic fracturing. In this presentation, we demonstrate a novel method to visualize smart foam rheology in crude oil displacement on a pore-scale micromodel. Specifically, we designed a heterogeneous porous media micro-fluidic device into which foam was injected to study the oil recovery process. We discovered that the responsive rheology of foam mitigates the deleterious effect of media heterogeneity and allows the sweeping fluid to displace lower permeability media than previously possible using a single phase. Foam separated into dry and wet phases in the presence of porous media with layered permeability such that the apparent viscosity in the higher-permeability region is greater than that in the lower-permeability region. Bubbles trapped in the higher-permeability region can divert fluid to displace oil in the lower-permeability region. Thus, the sweep efficiency is greatly improved compared to either gas or water flooding alone.

Tuesday 4:25 Sandhill Crane EF26

Applicability of time-temperature superposition and strain-rate frequency superposition for skin care products

Mariko Hasebe and Hy Bui
Applied Research, L'Oreal, Clark, NJ 07066, United States

We investigate the dynamic behavior of 11 anti-aging skin care products in three different emulsion systems such as Oil/Water, Water/Oil, and Silicone/Water by means of rheology. These emulsions are considered as soft glassy materials and exhibit solid-like behavior in linear viscoelastic regimes with extreme slow dynamics. An attempt to capture the terminal flow of emulsion system, the time-temperature superposition (TTS) was utilized. As a result, we observed that TTS can be applied to O/W and W/Si, while it was totally failed for W/O skin care systems. Additionally, the TTS master curves could not capture the slow structural relaxations of these skin care emulsion. It was reported that the strain-rate frequency superposition (SRFS) could cover both linear and non-linear regime for a wide range of materials including emulsions. This SRFS could detect the low frequency response of structural relaxation. Therefore, we employed the SRFS to investigate these three emulsion systems at the skin temperature (305K). The master curves of strain-rate frequency superposition (SRFS) may be well constructed for the O/W, W/O and W/Si emulsion products. Therefore, the slow relaxation dynamics of 3 type emulsions can be obtained. However, we discovered that the master curves of SRFS deviated from the frequency oscillation curve in the linear viscoelastic regime at 305K for most of studied samples. Only 4 skin care samples containing high molecular weight polymeric emulsifiers satisfied the superposition of SRFS with linear frequency oscillation curves.

Tuesday 4:50 Sandhill Crane EF27

Electrohydrodynamics of leaky dielectric drops in strong electric fields: Simulations and theory

Debasish Das and David Saintillan
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Weakly conducting dielectric liquid drops suspended in another dielectric liquid exhibit a wide range of dynamical behaviors when subject to an applied uniform electric field contingent on field strength and material properties. These phenomena are best described by the much celebrated Maylor-Taylor leaky dielectric model that hypothesizes charge accumulation on the drop-fluid interface and prescribes a balance between charge relaxation, the jump in Ohmic currents and charge convection by the interfacial fluid flow. Most previous numerical simulations based on this model have either neglected interfacial charge convection or restricted themselves to axisymmetric drops. In this work, we develop a three-dimensional boundary element method for the complete leaky dielectric model to systematically study the deformation and dynamics of liquid drops in electric fields. The inclusion of charge convection in our simulation permits us to investigate drops in the Quincke regime, in which experiments have demonstrated symmetry-breaking bifurcations leading to steady electrorotation. Our simulation results show excellent agreement with existing experimental data and small deformation theories.

Tuesday 5:15 Sandhill Crane EF28

Rheology of pollution preventing inks based on a combination of microemulsion and resin

Sudheshna Moka and Ashok N. Bhaskarwar

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The need for printed media, particularly offset printing, continues to grow consistently in spite of the exponential increase in the usage of electronic media. But the very amount of toxic chemicals released to the environment by the printing industry -more than 41 million pounds in the year 1995 in US alone - presses the need for environment friendly inks. Many VOCs and other toxic chemicals are used in the ink formulations and released to the environment during printing as well as during the cleaning of printing presses. Cleaning of inks in the printing presses employs further use organic solvents. The inks being reported use vegetable oils and other non-toxic chemicals but no VOCs. They are also plain water washable, hence completely eliminating pollution. The ink being reported consists of a combination of a water-in-oil microemulsion and a resin. The resin is made from a vegetable oil, pthalic anhydride, and glycerol. Resin improves the binding, rheological, and mechanical properties of the ink. Due to increase in viscosity, the flow of ink is better regulated. Experiments conducted to test the washing of ink showed that it is plain water washable, thus making it an absolutely zero-VOC ink. Stamp pad tests gave satisfactory results. The drying time required by this ink was shorter than that required by microemulsion based ink. Hence, the inks based on the combination of microemulsion and resin are better than only microemulsion inks. The procedures followed for preparation of the resin and microemulsion are described. The characteristic acid number of the resin was found to be 148. The inks were tested for two different compositions based on different weight ratios of the resin and microemulsion. The viscosity, storage and loss moduli of the microemulsion and resin are also compared.

Symposium SM
Polymer Solutions & Melts

Organizers: Carlos R. López-Barrón and Nicolas Alvarez

Tuesday 1:30 Snowy Egret SM20

PLA branching with multi-functional aziridine

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As a renewable, biodegradable and biocompatible polyester, polylactide (PLA) is finding applications in single-use disposable items, biomedical implants and drug delivery systems. However, due to its low melt strength, PLA usually shows unsatisfactory processability in melt processes like film blowing, thermoforming (sheet extrusion), and foaming. One of the most effective ways to increase melt strength is to introduce long chain branching (LCB) structure into the polymer. Strategies have been developed to branch PLA, including copolymerization with multifunctional co-monomers, high-energy irradiation, and reactive melt processing. Among those strategies, reactive melt processing using multifunctional chain extenders is preferred because of its low cost and high productivity. Currently, functional group reactions are mainly based on the reaction between multifunctional epoxide and carboxyl end groups of PLA chains. However, this reaction is slow and requires high temperature, which may result in too much polymer degradation. In this work, we strive to use aziridine, a faster functional group reaction to prepare long chain branched PLA. We compare three approaches: triaziridine plus commercial PLA, triaziridine plus PLA reacted with pyromellitic dianhydride to create multifunctional acid end groups, and multifunctional aziridine chain extender. Branching extent was evaluated with NMR, SEC, light scattering, shear and extensional rheology. Results are compared to the predictions from branching theory.

Tuesday 1:55 Snowy Egret SM21

Tunable rheology of dendronized polymers

Salvatore Costanzo[1], Leon Scherz[2], Thomas Schweizer[2], Martin Kröger[2], George Floudas[3], Dieter A. Schlüter[2], and Dimitris Vlassopoulos[1]

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We present a systematic investigation of the rheology and packing of dendronized polymers (DPs) with varying generation and backbone degree of polymerization. Results reveal unusually long thermal equilibration times due to the tendency of DPs to minimize local density gradients and promote intermolecular correlations, akin to a Velcro type of behavior [1]. Results from X-ray scattering show increased lateral backbone-backbone correlations with a columnar arrangement of backbones and a liquid crystalline underlying order. Linear and nonlinear shear measurements provide further evidence for the Velcro-fastening response, with a rubbery plateau due to intermolecular interactions and FENE-like nonlinear response, both reflecting absence of entanglements [2]. Functionalization of DPs with ureido-pyrimidinone (UPy) groups, which enhance intermolecular bonding and affect the annealing kinetics, provides further support for this picture, as revealed by rheological measurements.

[1] Pasquino et al. Macromolecules 2012, 45, 8813 [2] Costanzo et al. Macromolecules 2016, 49, 7054

Tuesday 2:20 Snowy Egret SM22

Strain hardening in immiscible PE/PP blends via interfacial reinforcement with PE-cb-PP comb-block copolymers

Carlos R. López-Barrón, Andy Tsou, Peijun Jiang, and Donna Crowther

ExxonMobil Chemical Company, Houston, TX, United States

Poly(ethylene-cb-propylene) (P(E-cb-P)), prepared by copolymerization of vinyl terminated atactic polypropylene and ethylene [Tsou et al., Polymer 104, 72-82 (2016)] was used to compatibilize immiscible blends of high density polyethylene (HDPE) and isotactic polypropylene (iPP). Addition of 5 wt% P(E-cb-P) resulted in microdomain size reductions and the concomitant increase in the elastic modulus, as typically observed in immiscible blends compatibilized with linear block copolymers. A more intriguing phenomena is the development of extensional strain hardening by the addition of P(E-cb-P) to the HDPE/iPP blends. This effect is stronger in blends with cocontinuous microstructure (50/50 HDPE/iPP) than in blends with matrix-droplet morphology (75/25 or 25/75 HDPE/iPP). We postulate that the enhancement in strain hardening observed in the compatibilized blends is due to strengthening of the interface via two mechanisms: (1) the increase in the blend interfacial area and (2) entanglement of the PE and PP blocks from P(E-cb-P) within the corresponding homopolymer phases.

Tuesday 2:45 Snowy Egret SM23

Influence of the entanglements on steady elongational viscosity for monodisperse polymer melts

Taisir Shahid[1], Christian Clasen[2], Filip Oosterlinck[3], and Evelyne Van Ruymbeke[1]

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While the linear viscoelastic properties of linear polymers are quite well understood and can be predicted at the quantitative level, many questions still need to be answered in order to understand and model their non-linear extensional rheology. The molecular picture presently used to represent the chain dynamics under extension does not allow capturing the different scaling laws observed experimentally. With the help of a tube model in order to distinguish the different processes contributing to the polymer relaxation, we revisit the extension rheological data provided in literature, and propose a different point of view to interpret them. In particular, we define different levels of stretch that a chain can reach in function of the extensional rate, and their implication in the steady viscosity value. We also discuss the important role played by reptation and contour length fluctuations in the dynamics of a stretched chain. We show that this simple approach well matches the experimental observations, providing new directions to explore, towards the understanding of extensional rheology.

Tuesday 3:35 Snowy Egret SM24

Polydisperse linear entangled polymer model incorporating the binary entanglement pair dynamics for the application to shear modification

David W. Mead[1], Saman Monjezi[2], and Joontaek Park[2]

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The linear rheology of virtually any entangled polymeric system is essentially understood quantitatively. This includes complex backbone architectures such as linear, star, comb and blends of thereof. Despite this satisfactory state of affairs for the linear rheology, the nonlinear rheology of even monodisperse melts of linear polymer is not well understood. This paper focuses on the nonlinear rheology of polydisperse linear polymers using the recent toy molecular model[1]. The polydisperse toy model incorporates entanglement dynamics and a conformation dependent friction coefficient into a molecular framework[1]. We demonstrate that the new polydispersity model adheres to the Cox-Merz rule, Gleissele's mirror relations and Laun's rule. Additionally, we show for the first time a molecular constitutive relation that can simulate and explain the interrupted shear experiments of Tsang & Dealy[2,3]. These experiments and their interpretation are related to "Shear Modification" which we also simulate for polydisperse systems of linear polymers in shear and extension. We are able to capture these phenomena principally by virtue of including entanglement dynamics into the model. Entanglement dynamics are missing from most other molecular models such as the MLD[4] and GLaMM[5] models and their derivatives.

1) Mead, D.W., N. Banerjee and J. Park, J. Rheol. 59, 335-363(2015). 2) Tsang, W.K.M. and J.M. Dealy, J. Non-Newt. Fluid Mech. 9, 203(1981). 3) Dealy, J.M. and W. K.W. Tsang, J. Appl. Poly. Sci. 26, 1149-1158 (1981). 4) Mead, D.W., R.G. Larson and M. Doi, Macromolecules 31, 7895-7914 (1998). 5) Graham, R.S., A.E. Likhtman, T.C.B. McLeish and S.T. Milner, J. Rheol. 47, 1171-1200 (2003).

Tuesday 4:00 Snowy Egret SM25

Nonequilibrium molecular dynamics simulations of entangled polymer melts and solutions undergoing planar elongational flows

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Tube based models predict that concentrated polymer solutions behave roughly the same as entangled polymer melts, if they have the same number of entanglements and if stress, strain rate and time are made dimensionless appropriately. But there are a lot of experimental works that show entangled polymer melts and solutions exhibit different behaviors when they are subject to extensional flows at high extension rates. Specifically

there is an upturn in extensional viscosity of polymer solutions at extension rates higher than the inverse of the Rouse time which has not been observed in polymer melts. Recent experiments of Wingstrand *et al.*[1], however, have demonstrated that using oligomers as solvent, polymer solutions could behave in a similar fashion as melts.

In this work we performed nonequilibrium molecular dynamics (NEMD) simulations of entangled $C_{700}H_{1402}$ and $C_{1000}H_{2002}$ linear polyethylene melts subject to planer elongational flows. We also simulated concentrated solutions of $C_{1000}H_{2002}$ in $C_{16}H_{32}$ as an oligomeric solvent with the same monomeric units in order to compare the behavior of polymer melts and solutions with roughly the same number of entanglements. Simulation results show that polymer solutions and melts exhibit roughly the same behavior at high extension rates. Specifically, similar to the melt, no upturn was observed in primary extensional viscosity of the solution, consistent with Wingstrand *et al*. experiments. Other system properties including chain orientation, chain stretch, and entanglement network properties and their potential connection to this finding will be discussed in this presentation. Preliminary results of extensional viscosity of concentrated solutions in small solvent molecules with various molecular architectures such as benzene will also be shown.

[1] Wingstrand, S.L., N.J. Alvarez, Q. Huang, O. Hassager, Phys. Rev. Lett. **115**, 078302 (2015).

Tuesday 4:25 Snowy Egret SM26

Affine vs. non-affine deformation in fast flow of entangled polymers: New insight from small-angle neutron scattering

Christopher N. Lam[1], Zhe Wang[1], Weiyu Wang[1], Jianning Liu[2], Kunlun Hong[1], Lionel Porcar[3], Wei-Ren Chen[1], and Yangyang Wang[1]
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[3]Large Scale Structures, Institut Laue-Langevin, Grenoble, France

During the last several decades, the study of the dynamics of entangled polymers has been focusing on the application of the tube model. Despite the tremendous success of this theoretical approach, a key hypothesis of the tube model concerning nonlinear viscoelasticity has not been fully validated by experiments. In their seminal 1978 paper, Doi and Edwards proposed a unique elastic deformation mechanism to account for the nonlinear rheological behavior of entangled polymers. This mechanism asserts that the external deformation acts on the tube, instead of the polymer chain. A direct consequence of this assumption is that the evolution of chain conformation of an entangled polymer in flow is *non-affine* beyond the Rouse time, with entanglement strands being oriented but hardly stretched. This hypothesis, being a keystone of the tube model, stands in stark contrast to the elastic deformation mechanisms of other alternative theoretical approaches where the *affine* deformation mechanism is adopted. Here we will describe our recent effort to elucidate the molecular deformation mechanism of entangled polymers by using small-angle neutron scattering (SANS) experiments. A new approach, based on spherical harmonic expansion analysis, has been developed to decompose the 2D anisotropic scattering pattern. This development makes it possible to unambiguously examine the deformation mechanism predicted by statistical and molecular models of entangled polymers at the microscopic level. Our SANS measurements on uniaxially stretched polystyrene melts show that neither the tube model nor the affine model could provide a satisfactory description of the Q-dependent spherical harmonic expansion coefficients determined from experiments. Implications from these new experiments and analyses will be discussed in this talk.

Tuesday 4:50 Snowy Egret SM27

Nonlinear stress relaxation of miscible polyisoprene/poly(p-tert-butyl styrene) blends in pseudo-monodisperse state

Yumi Matsumiya and Hiroshi Watanabe
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For miscible pair of polyisoprene (PI) and poly(*p-tert*-butyl styrene) (PtBS), the component molecular weights, composition, and temperature were tuned to prepare PI/PtBS blends in the *pseudo-monodisperse* state where the component PI and PtBS chains had the same terminal relaxation time. These pseudo-monodisperse blends had the linear viscoelastic moduli indistinguishable from the moduli of entangled monodisperse bulk homopolymers of particular molecular weights, and satisfied the time-strain separability in their nonlinear stress relaxation behavior under large step strains. The damping function h(?) of those blends was close to h_{DE}(????) calculated from the Doi-Edwards model and classified to be the type-A damping function, even though the major component (PI) in the blends had a large entanglement number per chain (N = 50). Highly entangled monodisperse bulk homopolymers having similarly large N are known to exhibit the type-C damping characterized by h(?) << h_{DE}(?), and this damping behavior was indeed confirmed for high-M bulk PI utilized as the blend component. Thus, the nonlinear damping behavior was different for the pseudo-monodisperse PI/PtBS blends and high-M bulk PI, despite the similarity in the entanglement number N for PI therein. This difference was discussed within the molecular scenario of Marrucci and Grizzuti in relation to the topological hindrance for PI segments due to PtBS segments having a much larger friction. This hindrance retarded the Rouse equilibration of the PI backbone in the blends, which possibly provided the highly entangled PI with a slow contour length fluctuation mechanism that competed with reptation. Such a competing mechanism smears the elastic instability underlying the type-C damping as suggested from the Marrucci-Grizzuti scenario, which possibly allowed the pseudo-monodisperse blends containing highly entangled PI to exhibit the type-A damping.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Audubon DEF PL3

Spontaneous flows in soft active matter

Zvonimir Dogic
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The laws of equilibrium statistical mechanics impose severe constraints on the properties of conventional materials assembled from inanimate building blocks. Consequently, such materials cannot exhibit autonomous motion or perform macroscopic work. Inspired by the remarkable properties of the biological cytoskeleton which is driven away from equilibrium by a conserved set of protein nanomachines, our goal is to develop soft active materials assembled from the bottom-up, using animate energy-consuming building blocks such as molecular motors and microtubule filaments. Released from the constraints of the equilibrium, these internally driven gels, liquid crystals and emulsions are able to change-shape, crawl, flow, swim, and exert forces on their boundaries to produce macroscopic work. In particular, we describe properties of an active isotropic fluid that upon confinement, transitions from a quiescent to a spontaneously flowing state. We characterize the properties of the emergent self-organized flows as well as how the transition to a flowing state depends on the properties of the confining geometry. We also describe the unique dynamics of active nematic liquid crystals, which exhibits complex streaming flows that are powered by continuous creation and annihilation of oppositely charged disclination defects. Our results illustrate how active matter can serve as a platform for testing theoretical models of non-equilibrium statistical mechanics, developing a new class of soft machines and potentially even shedding light on self-organization processes occurring in living cells.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Wednesday 10:00 Audubon B SC29

Pairwise interparticule interactions determine discontinuous shear thickening transition in non-coloidal suspensions

Jean Comtet[1], Guillaume Chatté[2], Antoine Niguès[1], Lydéric Bocquet[1], Alessandro Siria[1], and Annie Colin[2]
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The process by which suspensions go through an increase in viscosity at a critical shear stress is known as shear thickening. Although well-characterized on the macroscale, the microscopic mechanisms at play in this transition are still poorly understood. Using a quartz-tuning fork based Atomic Force Microscope, we characterize the pairwise force profile between two approaching PVC beads in solvent. Our set-up allows us to disentangle frictional and conservative interactions for both normal and tangential (shear-like) relative motion of the beads. We see a clear transition from (1) a low-friction regime, where the two beads support a finite normal load due to the entropic repulsion of the polymer brush while interacting purely hydrodynamically to (2) a high-friction regime characterized by hard repulsive contact between the beads and the presence of sliding friction. Critically, by continuously changing solvent properties, we show that the normal stress needed to enter the frictionnal regime at the nanoscale matches the critical stress at which shear thickening occurs in macroscopic suspensions. Our experiments thus bridge nano and macroscales, and provide long-time needed characterizations of the role of frictionnal forces in shear thickening.

Wednesday 10:25 Audubon B SC30

A rheological signature of frictional interactions in shear thickening colloids

John R. Royer[1], Daniel Blair[2], and Steve Hudson[3]
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Colloidal shear thickening presents a significant challenge because the macroscopic rheology becomes increasingly controlled by the microscopic details of short ranged particle interactions in the shear thickening regime. Our measurements here of the first normal stress difference over a wide range of particle volume fractions elucidate the relative contributions from hydrodynamic lubrication and frictional contact forces, which have been debated. At moderate volume fractions we find $N1 < 0$, consistent with hydrodynamic models; however, at higher volume fractions and shear stresses these models break down and we instead observe dilation ($N1 > 0$), indicating frictional contact networks. Remarkably, there is no signature of this transition in the viscosity; instead, this change in the sign of N1 occurs while the shear thickening remains continuous. We therefore introduce a simple model that combines these frictional and hydrodynamic contributions and accurately fits the measured viscosity over a wide range of particle volume fractions and shear stress.

Wednesday 10:50 Audubon B SC31

Tunable shear thickening: From understanding suspension thickening to controlling viscosity on the fly

Neil Lin[1], Chris Ness[2], Jin Sun[2], Ben Guy[2], Michiel Hermes[2], Wilson Poon[2], Mike Cates[3], and Itai Cohen[1]
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Whether contact forces play a role in shear thickening of colloidal systems where hydrodynamic contributions are thought to dominate remains highly controversial. By performing shear reversal experiments on silica and latex colloidal particles, we directly measure the hydrodynamic and contact force contributions to the suspension viscosity. We find that contact forces are not only present, but dominate the shear thickening response. More importantly, this finding directly suggests a strategy for active controlling the thickening viscosities of dense suspensions. We demonstrate that by strategic imposition of a high-frequency and low-amplitude shear perturbation orthogonal to the primary shearing flow, we can largely eradicate thickening. The orthogonal shear effectively becomes a regulator for controlling thickening in the suspension, allowing the viscosity to be reduced by up to two decades on demand.

Wednesday 11:15 Audubon B SC32

Towards a predictive description of shear thickening suspensions

Abhinendra Singh, Jeffrey F. Morris, and Morton M. Denn
Benjamin Levich Institute, City College of New York, CUNY, New York, NY, United States

The mechanism of shear thickening in dense suspensions has recently been shown to be consistent with a transition from lubricated rheology, where close interactions between suspended particles take place through a thin liquid film, to a frictional rheology, wherein particles experience frictional contacts. Particle simulations that led to this concept have been successful in quantitatively reproducing the non-Newtonian shear behavior of certain thickening suspensions, including discontinuous shear thickening. We still do not have a macroscopic continuum description of these suspensions that would enable prediction of the flow behavior under complex flow conditions, however. As a step towards developing a predictive theory we explore the effect of particle and fluid properties on the flow behavior using a mixing rule for lubricated and frictional rheologies that is applicable to both shear and normal stresses. We develop the full flow "phase" diagram for shearing motions and explore relations between the macroscopic flow behavior and such microscopic properties as the inter-particle force distribution, coordination number, and anisotropy in both force and contact networks.

Wednesday 11:40 Audubon B SC33

Rheological characterization of colloidal silica suspensions for 3D printing of optical glass monoliths

Nikola Dudukovic[1], Du Nguyen[1], Timothy Yee[1], Joel Destino[1], Cameron Meyers[2], Eric Duoss[1], and Rebecca Dylla-Spears[1]
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Gradient index (GRIN) optics, which rely on changes in material refractive index rather than optical figure to achieve a desired optical effect, have the potential to reduce optical finishing costs, as well as to reduce the number of optics required in a system. Currently, GRIN glass optics are produced by imparting compositional changes by diffusion, which in practice limits both the achievable optic size and the gradient profile. We instead employ a direct ink write (DIW) additive manufacturing process to 3D print monolithic structures of gradient composition using shear thinning colloidal suspensions (inks) of silica or titania-doped silica nanoparticles. The desired compositional gradient is obtained by inline mixing of two inks at appropriate ratios right before extrusion through a nozzle. The printed part is then dried and sintered to a fully dense glass. This approach offers advantages over conventional GRIN processing, such as the ability to achieve larger sizes in less time and to have precise compositional control of non-monotonic gradients. Formulation of inks for the inline mixing DIW process poses several main rheological challenges in the production of low-defect optical monoliths. (1) The viscoelastic properties of the doped and un-doped inks must be well matched to prevent variability during the printing process. (2) The elastic recovery upon extrusion must be controlled to obtain the desired leveling properties of the ink, such that the fabricated monolith maintains the desired form, while eliminating print line porosity. These aspects are critical for the control of the refractive index gradient and to attaining sufficient optical quality of the final product. We present approaches to quantify the rheological behavior of the inks during the DIW process and compare it to rotational and capillary rheology and tensiometry experiments.

*This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. *LLNL-ABS-705259

Symposium NF
Non-Newtonian Fluid Mechanics & Instabilities

Organizers: Sandra Lerouge and Becca Thomases

Wednesday 10:00 Audubon DEF NF6

Flow of viscoelastic fluids through a sharp microfluidic bend: Role of wormlike micelles structure

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Wormlike micellar solutions, prevalent in consumer products, drug delivery, and drag-reducing agents, exhibit interesting fluid dynamics and rheological behavior. We examine the flow and instabilities of viscoelastic fluids - a semi-dilute aqueous solution of polyethylene oxide and two wormlike micellar solutions of cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal) - through a microfluidic 90° bend, in which shear deformation and streamline curvature dominate. Similar to results reported by Gulati *et al.* [*Phys. Rev. E*, **78**, 036314,2008 and *J. Rheol.*, **54**(2), 375-392, 2010] for PEO solutions, we report a critical Weissenberg (Wi) number for the onset of lip vortex formation upstream of the corner. However, the decreased aspect ratio (channel height to width) results in a slightly higher critical Wi and a vortex that grows more slowly. We consider wormlike micellar solutions of two salt to surfactant concentration ratios, R=0.52 and R=0.75. At R=0.52, wormlike micelles are linear and exhibit strong viscoelastic behavior, but at R=0.75, wormlike micelles become branched and exhibit shear banding behavior. Microfluidic experiments on the R=0.52 solution reveal two unstable regimes. The first regime, at Wi=6, is characterized by the formation of a stationary lip vortex upstream of the bend; in the second regime, at Wi=20, the vortex oscillates and periodically changes size. The R=0.75 solution also exhibits two regimes. The first transition at Wi=4 is characterized by the intermittent appearance of lip and far outside corner vortices. Increasing the flow rate to Wi>160 results in a transition to a second unstable regime, where there is only a lip vortex that changes size periodically. The difference in flow transitions in PEO and wormlike micelles presumably arises from the additional contribution of wormlike micelle breakage and reformation under shear. Flow transitions in wormlike micelles are also significantly affected by chain branching.

Wednesday 10:25 Audubon DEF NF7

Viscoelastic fluid-structure interactions between a non-Newtonian fluid flow and flexible circular cylinder

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When a flexibly-mounted bluff body (such as a circular cylinder) is placed in Newtonian flows, the shedding of separated vortices at high Reynolds number can drive the motion of the structure. This phenomenon is known as Vortex-Induced Vibration (VIV) and has been studied extensively. If the same flexibly-mounted circular cylinder is placed in non-Newtonian flows, however, the structure's response is unknown. Unlike Newtonian fluids, the flow of viscoelastic fluids can become unstable at infinitesimal Reynolds numbers. For the flow of wormlike micelle solutions around a fixed circular cylinder, purely elastic flow instabilities have been observed. When these elastic flow instabilities occur in the vicinity of a flexible structure, the fluctuating fluid forces exerted on the structure grow large enough to cause a structural instability which in turn feeds back into the fluid resulting in a flow instability. We present an investigation into this type of coupled fluid-structure instabilities by subjecting a flexible circular cylinder to a high Weissenberg number flow of viscoelastic wormlike micelle solution. The static and dynamic responses of the flexible cylinder will be presented for a range of flow velocities and fluid rheology, along with measurements of velocity profiles and flow-induced birefringence, in order to quantify the time variation of the flow field and the state of stress in the fluid.

Wednesday 10:50 Audubon DEF NF8

Viscoelastic micellar material formation at the interface of immiscible fluids

Zahra Niroobakhsh[1] and Andrew Belmonte[2]
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A reactive gel-like micellar material is observed in an immiscible system of aqueous surfactant (cetylpyridinium chloride) solution and a particular oil, oleic acid. What distinguishes this system in the context of fluid flow is the presence of surface tension and growing micellar material together at the interface. We investigate the instabilities caused by this coupling in two fluid systems: a falling liquid column and a Hele-Shaw cell. In the liquid column experiment, we observe under different conditions the pinch-off of droplets, immobile and mobile cylindrical surfaces, buckling and wrinkling of these surfaces, as well as a breakout instability. In the Hele-Shaw experiment, we observe strikingly different patterns compared to classic Saffman-Taylor instability, as a function of concentration, surfactant injection rate, and type of oil. To characterize the viscoelasticity of the micellar interface, we measure its dynamic rheological properties using a double-wall ring interfacial rheometer.

Wednesday 11:15 Audubon DEF NF9

Growth of viscoelastic instabilities around a linear cylinder array

Xueda Shi and Gordon F. Christopher
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Using microfluidic channels, we have previously characterized new types of instabilities that occur at moderate viscoelastic Mach numbers around individual cylinders in rectangular channels. In that work, we hypothesized that the observed downstream and upstream instabilities were not independent phenomenon, but rather that the upstream instability was the growth in amplitude of the initial downstream disturbance. In this work, a linear array of cylinders in a rectangular microchannel is used to examine the development of the previously observed moderate viscoelastic Mach number instabilities and determine the mechanism causing observed behaviors.

Using streakline imaging and pressure drop measurements, instabilities in these channels are shown to start on the downstream face of a cylinder and grow upstream, eventually creating a vortex of slow moving fluid in front of the most upstream cylinder. It is shown that the downstream and upstream flow patterns all emerge due to the same mechanism related to the creation of secondary flow due to elastic waves. We note that as the instability moves upstream a number of interesting flow patterns can be observed in the space between adjacent cylinders. Furthermore, pressure drop measurements show that the relative importance of this phenomenon in terms of the excess pressure drop are mitigated for higher elasticity fluids. These results have importance in the role of elastic fluids in oil displacement form porous media during enhanced oil recovery.

Wednesday 11:40 Audubon DEF NF10

Elastic turbulence in channel flows at low Reynolds number

Boyang Qin and Paulo E. Arratia
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In this talk, the flow of a viscoelastic fluid is experimentally investigated using particle velocimetry methods in a micro-fluidic device. The device is a long and straight micro-channel that is 100- μm wide and deep; the channel has a short 3-mm region that contains a linear array of cylinders (perturbation region) followed by a 3-cm long and straight region (parallel shear region). We find that, both in the wake of the cylinders and far downstream in the parallel shear region, the flow is excited over a broad range of frequencies and wavelengths. These velocity fluctuations are consistent with the main features that characterize elastic turbulence at low Re. However, the decay of the initial elastic turbulence around the cylinders is followed by a growth downstream in the straight region. The emergence of distinct flow characteristics both in time and space suggests a new type of elastic turbulence, markedly different from that near the curved cylinders.

Symposium MF
Micro/Nano Fluidics and Probe Rheology

Organizers: Monica Oliveira and Gordon Christopher

Wednesday 10:00 White Ibis MF6

Microrheological characterization of covalently adaptable hydrogels pushed out of equilibrium

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Covalently adaptable hydrogels (CAHs) mimic aspects of the native extracellular matrix enabling cells to shear, degrade and apply traction similar to in vivo motility. We use multiple particle tracking to measure dynamic scaffold material properties during CAH degradation and the subsequent bond breakage and reformation as equilibrium is shifted by changes in the incubation pH. MPT measures the movement of particles embedded in the CAH and the resulting mean-squared displacement describes the network state and connectivity. The CAH is formed by self-assembly of 8-arm polyethylene glycol(PEG)-aldehyde and 8-arm PEG-hydrazine to form covalently adaptable hydrazone bonds. CAHs are made at both acidic (pH 4.3) and physiological (pH 7.4) pHs and incubated in a sink of buffer at a different pH or held pH 4.3. When the CAH is incubated the scaffolds are pushed out of equilibrium and hydrazone bonds begin to break, rearrange and reform. For a scaffold made at pH of 7.4 or 4.3 and incubated at pH 4.3, we measure degradation of the scaffold over several hours. As the degradation of the material precedes bonds reform several hours after the scaffold is pushed out of equilibrium, from a sol back to a gel. A scaffold that was polymerized at pH 4.3 and incubated at pH 7.4 has similar behavior but on a longer time scale. Degradation of this scaffold takes weeks and bonds within the material break and reform over a cycle of approximately a day, the material oscillates between a sol and loosely, cross-linked gel. Time-cure superposition is used to determine the critical time, tc, and critical relaxation exponent, n, during degradation. CAH degradation is also modeled using second-order reaction kinetics, to account for the initial degradation, rearrangement and reformation of hydrazone bonds, and the final hydrolytic degradation is modeled using first-order kinetics. This unique rheological behavior can be exploited to advance the use of these materials within the body, specifically, for sustained release of active molecules.

Wednesday 10:25 White Ibis MF7

Probing the structure of mucin gels using microscale and macroscale rheometry

Caroline E. Wagner[1], Bradley S. Turner[2], Gareth H. McKinley[1], and Katharina Ribbeck[2]
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Understanding the structural features of mucus, such as the average mesh size between interaction sites on its primary solid component, the large glycoprotein mucin, as well as the nature of these interactions is essential for understanding how mucus achieves its impressive barrier properties and how pathological cases arise. While the details of these features remain largely unresolved, it is known that the range of mechanical properties that mucus exhibits throughout the body depend on its intended physiological function, and arise because the local environment can mediate the strengths of a wide range crosslinking interactions which form the mucin network. In the present work we use a combination of macrorheological measurements and single particle tracking (SPT) probes in order to interrogate the details of the different association mechanisms from observed changes in the rheological response of a model system of 1wt% reconstituted MUC5AC mucins under various environmental conditions. Consistent with previous studies, our macrorheological tests show that the linear viscoelastic moduli of these mucin gels increase significantly as the pH is lowered from neutral to acidic. By studying the trajectories of individual particles of various sizes embedded in these gels, including the distributions of their step sizes and waiting times between steps, a clearer picture of the microstructural modifications leading to these bulk changes in mechanical properties can be gleaned. We show that even though traditional observations of ensemble-averaged microscopic thermal fluctuations in mucin gels are generally not predictive of their macroscopic linear viscoelastic response, detailed analysis of the non-Gaussian and non-Brownian nature of microparticle trajectories yields new insight into the structural and rheological details of mucin hydrogels.

Wednesday 10:50 White Ibis MF8

Serpentine channels: Micro-rheometers for fluid relaxation times of complex fluids

Anke Lindner[1], Laura Casanellas[2], Rob Poole[3], Sandra Lerouge[4], Manuel Alves[5], and Christian Wagner[6]
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We propose a novel device capable of measuring relaxation times of viscoelastic fluids as small as 1 ms. In contrast to most rheometers, which by their very nature are concerned with producing viscometric or nearly-viscometric flows, here we make use of an elastic instability that occurs in the flow of viscoelastic fluids with curved streamlines. To calibrate the rheometer we combine simple scaling arguments with relaxation times obtained from first normal-stress difference data measured in a classical shear rheometer. As an additional check we also compare these relaxation times to those obtained from Zimm theory and good agreement is observed. Once calibrated, we show how the serpentine rheometer can be used to access smaller polymer concentrations and lower solvent viscosities where classical measurements become difficult or impossible to use due to inertial and/or resolution limitations. The applicability of this device is discussed for polymer solutions with different levels of shear thinning.

Wednesday 11:15 White Ibis MF9

The role of sample rheology on matrix effect in microfluidic immunoassays

Ana I. Barbosa[1] and Nuno M. Reis[2]
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One of the biggest challenges to the development of affordable point-of-care (POC) diagnostic tests in the interference of biological sample components found in complex biological samples in the analytical sensitivity and performance of the test. POC diagnostics market is growing at double figures, and estimated as worth in excess of US$13billion per year, this growth is being driven by a shift from centralized lab diagnostics to near the patient. This has been triggered by the ability of miniaturized POC tests to deliver fast results. Sample preparation increases the complexity of the test, compromising the affordability and portability desirable for POC test. Our research group has recently laid a major step stone towards assays without sample preparation, by reporting for the first time microfluidic assays from whole blood (Barbosa et al, Lab Chip, 2014, 14, 2918). In order to understand the main parameters governing the so called "matrix effect", we have studied the role of sample rheology on performance and antigen-antibody equilibrium in a sandwich immunoassay in our novel fluoropolymer microfluidic devices containing 10 parallel microcapillaries with internal diameters between 128 to 378 µm. By spiking samples of increasing bovine serum albumin concentration with fixed amounts of antigen, we found that sample viscosity acted by adding a mass transfer resistance to antigen diffusion in the whole range of viscosities tested (1.0-3.5 Pa.s). Viscosity affected assay signal by delaying antibody-antigen equilibrium, resulting in longer incubation times with biological samples compared to assays in buffer. Surprisingly, the amount of albumin required to match the matrix interference typically found in undiluted human serum yielded a solution viscosity of 3.5 Pa.s against 1.6 Pa.s for human serum, suggesting sample viscosity is relevant yet cannot explain the observed matrix interference on its own. This is a major step in identifying parameters that control the matrix effect.

Wednesday 11:40 White Ibis MF10

Steady-state shape and moduli determination for an elastic capsule in a microfluidic T-junction

Abdollah Koolivand and Panagiotis Dimitrakopoulos
Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111, United States

The study of the motion and deformation of capsules and biological cells in microfluidic channels is motivated by a wide range of applications including drug delivery, cell sorting and cell characterization devices of microparticles and microcapsules with desirable properties, determination of membrane properties and of course its similarity to blood flow in vascular capillaries.

The determination of the elastic properties of the membrane of artificial capsules (i.e. the shear modulus Gs and area-dilatation modulus Ga) is essential for the better design of the various devices that are utilized. For this, several techniques have been developed including static compression and shear, extensional or centrifugal flow fields for milli-capsules as well as micropipette and atomic force microscope measurements, and flow in microfluidic channels and tubes for micro-capsules. We emphasize that the mechanical determination of membranes is a challenging task (especially for micro-capsules), while two experimental techniques are commonly required to account for the combined effects of the shear and area-dilatation moduli on the membrane deformation.

In this work, we investigate computationally the dynamics of a strain-hardening elastic capsule in a microfluidic T-junction. To achieve this, we utilize our interfacial spectral boundary element method for membranes which has been employed for the study of the capsule dynamics in various microfluidic devices. Our interest is concentrated on the effects of the flow rate on the capsule deformation and dimensions for different membrane hardness. We also develop a novel methodology to determine accurately and efficiently the shear modulus and area-dilatation modulus of the elastic membrane, independently of the fluids viscosity ratio and the membrane viscosity.

Symposium SM
Polymer Solutions & Melts

Organizers: Carlos R. López-Barrón and Nicolas Alvarez

Wednesday 10:00 Snowy Egret SM28

Linear rheology of entangled bulk polymers functionalized with metal-ligand interactions

Flanco Zhuge, Jérémy Brassinne, Charles-André Fustin, Jean-François Gohy, and Evelyne Van Ruymbeke
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The advent of supramolecular chemistry in the last decades has provided powerful tools to form "smart" materials with the ability of molecules to self-assemble. They rely on intelligent macromolecules or (supra-)molecular motifs to adapt their structure and properties towards external triggers.[1] However most of these self-assembled materials are studied in solution because commonly used polymers have a glass transition above the room temperature. But if the material is a fluid itself, i.e. flexible polymers with a glass transition below the ambient temperature, they can be investigated in bulk as soft materials.[2] Reversible polymeric networks obtained by functionalizing flexible polymer chains with associating units constitutes an interesting and useful class of soft material because of the richness in their rheological behavior such as stimuli-responsiveness, adaptability or healing feature.[3]

Here, we study the linear viscoelastic properties of a series of low dispersity poly (n-butyl acrylate) chains functionalized with 2,2';6',2"-terpyridine, able to self-associate through metal-ligand coordination. Depending on the topology and functionality of the chains, the polymers with low dispersity (Đ < 1.3) self-assemble into metallo-supramolecular bulk structures once metal ions are added. Upon self-assembly, linear building blocks form longer entangled chains while four-arm stars can form entangled networks. The properties of the obtained materials can be finely tuned depending on the length of the polymer chains and the type of metal. In this respect, a control is gained over the dynamics of this class of metallo-supramolecular assemblies. Hence, they are extremely interesting for specific applications such as adhesives or mechano-sensors.

1. *Gels* **2015**, 1, 235. *Macromolecules* **2014**, 47, 4514. 2. *Macromolecules* **2015**, 48, 7320. *Polymer* **2015**, 69, 233.

Wednesday 10:25 Snowy Egret SM29

Design and intuition with continuous spectra

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Design is often based on intuition. How can we improve our intuition so that we can better engineer and design with viscoelastic polymeric materials? Intuition here is challenging because even linear viscoelastic properties are function-valued, rather than constants as they are for more simple fluids and solids. Here, we consider the various representations of linear viscoelasticity (oscillatory, step, spectra) for (i) tactile intuition which is known to improve design quality, and (ii) design-appropriate predictive modeling to enable optimization and inverse problem solutions. We propose that continuous spectra, including relaxation spectra $H(\tau)$ and retardation spectra $L(\tau)$, may prove to be a key link between viscoelastic material behavior and our intuition to design these materials. Simple parameterizations, such as log-normal distributions, provide a particularly low-dimensional description of the high-dimensional viscoelastic behavior. Moreover, the concept of relaxation spectra connects directly to microstructural design in systems of polymer melts and solutions. This will allow for greater ease when understanding these systems and likewise for tuning system parameters for use-specific design.

Wednesday 10:50 Snowy Egret SM30

Dynamics of polyelectrolytes in shear and extensional flows

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Biological macromolecules like proteins, DNA and polysaccharides, as well as many industrial polymers, are classified together as polyelectrolytes as in solution, the repeat units in their backbone are decorated with disassociated charge-bearing ionic groups, surrounded by counter-ions. The shear and extensional rheology response of the charged macromolecular solutions are not as well understood as that of their uncharged counterparts. We describe a comprehensive set of study of polyelectrolyte dynamics in shear, extensional and interfacial flows using two model systems: sodium (polystyrene sulfonate) and poly(acrylic acid) that have diverse applications including energy storage, flocculants in waste water treatment, dispersants in home-care and food products, and rheology modifiers in inks and coatings. We characterize shear rheology response in terms of how intrinsic viscosity, relaxation time, zero shear viscosity and elastic modulus vary with change in polyelectrolyte and salt concentration. The extensional rheology response, and the influence of charge and concentration of polyelectrolytes on their pinch-off dynamics, is characterized using dripping-onto-substrate (DoS) rheometry technique.

Wednesday 11:15 Snowy Egret SM31

Continuous relaxation spectra for MAOS characterization

Luca Martinetti[1], Piyush K. Singh[1], Johannes M. Soulages[2], and Randy H. Ewoldt[1]
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We show how any analytical prediction for (strain-controlled) medium-amplitude oscillatory shear (MAOS) can be coupled with a continuous distribution of relaxation times. This applies to models that are not inherently time-strain separable, and is important for improved certainty when inferring molecular information from these bulk rheological measurements.

Here, we demonstrate inference using continuous spectrum MAOS with aqueous poly(vinyl alcohol) (PVA) transiently-crosslinked by sodium tetraborate (Borax) [Bharadwaj et al.]*. To gain physical insight into network microstructure and modeling, the frequency-dependence and sign changes of all four MAOS measures ([e1](ω), [e3](ω), [v1](ω), [v3](ω)) are considered. The mesoscopic network model contains a single nonlinear parameter (χ) for elastic strain-stiffening, hypothesized to arise from a combination of both (i) finite chain extensibility, and (ii) stretch-induced crosslink formation. The use of a continuous relaxation spectrum derived from the log-normal distribution dramatically improves the SAOS fit, but surprisingly makes the MAOS fit worse if the nonlinear parameter is assumed constant for all relaxation times. Qualitative and quantitative agreement with the asymptotically-nonlinear signature is achieved with the simple use of a step-function-type distribution for the nonlinear parameter χ that excludes the longer relaxation modes. Our results suggest that MAOS is more sensitive than SAOS to the longer relaxation times.

While the work here is focused on a specific polymeric system, it represents the broad potential contribution of continuous relaxation spectra and asymptotic, leading-order nonlinearities to enable structure-rheology insight, and model selection for soft materials in general.

* Bharadwaj N. A., Schweizer K. S., Ewoldt R. H., "A strain stiffening theory for transient polymer networks under asymptotically-nonlinear oscillatory shear", submitted (2016).

Wednesday 11:40 Snowy Egret SM32

Predicting flow properties of polymer melts via polymerization kinetic modeling and computational rheology

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The processability of plastic - how hard it is to move the molten polymer through extruders and dies and then compress or stretch it into its final form - strongly depends on the molecular weight and architecture of its molecular constituents. Industrially produced polymers generally present broad distributions of branched and linear molecules that are responsible for their unique flow properties. For instance, shear thinning is used to facilitate extrusion and strain hardening to improve bubble stability during film blowing operations.

Recent theoretical advances in computational rheology have enabled the prediction of polymer melt flow performance from molecular structure, leading to the Branch-on-Branch (BoB) model. In addition, the polymer molecular architecture can be predicted using polymerization kinetic modeling.

In this work, we demonstrate a modeling platform combining polymerization and computational rheology models for polyethylene and polypropylene samples. In particular, we relate the resin flow performance to the polymer branching distribution.

Wednesday Afternoon

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Wednesday 1:30 Audubon B SC34

Turning a microscope into a rheometer

Neil Lin[1], Matthew Bierbaum[1], Peter Schall[2], James Sethna[1], and Itai Cohen[1]
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I will introduce a new method called SALSA (Stress Assessment from Local Structure Anisotropy) to determine the stresses in hard-sphere colloidal suspensions at the single particle scale. In such systems, the force with which particles collide is related to the thermal energy. Therefore, using a time series of featured particle positions, we can deduce the thermal collision probability, and compute the stress arising from these collisions. Thus, SALSA can effectively transform your micorscope into a local rheometer measuring the 3D stress distribution in your suspensions. To illustrate the usefulness of SALSA, I will present some scientific applications ranging from visualizing the nonlinear stresses near crystalline defects to quantifying the stress heterogeneities in glasses.

Wednesday 1:55 Audubon B SC35

Microrheology as a powerful tool to monitor particulation of bovine serum albumin

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The applicability of Microrheology technique as part of dynamic light scattering was used to investigate rheological changes and aggregation during the nanoparticulation of dilute bovine serum albumin (BSA) prepared using the desolvation method with ethanol as a desolvating agent. Carboxylate melamine particles (0.650 µm) were used as a tracer because of compatibility of the tracer with BSA molecules. The results showed that storage modulus (G') increased when the ethanol to BSA solution volume ratio increased to 2 and higher. This suggests that the nucleation and particulation of BSA occurred when the ethanol concentration was 63% and higher. The maximum storage modulus was achieved in 80% ethanol solution. We conclude that Microrheology offers useful and predictive insights to determine the mechanism of particulation of colloidal biopolymers.

Wednesday 2:20 Audubon B SC36

Modelling the flow of suspensions with large inclusions, from one millimeter to one centimeter in size, in complex geometries: Application to the development of Standard Reference Materials for calibration of rheometers

Nicos S. Martys[1], Chiara F. Ferraris[1], William L. George[1], Steven G. Satterfield[1], and Didier Lootens[2]
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In this presentation I will discuss the development of standard reference materials (SRMs), using computer simulations and experiment, for calibrating rheometers utilized in measurements of suspensions composed of macro-sized particles (of order millimeter to centimeter in size) in a non-Newtonian fluid matrix. Such measurements are important, for example, in the cement and concrete industry where evaluation of the rheological properties of mortars and concrete is needed to predict its flow and placement. The first SRM described is composed of millimeter sized mono sized beads in a non-Newtonian fluid matrix similar in properties to a cement paste. A second SRM is made up of the first one with larger beads added, representative of a concrete. A smoothed particle hydrodynamics based simulation is carried out to determine the rheological properties of these suspensions. Simulation results are compared to experiments using rheometers with cylindrical, vane and spiral shaped impellers. Visualization of flows in such rheometers, based on simulation will be shown. The visualizations clearly indicate how discrepancies between modelling and experimental results depend on the impeller design.

Wednesday 2:45 Audubon B SC37

Adjusting the electrorheological effect in silicate cage structures: Changing the number of cyanopropyl functional groups attached to the T8-cages

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Two Polyhedral Silsesquioxane Cage Based Electrorheological fluids were prepared. One nanocage with 8 functional groups attached was synthesized using a hydrosilation method. This material was then compared to a similar silicate cage structure having only 1 functional group attached to the silicate cage. Both structures were characterized using NMR and FTIR techniques. Previous research has shown that sulfonated polyhedral silsesquioxane (sPOSS) material when mixed with silicone oil (PDMS) and cyanopropyl POSS (cPOSS) also exhibits a significant ER effect. Here we show the effect on the ER activity of cyanopropyl POSS(cPOSS) particles in silicone oil by varying the number of functional groups on the nanocage structure. The rheological properties with applied DC electric fields of the suspension is demonstrated through steady flow and oscillatory tests. The research also contributed answers to the effects of changing the concentration of cPOSS particles. The preyield, yield and postyield characteristics of the ER fluid were determined using the flow curves, small amplitude oscillatory tests, and thixotropic stress loop tests. These results were also compared to dielectric spectroscopy measurements of the two ER fluids.

Wednesday 3:35 Audubon B SC38

Rheology of hydrate particulate suspensions

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Hydrates are crystalline solids that form when a lattice of hydrogen-bonded water molecules is filled by guest non-polar molecules coming from an adjacent gas or liquid phase. Naturally occurring hydrates have gained a lot of attention as potential energy resources and carbon dioxide storage systems, while the formation of hydrate compounds during oil extraction from deep-water fields represents a flow assurance risk for operations if appropriate operating conditions are not established. In any of these applications, the mechanical behavior of hydrates both as bulk solids and as dispersed suspensions of solid particles is of interest and deserving of investigation. In this work we focus on the rheological behavior of hydrate particle suspensions, formed by in-situ heterogeneous nucleation of surfactant-stabilized emulsions containing cyclopentane (a hydrate former at ambient pressure). Hydrate formation is monitored through temporal changes in the linear viscoelastic behavior with a novel time-resolved technique that enables us to maintain a small mutation number during the entire transient process. Yielding and plastic flow are analyzed with creep tests and steady shear measurements at different shear rates, with care taken to eliminate the tendency of the material to slip. The rheological material response for different hydrate volume fractions is interpreted within the framework of a recently proposed model for time-dependent (or thixotropic) elasto-visco-plastic materials by connecting the model parameters to physical quantities that affect particle-particle interactions, the effective volume fraction and the maximum packing fraction of suspended hydrates. This rheological analysis helps to identify the differences observed between hydrate-particle and ice-particle suspensions, to understand the kinetics of hydrate cluster formation and eventually to design appropriate operating conditions whenever efficient transport of hydrate particles suspensions is required.

Wednesday 4:00 Audubon B SC39

Rheological properties of suspensions with red mud as a supplementary cementitious materials: Monitoring flow and consolidation

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The efforts for a large-scale application for red-mud in cementitious compositions has been stepped up in recent years, associated with a demand for new supplementary cementitious materials (SCMs). It is known that these materials can improve some hardened-state properties, but changes on the rheological behavior are very dependent of RM content. This work was carried out using Ordinary Portland Cement and red-mud from Alumar (Brazil). The pastes were prepared using 5, 10 or 20% of substitution (in weight), maintaining the water-to-solid ratio in 0.5. Stepped flow test and strain sweep test were used to monitor the rheological parameters and the gain of consolidation over time respectively, and Vicat test was used to quantify the setting time. The increase of red mud content, improve the amount of finer particles and the specific surface area, reducing consequently, the interparticle size separation distance (IPS). It is clear that all pastes have shear thinning behavior. There is a little reduction on yield stress and apparent viscosity with substitution of 5%-red-mud, but with higher RM-content, these rheological parameters increase. There is no correlation between the microstructure stiffening and yield stress in the setting time. For RM-content higher than 10% the rigidification is accentuated. This means that changes on the rheological parameters over time were clear, but not sufficient to explain the changes in the needle penetration and setting result.

Wednesday 4:25 Audubon B SC40

Dependence of rheological properties on filler size in particle-filled crosslinked systems

MRB Mermet-Guyennet[1], M Dingreve[1], M Habibi[1], N Martzel[2], R Sprik[1], Morton M. Denn[3], and Daniel Bonn[1]
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Nanosized filler particles enhance the mechanical properties of polymer composites in a size-dependent fashion. This is puzzling, because classical analyses are inherently scale-free, and models for the rheology of particle-filled systems do not predict a filler-size dependence. Here we study the industrially important system of silica-filled rubbers, together with a well-characterized model filled crosslinked polymer gel, and show that both the linear and non-linear rheological properties of these systems exhibit a unique scaling proportional to the cube of the volume fraction divided by the particle size. This remarkable behavior makes it possible to predict the full mechanical response of particle-filled rubbers for small but finite deformations based solely on the rheology of the matrix and the size and modulus of the filler particles.

Wednesday 4:50 Audubon B SC41

Effect of deformation history on capillary attractive particulate suspensions

Junyi Yang and Sachin Velankar
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Previous studies show that addition of small amounts of wetting fluid to particles suspended in a non-wetting fluid endows the suspension with yield stress. The yield stress is attributable to formation of a space-spanning network of particles bound by menisci of the wetting fluid, analogous to adding a small amount of water to dry sand. The rheology of such suspensions shows many similarities with attractive colloidal suspensions. However, such mixtures are far from equilibrium so that their structure and rheology depend on deformation history. We conduct a fundamental morphological and rheological study of such "pendular suspensions" using polymeric blends consisting of two immiscible molten polymers and silica particles.

Experiments are restricted to a composition regime where the polymer that preferentially-wets the particles is more dilute than the particles themselves. Rheological studies show that the linear viscoelastic modulus decreases if the suspensions are sheared at a high rate prior to the modulus measurement, but this decrease can be reversed by sufficient low rate shearing. Upon cessation of shear, elastic recoil strains on the order of only ~1% are observed, suggesting that such suspensions are weakly elastic. Beyond strain of ~1%, the suspensions yield plastically. The results are interpreted in terms of a micromechanical picture in which deformation and flow induces rupture of pendular menisci. Limited morphological studies confirm that menisci of the wetting fluid bond the particles together into large aggregates, which break and reform continuously under flow conditions. Higher rate shearing favors aggregate breakdown, consistent with modulus decrease observed rheologically. Lower rate shearing induces growth of the aggregates, and is also consistent with rheology results. The process of yielding appears to involve rupture of menisci between particle clusters rather than between individual particle pairs, i.e. yielding and flow appear to involve highly non-homogeneous deformation.

Wednesday 5:15 Audubon B SC42

Non-Newtonian rheological characteristics of oil-based metal oxide nanofluids

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Rheological properties of nanofluids play an important role in determining heat transfer capacity and pumping power of a fluid as they have the potential to improve key heat transfer characteristics over the corresponding base fluid. In this investigation, a clear understanding of how nanoparticle concentration, nanoparticle type, and nanoparticle diameter affect the viscosity of a nanofluid over a range of shear rates. The nanoparticles used for this investigation are aluminum oxide and titanium oxide with a base fluid of paraffin oil (white, CAS No: 8020-83-5). Nanofluids containing both single types and mixture of nanoparticles at 0.2 - 5 % volumetric concentrations are prepared using two step method with a sonication time of 12 hours. Viscosity was measured using Brookfield Dv2T rotational viscometer with a cone (cp-40Z) and plate apparatus. Results show that Newtonian behavior of the fluid changes to non-Newtonian (shear thinning) on increasing the particle concentration. The effect of mixtures of nanoparticles were also investigated to determine the effect particle type has on both the viscosity and the rheological behavior.

Symposium NF
Non-Newtonian Fluid Mechanics & Instabilities

Organizers: Sandra Lerouge and Becca Thomases

Wednesday 1:30 Audubon DEF NF11

Distinguishing shear banding from shear thinning in Taylor-Couette flows

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Shear banding is typically attributed to mechanical instability due to non-monotonic or discontinuous stress-rate constitutive behavior. However, such behavior is obscured in experiment by the significant spatial gradients in the shear stress inherent to most rheometric geometries, such as Taylor-Couette flow, which results in an apparent stress plateau with increasing shear rate. Moreover, these same stress gradients can produce banding-like velocity profiles, even when the fluid possesses a monotonic constitutive curve. This raises an important practical question: how do we distinguish whether a fluid is truly shear banding as opposed to strongly shear thinning? To answer this question, we report a model-free numerical approach to identify steady state shear banding through higher-order derivatives of the velocity profile. The approach is validated using flow calculations of the diffusive-Giesekus model, and then applied to rheology and flow velocimetry measurements on shear thinning and shear banding wormlike micelles in a Taylor-Couette device with systematically varying curvature (i.e., ratio of gap size to cylinder radius). The results of both simulation and experiment are used to identify several dominant features of shear banding, whose presence and quantitative behavior are relatively insensitive both to the applied shear rate and the degree of curvature of the flow geometry. By contrast, we find that many shear thinning fluids exhibit flows that resemble banding, but with features that are highly sensitive to the flow conditions and geometry. Our results provide clear, unambiguous criterion for identifying shear banding in complex fluids, and clear guidelines for performing flow velocimetry measurements to identify shear banding in complex fluids.

Wednesday 1:55 Audubon DEF NF12

Jetting flow of a shear banding fluid in a rectangular duct

Paul Salipante[1], Charles Little[2], and Steve Hudson[3]
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We present on the characteristics and causes of a jetting flow instability of shear banding worm-like micelle solutions in microfluidic channels with rectangular cross-sections over an intermediate volumetric flow regime. Particle tracking methods are used to measure the three-dimensional flow field in channels of differing aspect ratios, sizes, and wall materials. When jetting occurs, it is self-contained within a portion of the channel where the flow velocity is greater than the surroundings. We observe that the instability forms in high aspect ratio channels, and that the location of the high velocity jet appears to be sensitive to stress localizations. Jetting is not observed in a lower concentration solution without shear banding. Simulations using the Johnson-Segalman viscoelastic model show a qualitatively similar behavior to the experimental observations and indicate that compressive normal stresses in the cross-stream directions support the development of the jetting flow. Our results show that non-uniform flow of shear thinning fluids can develop across the wide dimension in rectangular microfluidic channels, with implications for microfluidic rheometry.

Wednesday 2:20 Audubon DEF NF13

Stress-concentration coupling in polymer solutions under strong flow

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A key assumption underlying many theoretical fluid mechanics studies of complex fluids is that the fluid composition remains homogeneous. Specifically, it is often assumed for polymeric solutions that the concentration of the polymer is independent of position in the rest state and remains so in the presence of flow. On the other hand, many industrial flows of complex fluids are nonhomogeneous.

In this work, we generalize the classical analysis of polymer fluctuations in shear flow to consider the same problem for general linear flows, with an emphasis on mixed (shear + extensional) flows. The theoretical foundation is that of the Helfand-Fredrickson mechanism in which polymer molecules can migrate up stress gradients, toward regions of higher concentration, hence providing a mechanism to enhance naturally occurring thermal fluctuations. We develop and apply a modernized version of the two-fluid model for highly entangled polymer solutions, which are well described by the Rolie-Poly constitutive model. The goal of this work is to use concentration fluctuation analysis to devise criteria by which one can ascertain whether being a "strong flow" is sufficient to make scattering patterns appear like a rotated version of pure extension. For the types of polymer solutions of interest to this work, our simulations reveal that scattering patterns under flows that are classified as "strong" (in which extension controls the chain dynamics) may deviate from the behavior expected under extensional flow and reveal a non-trivial influence of shear flow.

Wednesday 2:45 Audubon DEF NF14

Stability of shear banded flow for a viscoelastic constitutive model with thixotropic yield stress behavior

Yuriko Renardy and Michael Renardy
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We examine the stability of two-layer shear flow, one layer yielded and the other unyielded, for a PECN fluid. The PECN model is a viscoelastic constitutive model which combines the partially extending strand convection model (PEC) with a Newtonian solvent. We define ε to be the ratio of retardation time to relaxation time and focus on the case of small ε. A linear stability analysis is conducted of shear banded flows, and the interface is found to be unstable. The instability is driven by a normal stress difference across the interface. As for the Johnson-Segalman model, which has been studied in earlier literature, the PEC model has a higher normal stress in the high shear rate phase than in the low shear rate phase. To assess the importance of this property, we also investigate a model which is specifically designed to reverse this. It is found that instabilities still occur, although the range of unstable wave numbers is reduced.

Wednesday 3:35 Audubon DEF NF15

Surface textures and non-Newtonian fluids for decreased friction

Jonathon K. Schuh and Randy H. Ewoldt
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Surface texturing is used to reduce friction in lubricated sliding contact. Here we experimentally study the coupling of non-Newtonian fluid properties with varying texture profiles. Gap-controlled experiments with polymer solutions were performed on a tribo-rheometer configuration using textured parallel disks and gap separations below 300 µm. Gap control, rather than normal force control used in traditional tribology studies, is necessary to control the relevant dimensionless parameters of the experiment. These include the Reynolds Number, Weissenberg Number, and Deborah Number. The Deborah Number appears due to transient variations in the direction of flow due to surface texturing, whereas the Weissenberg Number is determined by the characteristic strength of flow (shear rate). We measure normal and shear loads up to a maximum Reynolds number with respect to gap height Reh=59.54. Previous experimental work tested with the rotating plate moving in only one direction. In our work here, we study bi-directional sliding motion to verify symmetry in the experimental setup and to study the directional-dependent normal and shear response. We show that the symmetry of the surface textures depth profiles must be broken to produce normal forces above the viscoelastic response, and that an optimal angle of asymmetry ß exists for decreasing friction with asymmetric surface textures and viscoelastic lubricants.

Wednesday 4:00 Audubon DEF NF16

Viscosity measurement of rapidly evolving biopolymer solutions and modeling of laminar pipe flow – mixing, MRI-velocimetry, and simulation

William H. Hartt, Emilio Tozzi, Shripad D. Joshi, Robert D. Johnson, and Lori A. Bacca
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Rapidly evolving rheological properties are prevalent in processing applications with dissolving or reacting polymers. When polymeric particles are incorporated into solvents, viscosity changes of 1000x may occur in seconds. These dramatic changes in viscosity present challenges for process control, mixing, and scale-up. We present techniques and results for measuring rapidly changing viscosities in non-Newtonian fluids and modeling flows with rapidly changing viscosities. We also present flow imaging for validation of models.

First, NMR-velocimetry is used to show the effects of rapidly changing viscosities on laminar flows in process equipment. This information is used to formulate a model that determines transport properties needed for scale-up and prediction of equipment performance. Impacts of rapidly changing viscosity on laminar pipe flow are shown experimentally.

Second, after determining which time dependent transport properties are needed for objective scale-up we demonstrate and validate a method for measuring time dependent viscosity. We use analysis utilizing the Metzner-Otto rule for stirred tanks (impeller in a rheometer) and flow through static mixers. Both methods result in similar viscosity and time dependent measurements. We explore time dependent growth models from various technical fields to best fit the data. We also use these models to objectively determine temperature and strain rate dependence. The resulting models are then used in a variety of flow models.

Finally, we present laminar pipe flow models with three levels of hierarchy. Dimensional analysis leads to scaling behavior and we are able to collapse all data onto one master curve. The second level of complexity is the axially dependent evolving viscosity flow model, which is easy to use and predicts many features of the flow. The final level of complexity is a three-dimensional CFD model with evolving viscosity. We show the accuracy and practicality of using each of these models.

Wednesday 4:25 Audubon DEF NF17

A high-order immersed boundary method for solving polymeric flow problems on arbitrary smooth domains

David B. Stein[1] and Becca Thomases[2]
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We present a robust, flexible, and high-order Immersed Boundary method for simulating fluid flow, including many models of viscoelastic flow, e.g. the Stokes-Oldroyd-B equations. The solution to the PDE is coupled with an equation for a smooth extension of the unknown solution; high-order accuracy is a natural consequence of this additional global regularity. Low and zero Reynolds number problems are handled efficiently and accurately. We demonstrate pointwise convergence of the polymeric stress for flows in complex domains, in contrast to the standard Immersed Boundary method, which generates large errors in the polymeric stress near to the boundaries. We demonstrate the method on standard benchmark problems, including flow around a cylinder.

Wednesday 4:50 Audubon DEF NF18

Large-amplitude oscillatory shear flow from Oldroyd 8-constant framework: Normal stress differences

Chaimongkol Saengow and Jeffrey Giacomin
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We use the Oldroyd 8-constant continuum framework to investigate polymer melts in large-amplitude oscillatory shear (LAOS) flow. In this flow, the normal stress differences respond as Fourier series, the higher harmonics of which are caused by the fluid nonlinearity. We choose this framework for its rich diversity of special cases (we tabulate 13 of these). Deepening our understanding of this Oldroyd 8-constant framework thus deepens our understanding of every one of these special cases. Previously [Macromol Theor Simul, 24, 352 (2015)], we arrived at an exact analytical solution for the normal stress difference response for the corotational Maxwell model in LAOS. Here, we derive the exact analytical expression for the Oldroyd 8-constant framework for the first and second normal stress difference responses. Our exact solution reduces to our previous solution for the special case of the corotational Maxwell model, as it should. Our worked example examines the special case of the corotational Jeffreys model, allowing us to explore the role of infinite shear viscosity on the normal stress difference responses of polymeric liquids in LAOS.

Wednesday 5:15 Audubon DEF NF19

A finitely extensible coil model for nonlinear viscoelasticity

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Non-Newtonian flow has been a topic of academic studies for over 100 years and is highly relevant to many industrial processes. Various microstructure and/or continuum mechanics frameworks have been proposed in the literature to model the nonlinear elastic effects in polymer flow. However, accurate modeling of 3-D viscoelastic flow with high Deborah and Weissenburg numbers still remains a substantial challenge, and constitutive models with minimal fitting parameters are particularly desired in modeling of realistic flow problems in polymer processing. In this work, a hybrid microstructure/continuum formulation is developed for a finitely extensible polymer coil that interacts with surrounding molecules through entanglement and disentanglement. A polymer coil is considered as an ellipsoid in the continuum domain and its microstructural effects on relaxation and hardening are tackled through finite stretch. A rotational recovery process is additionally introduced to the evolution equation for the conformation tensor using continuum mechanics principles so that the difference between rotational flow (such as shear) and purely extensional flow can be naturally handled in 3D flow. The resulting model contains 3 major parameters: one for finite stretch dictated by a ceiling stretch of the coil, a second one for rotational recovery, and a third one for adjusting stretch hardening of the rubbery coil. Each model parameter is linked to a corresponding physical process and can be readily determined from normal rheological plots. The new model, even in a single mode, is able to simultaneously predict practical material functions in simple shear and coaxial extension and to fit well to representative experimental data. Particularly in the steady-state (or quasi-steady state) flow case, a nearly closed-form stress to velocity gradient relationship can be derived with which shear thinning and elongational thickening can be simultaneously considered while computational advantages of a classical GNF model is retained.

Symposium MF
Micro/Nano Fluidics and Probe Rheology

Organizers: Monica Oliveira and Gordon Christopher

Wednesday 1:30 White Ibis MF11

Bubble pinch-off mechanisms in a microfluidic expansion channel

Daniel Vecchiolla, Vidya Giri, and Sibani Lisa Biswal
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Paramount to the optimal design of foam generation systems is the understanding of the complex dynamic interactions that govern bubble breakup. Recent experimental work has demonstrated that close confinement of bubbles can facilitate neighbor-neighbor bubble pinch-off (i.e. the breaking of a central elongated bubble from the strong interactions of two or more neighboring bubbles). This "structure-induced capillary instability" elucidated the process of bubble breakup in sheared foams and manifested in the discovery of two novel pore-level mechanisms of foam generation in porous media. The present work studies the mechanism of neighbor-neighbor pinch-off of monodisperse bubbles in the expansion region of a wide (1600 μm) collection channel. The relationship between capillary number and pinch-off, as well as the resulting size segregation, is examined. Pinch-off is metronomic at sufficient capillary numbers, assisted by a clear templating effect from the bubbles in the expansion. The banded bubble size distributions of fragmented and intact bubbles are largely influenced by the geometry of the channel. The optimal design for the formation of a bidisperse foam will also be discussed.

Wednesday 1:55 White Ibis MF12

Microliter-scale phase separating polymer droplets to estimate partition coefficients of single walled carbon nanotubes

Christopher W. Nelson and Shelley L. Anna
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Passive separation and purification methods for nanoscale materials like carbon nanotubes can be beneficial by reducing the need for high cost and energy/labor intensive equipment and processes. Phase separating mixtures of polymers and surfactants have been used to purify single wall carbon nanotubes, but there is a lack of data relating the partition coefficient of a desired nanotube species to the polymer-surfactant mixture composition. We use a microliter droplet-based fluid handling system coupled with inline absorption spectroscopy to rapidly determine the partition coefficient as a function of mixture composition. This approach takes advantage of small sample volumes, rapid mixing of viscous phases in the high shear microscale droplet formation process, use of viscosity contrast to orient the polymer rich compartments in the confined flow, and the ability to generate high resolution composition gradients along a train of droplets. Inline absorbance measurements are used to identify and quantify the nanotube concentration in each phase as well as to estimate the amount of residual material pinned at the compartment interface. Along with complementary droplet-based approaches to measuring the phase separation behavior of multi-component mixtures, we are able to fully quantify the separation behavior of various carbon nanotube species, enabling the design and optimization of industrial-scale liquid-liquid separation processes.

Wednesday 2:20 White Ibis MF13

Elasto-inertial separation of particles by size in straight rectangular microchannels

Di Li, Xinyu Lu, and Xiangchun Xuan
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We present in this work a continuous sheath-free separation of both a binary and a ternary particle mixture in viscoelastic polymer solutions through straight rectangular microchannels. This label-free separation arises from the flow-induced elasto-inertial lift force that directs particles towards size-sensitive equilibrium positions. We perform a comprehensive parametric study of the effects of flow rate, solvent viscosity, polymer concentration, polymer type and channel aspect ratio on the binary particle separation. To explain the observed shifting of particle equilibrium positions, we propose to break down the elastic lift into a center-directed component due to the fluid elasticity effects and a wall-directed component due to the fluid shear thinning effects. These two components of elastic lift scale differently with the experimental parameters, which work with the inertial lift to produce the differential elasto-inertial particle focusing in straight rectangular microchannels.

Wednesday 2:45 White Ibis MF14

Reducing transport energy barrier in crowded environments with weak interactions

Yeng-Long Chen, Fan-Tso Chien, Wei Chien, and Po-Keng Lin
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Macromolecular transport in crowded micro-environments typically slows as the surrounding becomes more crowded and less free volume is available. In crowded nanoslit micropost arrays, We found enhanced transport of DNA molecules in more crowded arrays, contrary to the expectation of slower diffusion. The nanofabricated post arrays are weakly attractive and emulate crowded interactive environments, resulting in weak DNA adsorption. The coupling between DNA diffusion with adsorption to the microposts results in increased mobility with increasing post density, in contrast to studies of decreased DNA/protein mobility in dense gels. Hidden Markov analysis was employed to identify the apparent free energy barriers, which is in agreement with theoretical estimates of based on polymer conformation fluctuations between posts. We also performed Langevin dynamics simulations of macromolecular transport in micropost arrays, which found lowered free energy barriers and enhanced diffusion in denser arrays. Faster DNA diffusion and hopping in crowded systems have important implications for biological systems and for technological applications such as macromolecule purification, and targeted drug delivery.

Symposium SL
Solids & Composites

Organizers: Jon Seppala and Cathy Jackson

Wednesday 3:35 White Ibis SL1

Questions in non-equilibrium materials: Is there an ideal glass transition and are colloidal dispersions good models of glasses?

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The glass transition is often taken to be a manifestation of an underlying thermodynamic transition, perhaps 50-100 K below the laboratory measured glass temperature. One evidence of this is found in the super-Arrhenius behavior of viscosity or relaxation time as a function of temperature. The so-called Vogel-Fulcher extrapolation of the measured dynamic property leads to an apparent finite-temperature divergence

some 50 K below the nominal glass temperature. By performing experiments on glasses aged for very long times (20 million year old amber) we [1] have been able to probe the upper bounds to the equilibrium dynamics to 43.6 K below the glass temperature. We find that the finite-temperature divergence does not exist, rather the glass exhibits an apparent Arrhenius behavior, suggesting that theories based on a finite temperature divergence of the relaxation times need to be re-evaluated. Also, there is considerable activity in the Soft Matter community using concentrated colloidal dispersions as models of glass-forming systems. Here we visit this problem in a series of concentration-jump experiments using PNIPAM-particle colloids to mimic the classic temperature-jump experiments that Kovacs used to characterize structural recovery in molecular glasses. We use diffusing wave light scattering spectroscopy and classical rheological methods to examine "intrinsic" isotherm, asymmetry of approach, and the memory signatures and compare the colloidal system with the molecular glass. We find that the colloidal systems while exhibiting some of the features seen in molecular glasses, in detail show surprising differences in their structural recovery signatures [2].

[1] J. Zhao, S.L. Simon, G. B. McKenna, "Using 20-million-year-old amber to test the super-Arrhenius behavior of glass-forming systems," Nature Comm., 4, 1783-1 - 1783-6 (2013). [2] X. Peng and G.B. McKenna, "Physical Aging and Structural Recovery in a Colloidal Glass Subjected to Volume Fraction-Jump Conditions," Physical Review E., 93, 042603 (2016).

Wednesday 4:00 White Ibis SL2

Theory of spatially heterogeneous activated relaxation, elasticity and vitrification in free standing thin films

Ken Schweizer and Steve Mirigian
Materials Science Department, University of Illinois at Urbana-Champaign, Urbana, IL, United States

Building on the no adjustable parameter force-level Elastically Collective Nonlinear Langevin Equation approach for bulk glass-forming liquids, we have constructed a quantitative statistical mechanical theory for how confinement in free standing thin films introduces a spatial gradient of the alpha relaxation time as a function of temperature, film thickness and location in the film. The crucial idea is that relaxation speeds up due to the reduction of both near surface barriers because of a loss of local cage neighbors, and the cutoff and dynamical softening near the vapor interface of the spatially longer range collective elasticity cost for large amplitude hopping. These two effects are strongly coupled. Predictions are made for how an apparent glass temperature depends on film thickness, the emergence of a two-step decay and mobile layers in time domain measurements, the dependence of film-averaged relaxation times on temperature and thickness, surface diffusion, and differences between kinetic and pseudo-thermodynamic measurements. A realistic vapor interfacial width significantly enhances the film-averaged glass transition temperature reduction. How film thickness impacts dynamical properties under non-isothermal conditions, where temperature is fixed relative to the thickness-dependent Tg, is contrasted with isothermal behavior. Modest differences are found if Tg is defined dynamically. However, adopting a pseudo-thermodynamic measure leads to a qualitatively new form of the relaxation time gradient where mobile layers near the film surface coexist with vitrified regions in the film interior. As a consequence, the film-averaged shear modulus can increase with decreasing film thickness, despite the Tg reduction and presence of a mobile surface layer, in contrast to universal mechanical softening behavior under isothermal conditions.

Wednesday 4:25 White Ibis SL3

Imaging the microstructural indentation response of thin films on glass

Lena R. Bartell[1], Neil Lin[2], Jennifer L. Lyon[3], Michael L. Sorensen[3], G. Scott Glaesemann[3], Donald A. Clark[3], Mark J. Lockhart[3], Michael E. DeRosa[3], and Itai Cohen[2]
[1]School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14850, United States; [2]Physics department, Cornell University, Ithaca, NY, United States; [3]Science and Technology Division, Corning Incorporated, Corning, NY 14830, United States

Thin film protective coatings are widely used in a variety of technological areas, including for chemical stability enhancement, corrosion protection, and mechanical damage inhibition. Characterizing how thin films respond to external contact is crucial for understanding their protective abilities and designing new coating materials. Conventional indentation techniques can be used to create such surface damage. However, measuring the film's microscale structure in 3D, especially during the indentation event, would be extremely helpful in understanding the films response to contact. Thus, we designed a custom indentation apparatus mounted on a confocal microscope and experimentally investigated the microscale indentation-flow response of thin epoxy films coated on glass substrates. This instrument allowed us to simultaneously indent the sample, image its 3D structure over time, and measure the corresponding macroscopic force response. By tracking micron-sized fluorescent tracer particles embedded in the film, we characterized and compared the flow behaviors for plain epoxy films and films filled with silica nanoparticles. In both samples, we visualized the development of the pile-up around the indenter tip. Additionally, we found that filled samples exhibit a notable wall-slip near the glass substrate in the last stages of indentation, while plain samples did not. Overall, this method provides unprecedented access to quantitative information about the microscale processes in films during indentation.

Wednesday 4:50 White Ibis SL4

The effect of testing conditions on the mechanical properties of polymers during fatigue testing

Denis Rodrigue[1], Valerian Hirschberg[1], and Manfred Wilhelm[2]
[1]Chemical Engineering, Université Laval, Quebec, Quebec G1V0A6, Canada; [2]Institut für Technische und Polymerchemie, Karlsruhe Institute of Technology, Karlsruhe, Baden-Würtemberg 76128, Germany

In this work, the effect of frequency and notch position on the fatigue behavior of polymers in the solid state was investigated. In particular, polylactic acid (PLA) was selected as a typical semi-crystalline thermoplastic sample and the tests were performed at room temperature using a torsion rectangular geometry. In particular, strain controlled tests were analyzed under large amplitude oscillatory shear (LAOS) at different frequencies (?/2p = 0.5, 1 and 2 Hz). Also, the notch position was changed from the middle of the long side towards the extremities of the sample (holding position). Using transient tests, the torque signal from an ARES rheometer was recorded and analyzed via Fourier-transform to obtain the fundamental and higher harmonics intensities. From the data gathered, typical linear mechanical parameters such as the storage (G') and loss (G") moduli were obtained, as well as the relative intensity of the second ($I_{2/1}$) and the third ($I_{3/1}$) harmonics as a function of time. The trends for each parameter were used to determine and understand typical fingerprints in the stress response leading to specific events such as crack initiation and crack propagation. The main idea is to detect some criteria leading to failure onset. The results obtained show that an important frequency effect on the Woehler curves exists with negligible effect on the linear mechanical parameters as a function of time. In contrast, different notch positions, and thereby stress distribution in the sample, were found to have a high impact on Woehler curves and the time dependent behavior of the mechanical parameters (mainly $I_{3/1}$). By shifting the notch position towards the extremities of the samples, $I_{3/1}$ values were found to increase with a change of slope until the creation of a macroscopic crack, which was confirmed by visual observation (video camera).

Wednesday 5:15 White Ibis SL5

Multiplicity of morphologies in poly (L-lactide) bioresorbable vascular scaffolds

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

Multiplicity of Morphologies in Poly (L-lactide) Bioresorbable Vascular Scaffolds Authors: Karthik Ramachandran1 and Julia A. Kornfield1 1Division of Chemistry and Chemical Engineering, California Institute of Technology 1200 E Colorado Blvd, Pasadena, 91125, CA, USA Bioresorbable vascular scaffolds (BVSs) are a promising new treatment for Coronary Heart Disease (CHD), the leading cause of death in the world (>7 million/year). In contrast to permanent metal stents, BVSs support the occluded artery for the first 6 months, but are completely resorbed in 2-3 years, leaving behind a healthy artery. The material at the heart of the BVS is the polymer poly L-lactide (PLLA), which hydrolyzes to L-lactic acid, a metabolic product processed by the body. The transient character of the BVS restores arterial vasomotion and eliminates the risk of late stent thrombosis. The clinical success BVSs is surprising given the inherent brittleness of PLLA (elongation at break <10% at physiological conditions). It is remarkable that a scaffold made of pure PLLA survives strains in excess of 50% when crimped onto the balloon catheter and upon subsequent deployment in the artery. Using a combination of polarized light microscopy and X-ray microdiffraction, we discovered that crimping creates a multiplicity of morphologies in the BVS; PLLA chains change orientation from the radial to the hoop-direction over distances of 100μm. This unique morphology facilitates a low-stress response upon deployment, protecting the scaffold from fracture and imparting the strength needed to support the artery. Therefore, the BVS takes advantage of structural transformations during crimping to exhibit ductile character upon deployment.

Symposium AT
Advanced Techniques and Methods

Organizers: Anthony Kotula and Matthew E. Helgeson

Wednesday 1:30 Sandhill Crane AT1

Frequency-sweep MAOS: Faster and cheaper medium-amplitude oscillatory shear

Piyush K. Singh[1], Johannes M. Soulages[2], and Randy H. Ewoldt[1]
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Medium-amplitude oscillatory shear (MAOS) is asymptotically-nonlinear and a valuable tool for inferring structure from rheology. However, a drawback of conventional MAOS is the time and material intensive nature of experiments. Many strain amplitude sweeps, and typically multiple sample loadings, are required to obtain frequency-dependent properties. Here, we propose a new MAOS methodology that is faster (fewer data points) and cheaper (fewer material loadings): the frequency-sweep MAOS. Similar to conventional small amplitude oscillatory shear (SAOS), we use only a frequency-sweep at a suitable strain amplitude. A key challenge is that measurable MAOS data lives between the instrument resolution (at small strains) and strongly nonlinear behavior beyond asymptotic nonlinearity (at large strains). We propose criteria to validate MAOS data taken at a single strain amplitude, and additionally provide quantitative estimates of the measurement uncertainty. Full characterization of all four MAOS measures requires two frequency sweeps: one frequency sweep for the third-harmonic measures and two frequency sweeps (at different input strain amplitudes) for the first-harmonic measures. The proposed method is validated for a linear polyethylene melt. This new, faster, and material economical MAOS approach will be beneficial for precious samples such as model branched polymers which are typically available in very limited quantities. Additionally, the lessons learned are extended to frequency-sweep SAOS for generating confidence that the measures are indeed in the linear regime.

Wednesday 1:55 Sandhill Crane AT2

Natural decomposition of the relaxation spectrum through combined implementation of Fourier, Laplace and Z transforms

Donggang Yao
School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, United States

Accurate determination of the inherent relaxation spectrum in linear viscoelasticity is of an immense importance in polymer science and engineering since it is linked to the polymer molecular structure, on one hand, and serves as a ubiquitous vehicle in solving different types of deformation and flow problems, on the other hand. Increasing evidences also indicate that an accurate relaxation spectrum is the foundation for nonlinear viscoelasticity; improper framing of relaxation modes can lead to peculiar predictions in large-Weissenberg flow (both in transient and steady state flow). However, the calculation of the relaxation spectrum from experimental data is classically regarded as an ill-posed inverse problem. Different data fitting methods can lead to vastly different relaxation spectrums. More recent work has thus been directed towards incorporating additional criteria or constraints (e.g., the 'parsimonious' spectrum by Baumgaertel and Winter, and the linearization procedure by Malkin and Kuznetsov) in data fitting with a hope to uncover a more natural relaxation spectrum. However, the general problem still remains open. In this work, we developed a data analysis procedure by a combined implementation of Fourier, Laplace and Z transforms to eliminate the ambiguity of the inverse problem and decompose the continuous spectra into natural discrete modes. Briefly, a frequency data is first converted into a time data through transfer function analysis and Fourier transform. Z transform is then performed on the discretized time data to obtain a region of convergence. Modes of relaxation are then progressively decoded using coupled convergence and sensitivity analysis. The presentation covers the mathematical foundation of the above procedure and provides case studies in fitting of experimental data.

Wednesday 2:20 Sandhill Crane AT3

Extremely strong depth dependence of the hardness of PDMS: Analysis of effects of false surface detection

Zhiyuan Qian and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

Depth dependence effects or size effects have been observed in metals as well as polymers with nanoindentaton tests. Several fold changes in modulus and hardness have been reported for glassy polymers such as Polystyrene (PS), Polycarbonate (PC), or Polymethyl methacrylate (PMMA), as well as semicrystalline polymers. However, the results of soft polymers such as Polydimethylsiloxane (PDMS) are more complicated, where multiple order of magnitude changes, several fold changes, and no changes have been reported by different groups in literature. In the present work, we examine the problem of one potential artifact in the testing of soft materials, that of the difficulty of detecting the surface or "true zero" in the nanoindentation test. We provide a quantitative estimate of the effects of error in surface detection on the measured force-displacement curves for the Berkovich tip geometry and find that the observed apparent stiffening is in agreement with our analysis. The significance of the results for testing of soft materials by nanoindentation is discussed. It is also shown that for hard/stiff materials the induced errors are smaller, but may still be significant in some circumstances.

Wednesday 2:45 Sandhill Crane AT4

Prediction of cryogenic viscosities: Arrhenius or erroneous?

Christine Roberts[1], David Barringer[1], Alan L. Graham[2], and Alex Mertz[2]
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Environmental sensing devices that sense acceleration can use low viscosity liquids as damping fluids that must operate over a wide temperature range down to as low as (?40 oC to 150 oC). The accuracy and fidelity of these environmental sensing device measurements depends on an accurate knowledge of the material properties. Properties at cryogenic temperatures are often predicted from extrapolations of measurements at higher temperatures. Here we focus on high-precision measurements of dynamic and kinematic viscosities using a variety of techniques at cryogenic temperatures for low-viscosity, linear polymeric fluids. We find that polydimethylsiloxane fluids can be accurately predicted from high temperature measurements. However, for perfluoropolyether fluids the increase of viscosity with decreasing temperature is highly non-linear. Arrhenius predictions lead to erroneous results and under predict the viscosity by over 150%.

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

Wednesday 3:35 Sandhill Crane AT5

Polymer chain stretching during uniaxial deformation: An in-situ, time-resolved SANS study in polymer melts

Carlos R. López-Barrón[1], Jeffrey J. Richards[2], and Yiming Zeng[3]
[1]ExxonMobil Chemical Company, Houston, TX, United States; [2]NIST Center for Neutron Research, Gaithersburg, MD, United States; [3]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, United States

Understanding the interrelation between stress response and microstructural evolution in polymers during deformation is key for engineering premium products from a bottom-up approach. We use a suite of in-situ probes to investigate different aspects of structure development during uniaxial deformation in semicrystalline polymers and polymer melts. In particular, small-angle neutron scattering (SANS) is a very powerful tool, as it provides information about single chain conformation as well as orientation and alignment induced by external fields such as shear flow or elongation. In this talk, I will present an example of the use of in-situ time-resolved SANS measurements during uniaxial deformation of polymer melts subjected to startup and cessation of uniaxial extensional flow. The fast relaxation of the melts constitutes a challenge for time-resolved SANS measurements. I will discuss the approach we use to overcome such challenges, which include the use of state-of-the-art protocols for stroboscopic SANS data collection in combination with modified commercial rheometers. Our measurements allow us to correlate chain alignment and extensional rheology of a series of bimodal polystyrene blends, which led to the development of a stress-SANS rule in extension. The stress-SANS rule, an analogous to the stress-optical rule, is obeyed at the early stages of stress growth (during flow startup) and at the late stages of stress relaxation (after cessation of flow). The implications of our analysis and the limitations of our method will be discussed in this talk.

Wednesday 4:00 Sandhill Crane AT6

Unearthing the power of small-angle neutron scattering for molecular rheology of polymers

Zhe Wang, Christopher N. Lam, Wei-Ren Chen, and Yangyang Wang
Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

Small-angle neutron scattering (SANS) is a unique and powerful method for investigating the conformational properties of flowing polymers. Despite a long history of application of SANS in rheology, the full power of this technique is yet to be unearthed. In this talk, we will describe a new approach, based on spherical harmonic expansion (SHE), for analyzing the anisotropic 2D SANS spectra of polymers in flow. This spectrum decomposition method not only provides a convenient way for comparing experimental results with the predictions from statistical and molecular models, but also allows many new questions to be asked, including the affineness, symmetry, and heterogeneity of the macromolecular deformation. The usefulness of the SHE approach is demonstrated by several examples from our recent studies.

Wednesday 4:25 Sandhill Crane AT7

Development of μRheo-SANS at NIST

Daniel Seeman[1], Javen Weston[2], Daniel Blair[2], Paul Salipante[3], Steve Hudson[3], and Katie Weigandt[1]
[1]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20878, United States; [2]Dept. of Physics Georgetown University, Washington, DC, DC, United States; [3]Polymers & Complex Fluids Group, NIST Materials Science & Engineering Division, Gaithersburg, MD, United States

There is a critical unmet need for characterization techniques capable of simultaneous measurements of structure and rheology, particularly at extremely high shear rates, in excess of those accessible via Couette rheometers. Many applications require channeling fluid through narrow openings, as with injectables, hydraulic fracturing fluids, or polymer extrusion - which can generate rates of shear far greater than those that can be measured in traditional rotational rheometers. We report development of a microfluidic slit rheometer as a sample environment for neutron scattering (μRheoSANS). We measure the structure of a semi-dilute surfactant solution of wormlike micelles during flow with the prototype μRheoSANS instrument. Using a fluid mechanics-based data analysis technique we are able to show that SANS measurements made in our Poiseuille flow cell are consistent with those obtained using a standard Couette RheoSANS device. The new instrument measures the rheology also at higher shear rates, where shear thinning and structural adjustments continue. This μRheoSANS capability will enable new studies of the structure and properties of complex fluids at high shear rate.

Wednesday 4:50 Sandhill Crane AT8

Flow elasticity of driven colloidal suspensions

Zhe Wang[1], Lionel Porcar[2], Yangyang Wang[1], Luis E. Sanchez-Diaz[1], Christopher N. Lam[1], Yun Liu[3], Takuya Iwashita[4], Takeshi Egami[1], and Wei-Ren Chen[1]
[1]Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States; [2]Large Scale Structures, Institut Laue-Langevin, Grenoble, France; [3]National Institute of Standards and Technology, Gaithersburg, MD 20899, United States; [4]Oita University, Oita, Japan

The development of mode-coupling theory (MCT) for addressing the deformation behavior of non-Newtonian liquids is relatively new. While the existing approximation can predict certain fundamental rheological behaviors that are characteristic of hard-sphere suspensions, there remains some ambiguity as to whether or not this theoretical framework can be extended to address the rheological properties of strongly interacting colloidal suspensions, which are commonly found in nature and a wide variety of applications. Using neutron scattering and rheological measurement, we demonstrate the flow behavior of charge-stabilized colloidal suspensions is a consequence of localized elastic response generated by particle interaction. We show how this short-lived, localized mechanical coherency determines the rheological behaviors, transport properties and glass phenomenon of driven colloids. Our finding sheds new light on understanding the nature of nonlinear colloidal rheology and provides a new theoretical ingredient for the development of first-principle constitutive equations for soft matter systems.

Wednesday 5:15 Sandhill Crane AT9

Dielectric RheoSANS: An instrument for the simultaneous interrogation of rheology, microstructure and electronic properties of complex fluids

Jeffrey J. Richards[1], Julie B. Hipp[2], Norman J. Wagner[2], and Paul D. Butler[1]
[1]NCNR, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States; [2]Chemical & Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

In situ measurements are an increasingly important tool to inform the complex relationship between nanoscale properties and macroscopic measurements. For conducting colloidal suspensions, we seek intrinsic relationships between the measured electrical and mechanical response of a material both in quiescence and under applied shear. These relationships can be used to inform the development of new materials with enhanced electrical and mechanical performance. In order to study these relationships, we have developed a dielectric rheology instrument that is compatible with small angle neutron scattering (SANS) experiments. This Dielectric RheoSANS instrument consists of a Couette geometry mounted on an ARES G2 strain controlled rheometer enclosed in a modified Forced Convection Oven (FCO). In this talk, we outline the development of the Dielectric RheoSANS instruments and demonstrate its operation using two systems - a suspension of carbon black particles in propylene carbonate and poly(3-hexylthiophene) organogel - where there is interest in how shear influences the microstructure state of the material. By monitoring the conductivity and rheological response of these materials at the same time, we can capture the entire evolution of the material response to an applied deformation.

Symposium SM
Polymer Solutions & Melts

Organizers: Carlos R. López-Barrón and Nicolas Alvarez

Wednesday 1:30 Snowy Egret SM33

Melt extensional rheology: SER vs. FSR and internal energy buildup

Panpan Lin[1], Z.C. Zhao[1], Jianning Liu[1], Zhen-Gang Wang[2], and Shi-Qing Wang[1]
[1]University of Akorn, Akron, OH, United States; [2]Caltech, Pasadena, CA, United States

In this presentation, we discuss extensional rheological behavior of various polymer melts using either SER (Sentmanat Extensional Rheometer) or Instron. After discussing the physics behind the emergence of tensile strain localization, we provide evidence for lack of fully developed flow state in such a global extensional test. While SER ensures homogeneous extension until the onset of extensional failure, FSR (filament stretching rheometer) does the opposite by applying non-uniform extension. Thus, SER is to simple shear achieved in small gap approximation of parallel-plate displacement as FSR is to capillary extrusion that merely supplies a constant throughput. By monitoring the temperature of the specimens in melt extension, we detected a sizable level of internal energy that can be as high as a significant fraction of the total mechanical work. Moreover, the internal energy build-up continues monotonically until the onset of specimen breakup. We conclude that well-entangled melts cannot transform from the initial state of rubbery-like elastic deformation to a flow state in uniaxial extension, contrary to the claims based on the FSR measurements that a steady extensional flow state is accessible in uniaxial melt extension. Finally, we disclose additional evidence concerning the origin of the internal energy storage.

Wednesday 1:55 Snowy Egret SM34

The melt rheology of poly(ethylene oxide) powder mixtures of varying initial molecular weight distribution subject to non-oxidative thermal degradation

Craig D. Mansfield, Mubashir Q. Ansari, and Donald G. Baird
Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States

The chemical kinetics of the non-oxidative thermal degradation of (poly(ethylene oxide) (PEO) are well characterized in the literature. However, the rheological behavior of PEO subject to these conditions has not previously been addressed. The rheology of melt material streams plays an important role in predicting the optimal performance of melt processes, such as the co-extrusion process. Connecting the rheology of degrading PEO to the governing kinetics is of fundamental importance to predicting composition and rheological behavior as a function of processing conditions.

In this work, the rheological behavior of melts formed from PEO powder mixtures of varying molecular weight was characterized using a combination of dynamic small amplitude oscillatory shear (SAOS) tests and inception of steady shear tests. SAOS tests were used to eliminate shear induced mixing, which was studied separately with inception of shear tests. The SAOS test scheme used allowed for isolation of thermal degradation effects during data analysis. The effect of degradation on the rheology of PEO will be discussed. In addition, a model for non-oxidative thermal degradation connecting the observed rheological behavior to the governing chemical kinetics will be introduced.

Wednesday 2:20 Snowy Egret SM35

Polymer orientation contributions

Peter H. Gilbert and Jeffrey Giacomin
Chemical Engineering, Queen's University, Kingston, ON, Canada

Previously, we explored the dynamics of a dilute suspension of rigid dumbbells as a model for polymeric liquids in large-amplitude oscillatory shear (LAOS) flow. We derived the expression for the polymer orientation distribution, and then we decomposed this function into its first five harmonics (the zeroth, first, second, third and fourth harmonics), and then, we further separated the harmonics into their components in-phase and out-of-phase with cos n?t. In this work, we deepen our understanding of the relationship between the orientation distribution function and the shear stress and normal stress differences. We also investigate the components of orientation that do not contribute to either rheological measurement. We create three-dimensional plots of orientation to investigate the components of orientation that contribute to each rheological measurement. We discover that one orientation component contributes to all rheological measurements, while several components contribute to none of the rheological measurements.

Wednesday 2:45 Snowy Egret SM36

A force-level theory of tube deformation, microscopic yielding, emergent convective constraint release and nonlinear rheology of entangled polymer liquids

Ken Schweizer[1] and Daniel Sussman[2]
[1]Materials Science Department, University of Illinois at Urbana-Champaign, Urbana, IL, United States; [2]Physics Department, Syracuse University, Syracuse, NY, United States

We develop a force-level statistical mechanical approach to self-consistently construct the anharmonic tube confinement field for entangled fluids of needles and primitive-path (PP) chains. The latter is analyzed in two limiting situations where stretch is either fully relaxed or unrelaxed. The mechanical response is first studied in a nonlinear elastic limit where irreversible relaxation processes are turned off. Gaussian level analysis of transverse dynamic displacements predicts polymer orientation dilates the tube, but if chains are stretched the tube is compressed. A finite maximum entanglement force transversely localizing polymers is generically predicted, implying tube destruction can occur corresponding to microscopic yielding. The latter is directly relevant to nonlinear step strain and creep measurements. For needles and contour-relaxed PP chains, such yielding occurs at a stress of order the equilibrium shear modulus and a strain of order unity, suggesting a mechanically fragile network. But for stretched chains, tube compression strengthens transverse confinement, suggesting the onset of irreversibility requires chain retraction to initiate disentanglement. A full theory for startup continuous shear rheology of needle fluids is constructed where relaxation occurs only via deformation-perturbed reptation which is self-consistently coupled to tube dilation and macroscopic stress. With increasing strain, entanglements are lost, reptation speeds up, and a stress overshoot emerges due to very large tube dilation. Just beyond the overshoot, the longest relaxation time scales as the inverse shear rate, corresponding to a generic and emergent form of convective constraint release. The steady state flow stress and shear thinning behavior are quantitatively sensible. The non-classical physics predicted for entangled needles is likely relevant to chain melts at low Rouse Weissenberg numbers if stretch equilibration is fast.

Wednesday 3:35 Snowy Egret SM37

From wall slip to shear banding: A journey through creep

Sirui Ge, X.Y. Zhu, M. C. Wang, and Shi-Qing Wang
University of Akorn, Akron, OH, United States

We report wall slip, shear banding in rate-controlled startup shear on one set of polybutadiene (PB) solutions and entanglement-disentanglement transition during creep without any shear strain localization on another set of PB solutions. The new data provide a more comprehensive description of wall slip, show shear banding in absence of edge instabilities, and demonstrate that creep produces a truly meaning overshoot in the transient viscosity and is a particular insightful mode to learn about the nonlinear responses of highly entangled polymers to shear deformation.

Wednesday 4:00 Snowy Egret SM38

Shear-banding of entangled polymer solutions under planar large amplitude oscillatory shear

Seunghwan Shin, Kevin D. Dorfman, and Xiang Cheng
Chemical Enginnering, University of Minnesota, Minneapolis, MN 55455, United States

Using high-resolution confocal rheometry, we study the shear profiles of well-entangled DNA solutions under large amplitude oscillatory shear (LAOS) in a planar Couette cell. With increasing shear strains and Weissenberg numbers (Wi), we observe a clear transition from normal Newtonian linear shear profiles to wall-slip dominant shear profiles and finally to shear-banding profiles at high Wi. To investigate the microscopic origin of the observed shear banding, we study the dynamics of micron-sized tracers embedded in DNA solutions. Surprisingly, the motions of tracer particles in the shear frame exhibit a strong dynamic heterogeneity within the high-shear-rate band of the shear-banding flows. We show that the probability distribution functions of particle displacements follow a power-law scaling at large displacements, indicating Levy-flight-type motions of particles. Our experiments suggest that the shear banding of concentrated DNA solutions under LAOS arises from the local breakage of the entanglement of polymer networks.

Thursday Morning

Symposium AP
Award Presentations

Metzner Award Presentation

Thursday 8:00 Audubon DEF AP1

From simple polymers to supramolecular assemblies: Understanding and predicting the rheology of complex polymeric structures

Evelyne Van Ruymbeke
Bio and Soft Matter, Inst. on Cond. Matter and Nano-science, Université catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

Understanding and tailoring the viscoelastic response of polymer melts or concentrated solutions from the knowledge of their molecular structure (architecture) represents a formidable challenge and remains a prime field of soft matter research, with several important and fundamental questions still open. To this end, we have developed a general coarse-grained approach based on the tube model, that we are now using as a predictive tool in order to investigate the viscoelastic properties of complex, entangled polymer architectures and to elucidate the molecular origin of their relaxation processes. In this presentation, we first outline the construction of the time marching algorithm, and then discuss some selected examples. We investigate the viscoelastic properties of polymer blends composed of monodisperse linear, star- or H- chains moving in a short linear matrix, which are of particular interest since these blends are governed by two distinct dynamics and since the motions of the slower chains are directly related to the dynamics of the short chains: depending on the time scale investigated, the latter can act either as part of the constraining environment, or as solvent for the long chains. In order to quantify the influence of this dynamic dilution process, we propose a new relaxation mechanism, which accounts for the tension equilibration along the long chain and provides an accurate description of their viscoelastic properties. Next, we implement this predictive toolbox to the complex rheology of entangled macromolecular self-assemblies built from sticky polymers (telechelic or randomly functionalized). These systems are modular, exhibiting reversible structural changes under the influence of temperature or deformation, and are usually thermorheologically complex. Their dynamic response is often characterized by two distinct processes, whose signature is the presence of two clear rubbery plateaux, yet the respective relaxation mechanisms bear similarities with those of simple binary blends.

Symposium SC
Suspensions, Colloids and Granular Media

Organizers: Jason Butler and Jeremie Palacci

Thursday 8:40 Audubon B SC43

Rheological properties of CNC and hydrophobic CNC suspensions in a polar solvent

Helia Sojoudi, Marie-Claude Heuzey, and Pierre J. Carreau
CREPEC, Chemical Engineering Department, Polytechnique Montreal, Montreal, Quebec H3C3A7, Canada

The rheological behavior of suspensions of CNCs and modified CNCs (mCNCs) in dimethyl sulfoxide (DMSO) was investigated. The efficiency of the surface modification of CNCs by grafting an organic acid chloride to produce hydrophobic CNCs has been verified by X-ray photoelectron spectroscopy (XPS). The 1 wt % CNC suspension in DMSO underwent gelation at 70 °C after one day. This network formation did not occur at room temperature. For gels containing 3 wt% CNCs, the low frequency complex viscosity at 70 °C increased by almost 4 decades after one day. For the mCNC suspensions a weak gel was formed from the first day; temperature did not affect gelation and aging effects were marginal. Finally, the rheological properties of suspensions in a 10 wt% of polylactic acid (PLA) solution were investigated. Adding 1.9 wt% CNCs and mCNCs to the PLA solution changed the rheological behavior from Newtonian to shear-thinning. The rheological properties of both types of suspensions increased during the first and second days and the presence of PLA did not prevent the gel formation. However, the relative viscosity of the CNC gels containing PLA was lower than that of samples without PLA, attributed to a decrease of the CNC nanoparticles interactions by the PLA chains. Also, for the PLA/mCNC systems, the PLA chains did not interfere in the network formation, but the relative viscosity of these suspensions was much lower than that of the PLA/CNC suspensions.

Thursday 9:05 Audubon B SC44

Quantitative nonlinear thixotropic model with stretched exponential response in transient shear flows

Yufei Wei, Michael J. Solomon, and Ronald G. Larson
Chemical Engineering, University of Michigan, Ann Arbor, MI, United States

We present a phenomenological rheological model for ideal thixotropy [1]. The model introduces a spectrum of structure parameters that collectively relaxes as a stretched exponential. It retains time-invariance symmetry with only a stretching exponent as an additional model parameter relative to conventional single-structure-parameter models. The kinetic equations for structure parameters are formulated systematically based on experimental results. They are nonlinear in both the structure parameters and the flow parameters of strain rate or stress. Through introducing multiple structure parameters, the model successfully captures the stretched-exponential and non-monotonic evolution of stress or shear rate in intermittent step tests. By using nonlinear kinetic equations, the model correctly predicts relaxation times' dependence on both the initial and final values of shear rate or stress in step tests. The model is tested in both shear-rate-controlled and stress-controlled rheological tests. We further show that this ideal thixotropic model can be combined with existing methods of introducing viscoelasticity and flow-induced anisotropy so as to extend its range of validity. Next, we report a brief comparative study between this ideal thixotropic model and a simple population balance model which calculates the bulk rheological property based on the dynamics of the aggregates size distribution.

[1] Y. Wei, M. J. Solomon, R. G. Larson, Journal of Rheology, 60 (2016)

Thursday 9:30 Audubon B SC45

Percolation behavior of carbon black suspensions in polar aprotic solvents

Julie B. Hipp[1], Jeffrey J. Richards[2], and Norman J. Wagner[1]
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In this work, the microstructural origin of the rheo-electric behavior of carbon black gels and suspensions is studied. These materials find widespread use as conductive fillers in composites and slurry-based electrochemical energy storage technologies. In these applications, both the viscosity and electrical conductivity are key design parameters determined by their microstructure. Using small angle neutron scattering (SANS) and electron microscopy, we perform detailed structural analysis on carbon black suspensions as a function of volume fraction for two commonly used conductive additives - KetjenBlack and Vulcan. From these measurements, the static structure factor is determined and characterized at low-Q by a power-law scaling, $I(Q) \sim Q^{-3}$. Similar to depletion gels, this scaling confirms that carbon black gels form as a result of arrested phase separation. We characterize the onset of gelation using oscillatory rheological measurements and identify the percolation threshold associated with the jamming transition. While the onset of mechanical percolation is commonly associated with the electrical percolation threshold for these materials, results from impedance spectroscopy measurements show that the electrical percolation threshold occurs at far lower volume fractions. Further, the power-law scalings associated with the yield stress and elastic moduli are not consistent with that extracted from the conductivity. These results suggest a rich relationship between electrical conductivity and the fluid properties of carbon black dispersions that could improve the design of future low-viscosity, high conductivity conductive additives for electrochemical flow applications.

Thursday 10:25 Audubon B SC46

Kaolinite suspension as a model fluid for fluid dynamics studies of fluid fine tailings

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The rheology of fluid fine tailings is studied, and compared with that of kaolinite suspensions having the same zeta potential, solids volume fraction, and relatively similar particle size distribution. The suspensions were examined under shear and oscillatory deformation fields and by means of a coupled rheometry-velocimetry technique to investigate their yielding, ageing, and steady-state flow behaviour under shear rate and stress controlled conditions. Using dynamic strain sweep experiments, it is shown that the samples exhibit a maximum in their loss modulus during yielding while they exhibit two different regimes of strain dependency in their fluidized regime. Samples are found to exhibit a plateau region in their stress-strain curves measured by the dynamic strain sweep experiments, due to presence of flow instabilities. Small amplitude oscillatory tests are performed to study ageing behaviour of the suspensions with different shear histories. The ageing process is found to depend strongly on the shear history of the samples prior to rest. Shear flow experiments under stress-controlled conditions show that both suspensions exhibit a plateau in their flow curves where a slight increase of the shear stress results in a dramatic change of the shear rate, implying the occurrence of shear-banding flow instability which is further confirmed by the measurement of the velocity profiles of the samples in a wide gap rheometer. This agrees with the behaviour observed in the oscillatory deformation mode and implies that below a critical shear stress no stable flow can be achieved in the suspensions. Fluid fine tailings and kaolinite suspensions are found to exhibit fairly similar rheological behaviour, when their zeta potentials, solids volume fractions, and particle size distributions are matched.

Thursday 10:50 Audubon B SC47

The effect of pre hydration on the rheological properties of Portland cement with and without superplasticizer

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It's common to find in several industrial process, the usage of pre hydrated cement in formulation of mortar and concrete, because there is not effective control on the cement's storage, resulting on pre hydration during the production of the cement, grinding, transportation and the subsequently storage. Previous studies shows that pre hydration has a negative impact on compressive strength, especially in the early ages, increasing the setting time and affecting the workability, but it is not a consensus because the setting time can be reduced. Levels of pre-hydration higher than e 0,3% can reduce considerably the clinker re-activity and also modify the cement performance. This study assessed changes in the rheological properties of Portland cement exposed to relative humidity (RHs) of 90%, by exposing the cement samples on an environment of NH4Cl saturated solution in order to evaluate the impact of pre-hydrated cement versus non pre-hydrated cement on the rheological properties of the paste with and without superplasticizer. On the fresh state the paste was evaluated on plate-plate rheometer the viscosity, yields stress and hysteresis area of each cement on a cement ratio 0,4 by using a fixed admixture dosage. Along the time it was conducted the oscillatory rheometry to evaluate the storage modulus (G') of the paste comparing the consolidation with the hydration kinetics obtained by calorimetric evaluation of the same pastes. Based on the previous rheometer results the shear stress response to applied shear rate, indicates that the pre-hydrated sample presents lower level of shear stress than the non-pre hydrated sample, it's because of the higher reactivity of the non-pre hydrated sample, but these results are not enough to explain the rheological changes, so oscillatory evaluation is needs to corroborate with his study as well as isothermal calorimetry.

Thursday 11:15 Audubon B SC48

The effect of polysaccharide gum on large amplitude oscillatory shear (LAOS) behavior of corn starch suspensions

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Many suspensions in food industry contain rigid or deformable particles in a liquid medium can show a very wide range of rheological behavior depending on constituents, concentration and the particle size and distribution. The rheological behavior of food suspensions may vary: Newtonian to non-Newtonian, thixotropic to antithixotropic, etc. Corn starch is a well-known shear thickening material at high solid content. Handling a shear thickening in production lines can often cause problems like jamming the small openings. During different kinds of processing, the food products are often subjected to large deformations, therefore LAOS can offer a better understanding of the structural changes of material. The aim of this study is to investigate the change in LAOS behavior of a shear thickening fluid by adding polysaccharide gums used in food industry which exhibit shear thinning behavior. This study includes determination of change in LAOS behavior of corn starch suspensions with different types and concentrations of polysaccharide gums (0.2%, 0.4%, and 0.6% wt) to understand how to adjust flow behavior of a suspension with high solid content. The rheological parameters (G'M, G'L, ?'L, ?'M, e3/e1, v3/v1, S and T) which were introduced by Ewoldt and McKinley (2008) were evaluated for the samples at a strain in the range of 0.01-200%. Lissajous-Bowditch curves were utilized to evaluate the elastic component and viscous component of the strain separately, to provide a visualized and qualitative study of the material transition process under increasing strain. Concentrated corn starch suspension showed shear thickening and shear softening properties (evidenced by positive value of v3/v1 and negative value of e3/e1 at higher strain), while after addition of polysacchride gum solution, the samples showed shear thinning and shear softening properties (negative value of v3/v1 and negative value of e3/e1 at higher strain).

Thursday 11:40 Audubon B SC49

Effect of HEC on gelling properties of CNC and ECNC suspensions

Gilles Lenfant[1], Marie-Claude Heuzey[1], Theo T. van de Ven[2], and Pierre J. Carreau[1]
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Electrosterically stabilized nanocrystals of cellulose (ECNCs) aqueous suspensions were shown to have no phase transition from the dilute to the concentrated regime compared to nanocrystals of cellulose (CNC) suspensions. Since they are liquid-like up to their gelation (˜10 wt%), we added hydroxyethyl cellulose (HEC) to induce gelation at lower ECNC contents, as already observed for CNCs. HEC was found to adsorb up to 450 and 250 mg/g on CNCs and ECNCs, respectively. HEC had a great impact on CNC suspensions. For a 4 wt% CNC suspension, adding 0.1 to 0.5 wt% HEC led to the formation of strong gels with a storage modulus of about 100 Pa independent of the frequency. We could also induce gelation of CNC suspensions at CNC content as low as 0.2 wt% when adding HEC in a ratio of 1:1 with respect to CNCs and in presence of 1 mM CaCl2. These CNC suspensions exhibited a strong non-Newtonian character and their steady-shear data had to be corrected due to fast structure build up kinetics. The onset of the viscoelastic properties was observed in ECNC suspension at 4wt%, but time-dependence was not as important as for CNC suspensions.

Symposium NF
Non-Newtonian Fluid Mechanics & Instabilities

Organizers: Sandra Lerouge and Becca Thomases

Thursday 8:40 Audubon DEF NF20

Revolving flow and heat transfer of a non-Newtonian fluid over an infinite stretchable disk

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The revolving flow problem, where the fluid rotates like a rigid body at a larger distance from an infinite stationary solid disk was studied by Bodewadt. The flow can be well explained by the simple 'Tea cup experiment'. The radial pressure gradient being balanced by the centrifugal forces. Fluid flows towards the axis of rotation and swepts upwards. The boundary layer, which develops on the disk, produces a secondary flow of the wake type. This secondary flow is the reason of accumulation of tea leaves at the center of the tea cup after a vigorous stirring. In this paper, the revolving flow and heat transfer of a non-Newtonian Reiner-Rivlin fluid over a stationary stretchable surface has been studied numerically. The radial variation of the disk's surface temperature follows a power law. The resulting coupled and highly nonlinear system of equations are solved numerically, using the finite difference method. It is observed that the disk stretching has a prominent effect on both momentum and thermal boundary layers. The solutions indicate that the strength of the induced secondary flow in the boundary layer decreases significantly with an increase in the stretching parameter. The oscillatory nature of the velocity profiles vanishes completely by the action of even moderate radial stretching. As a result of reduction in the momentum boundary layer, the thermal boundary layer thickness decreases significantly with an increase in the radial stretching. The radial distribution of the disk surface temperature makes significant effect on the temperature profiles in the boundary layer. For zero stretching, they are decreasing for the decreasing disk temperature, practically constant for the isothermal disk, and increasing in the vicinity of the wall for the increasing disk temperature. Stretching causes heat transfer enhancement and an increase in the radial shear stresses at the disk surface.

Thursday 9:05 Audubon DEF NF21

Understanding viscoelastic suspensions via numerical simulation

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There are no comprehensive simulation-based tools for engineering the flows of viscoelastic fluid-particle suspensions in fully three-dimensional geometries. On the other hand, the need for such a tool in engineering applications is immense. Suspensions of rigid particles in viscoelastic fluids play key roles in many energy applications and advanced manufacturing applications. In the present work, we describe the development of an Immersed Boundary Method (IB) to simulate the viscoelastic flow in suspensions of nonBrownian spheres. Since the phenomomena of interest occur typically at O(1) values of the flow Weissenberg or Deborah number, we describe the methods necessary to obtain accurate resolution of the stress boundary layers near the particle surface even in the IB framework. Since the code is massively parallel, we demonstrate the simulation of a few hundred particles with the code, and examine in detail two problems where the multi-particle viscoelastic interactions provide unique physical results: 1) The sedimentation of spheres in orthogonal shear in a Taylor Couette Cell and 2) The rheology of a sphere suspension in a viscoelastic fluid in a parallel plate device. We examine these suspensions up to 5% volume fraction and demonstrate that, in each case, the dilute approximation is poor even at very low volume fraction because of the finite Wi wake interactions between particles.

Thursday 9:30 Audubon DEF NF22

Drag reduction and rheological properties of a viscoelastic mixed cationic / zwitterionic surfactant system exhibiting dilution precipitation

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In this study we describe a novel mixed cationic / zwitterionic drag reducing surfactant system with an added counterion (sodium salicylate) dissolved in distilled water which displays unusual properties. At certain compositions the solution is strongly viscoelastic and drag reducing over a wide range of temperatures. Surprisingly, precipitation of much of the mixture is observed upon dilution with distilled water. The solution also exhibits shear precipitation when sheared if the composition is near the precipitation region. The mass fraction of solute present in the precipitate depends on the original composition. When the precipitate and supernatant are separated by decanting or filtration, the liquid phase is water like, and a solution made by dissolving the precipitate in the original volume of water is viscoelastic. Ternary phase diagrams were created. Rotational rheometry was used to characterize the shear viscosities and first normal stress differences of the original solutions, precipitate solutions, and supernatants from various original compositions. Extensional viscosities were measured using a modified RFX. FTIR, H-NMR, and mass spectrometry measurements were used to characterize the compositions of the phases.

Thursday 10:25 Audubon DEF NF23

Ink transfer of non-Newtonian fluids in gravure printing: The effect of shear and extensional deformation

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Roll-roll pattering of nanoscale features on flexible substrates is of great industrial and commercial importance due to its low cost and high throughput. Gravure printing is a roll-roll processing technique used to coat/print thin films less than 50 µm for a variety of commercial applications. We present the study on the effect the complex fluid rheology can have on the dynamics of liquid transfer from an idealized gravure cell to a flat rigid substrate. During the ink transfer process, as the ink is deposited onto the substrate, the liquid bridge experiences complex kinematics; a combination of shear and extension due to relative motion between the gravure cell and web. Previously, we have investigated the ink transfer behavior of shear-thickening and viscoelastic fluids while modeling the ink transfer process as a pure extensional flow. Shear can become important when there is a relative motion between the two rollers. In this talk, we will present an extension of our previous studies on shear-thickening and viscoelastic fluids, to investigate the importance of shear in ink transfer from gravure cells. The model viscoelastic fluids used in the study are aqueous polyethylene oxide solution in water and the shear thickening fluids used are fumed silica nanoparticle dispersions in polypropylene glycol (PPG). The fluid pickout from the gravure cell was studied as a function of extensional and shear deformation rates. The fluid filament interface profile evolution during the pickout process was also examined. For the shear thickening fluid, the pickout from pure extensional flow was found to be enhanced compared to Newtonian fluids at moderate velocities, due to extensional thickening of the fluid. The fluid pickout of the shear thickening fluid resulting from a pure shear exhibited a qualitatively similar trend to that of the extensional pickout although the pickout was significantly smaller. At large rates, shear was found to negatively affect the fluid pickout by causing an early onset of extensional thinning.

Thursday 10:50 Audubon DEF NF24

Quantitative predictions of the breakup times of inviscid-elastic filaments of dilute polymer solutions

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The applicability of dilute polymer solutions in free surface flow processes that involve a strong extensional component depends to a large extend on the longevity of the filament that forms after the development of a Rayleigh instability on an initial liquid bridge and that connects two consecutively forming droplets. Based on the analysis of V. Entov and J. Hinch [1], the stability and thinning dynamics of this liquid bridge has been described theoretically in great detail, and the predicted dynamics have been confirmed experimentally in several publications. In particular, a recent publication by C. Wagner et al. [2] describes an analytical solution for this elastocapillary (EC) balance regime, that allows a quantitative description of the breakup time for a known relaxation time and finite extensibility of the polymer in solutions, once the onset point of this EC regime I known. However, their analysis for the description of this onset point was based on the assumption of a viscid fluid. Since many dilute polymer in practical applications involve solvents that behave inviscid during filament thinning, we present in this paper an analytical solution for the evolution of the polymer stretch in an inviscid solvent, based on the FENE-P model, that allows us to quantitatively predict the breakup time of inviscid-elastic filaments. Predictions of this model are compared to experimental results for a number of model polymer solutions that span the relevant range of intrinsic Deborah and Elastocapillary numbers for actual applications.

[1] V.M. Entov, E.J. Hinch, JNNFM 72 (1997), 31-53. [2] C. Wagner, L. Bourouiba, G.H. McKinley, JNNFM 218 (2015), 53-61.

Thursday 11:15 Audubon DEF NF25

Non-uniform flow of glasses: The “shear-gradient concentration coupling instability”

Jan K. Dhont

Forschungszentrum Juelich, Jülich, Germany

There are several types of shear-induced instabilities in soft-matter systems, like vorticity- and gradient-banding. The microscopic origin of these two instabilities is by now reasonably well understood. There is, however, an instability that can be referred to as "the Shear-gradient Concentration Coupling instability" (the SCC-instability) that has been largely ignored due to the lack of understanding of its microscopic origin. This instability is due to a postulated shear-gradient induced mass flux together with a strong coupling of the stress to concentration. The origin of the shear-induced mass flux resulting from direct interactions is so far not understood, and explicit expressions for the corresponding transport coefficient have therefore not been derived. In this presentation, the origin of this mass flux is discussed, an explicit expression for the corresponding transport coefficient is presented, and numerical results are discussed for the stationary non-uniform flow profiles and concentration profiles of an initially SCC-unstable system, which will be compared to experiments on hard-sphere glasses [H. Jin, K. Kang, A.K. Hyun, J.K.G. Dhont, Soft Matter 10 (2014) 9470].

Symposium SL
Solids & Composites

Organizers: Jon Seppala and Cathy Jackson

Thursday 9:05 White Ibis SL7

The quest for an effective viscosity model for polymer nanocomposites

Marissa Giovino[1], Julia Pribyl[2], Brian Benicewicz[2], and Linda Schadler[1]
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Polymer nanocomposites have been shown to display improved thermal, mechanical and electrical properties over polymer matrices even at low loadings. Dispersion has proven to be a key factor in property enhancement for these materials. One method of achieving good dispersion is to densely graft a short brush to prevent enthalpic attraction and a sparsely grafted long brush to provide entanglements with the matrix. Effectively processing these materials is challenging. Currently there are equations to predict the viscosity of colloidal suspensions. These equations don't work well for polymer grafted nanoparticles, which are necessary to achieve good dispersion in high molecular weight polymer matrices. The complex rheology of these materials needs to be understood to effectively process them. Towards this end, the viscosity of a model system has been measured. The model system consists of SiO2 nanoparticles grafted with two populations of polystyrene brushes: one short brush and one long brush. These were dispersed into two homopolymer matrices (96 kg/mol and 190 kg/mol) at different loadings. The composite viscosity was measured for each sample using oscillatory rheology. It was found that the composites have significantly different glass transition temperatures. To normalize this effect the viscosities were shifted to an isohomologous temperature. The shifted data was fit by two different models: the Batchelor model and an empirical model developed for star polymer-linear polymer blends. This presentation will report our progress in determining the best model for prediction and the implications for what polymer physics is driving the rheological behavior.

Thursday 9:30 White Ibis SL8

Shear and extensional rheology of linear low density polyethylene/graphene nanocomposites

Sung Cik Mun and Christopher W. Macosko
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We investigated the shear and extensional rheology of melt-compounded linear low density polyethylene (LLDPE)/graphene nanocomposites with different concentrations of graphene nanoplatelets. It is observed that small quantities of graphene (< 5.0 wt%) with high aspect ratio significantly alter the shear and extensional flow behavior of LLDPE melt. Small angle oscillatory shear measurements indicate the terminal relaxation behavior at low frequencies changes from liquid-like to pseudo-solid-like response by the formation of graphene networks with increasing concentration. The transient extensional viscosity of the nanocomposites presents strain hardening over a wide range of Hencky strain rates at low concentrations (0.25 and 0.50 wt%), whereas LLDPE melt does not exhibit strain hardening. On the other hand, higher loadings of graphene (> 1.0 wt%) diminish strain hardening, while the extensional viscosity increases over a broad range of strains but reaches a plateau at large strains. These concentration-dependent rheological properties are correlated to the dispersion and size of graphene as well as the electrical conductivity of nanocomposites.

Thursday 10:25 White Ibis SL9

Stress growth and fiber orientation dynamics of glass-fiber reinforced polypropylene under non-lubricated squeeze flow

Gregory M. Lambert and Donald G. Baird
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Although fiber-reinforced plastics have been useful, their processing presents several challenges. Wet-laying can be used to manufacture parts with simple geometries, but more complex shapes require injection molding. This process is highly destructive to the fibers and causes them to reorient as the mold is filled. Thus, the ability to predict and control fiber attrition and orientation during processing - and by extension the mechanical properties of the molded part - is highly important to the process design.

Orientation models have been developed but these all rely on empirical parameters. In standard practice one obtains the parameters by fitting to orientation data in a molded part, tying the parameters to the injection conditions. Any change in the conditions (change in screw rotational speed, change in screw back pressure, etc.) requires new data. Obtaining quality orientation data is not a trivial matter and evaluating multiple conditions can easily add weeks to the process design phase.

Transient rheological flows such as the startup of simple shear or extension could be used as an alternative. One theoretical shortcoming of this approach is the fact that fibers are not expected to flex under homogeneous flows. Injection molded parts often contain a small portion of flexed fibers, but the rheological technique is incapable of replicating this behavior.

This work is concerned with the continuation of efforts to evaluate orientation models by investigating squeeze flow through a planar channel. This flow is of particular interest because it is a controllable, measureable, inhomogeneous flow. Orientation evolution will be presented alongside stress growth data and the ability of the test to reproduce fiber flexing will be evaluated. The effect of fiber length and flexibility on the rheology

and evolution of orientation is also considered. Furthermore, the ability of the bead-rod model to model the flow of semi-flexible fibers is compared to the conventional rigid fiber model.

Thursday 10:50 White Ibis SL10

Study on thixotropic behavior of ballistic clay backing materials by rubber process analyzer

Ran Tao, Kirk D. Rice, and Aaron M. Forster
Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

Clay is historically used as the backing material for standards-based ballistic evaluation of soft body armor based on both penetration and deformation effects after ballistic impact. However, clay is known to be a highly thixotropic material, whose rheological properties depend strongly on thermomechanical history and are only partially reversible. Therefore, a complete knowledge of rheological properties of clay is desired. In this work, we perform measurements to characterize rheological properties using a rubber process analyzer. Test methods employed include oscillation strain sweep, frequency sweep, aging stress relaxation, and oscillatory strain ramp and recovery. The results show that the material becomes softer under dynamic deformation and partially recover when the deformation is discontinued. The results also indicate that slow changes in microstructure upon aging also depend on the deformation history as well as temperature. Experimental protocols developed in this study for thixotropy research are applied to characterize other synthetic clay systems. In addition, large amplitude oscillatory shear (LAOS) fingerprints of those materials are obtained and discussed.

Thursday 11:15 White Ibis SL11

Assessing the orientation relaxation of thermotropic liquid crystalline polymers below their melting point using dynamic mechanical analysis

Mubashir Q. Ansari, Craig D. Mansfield, and Donald G. Baird
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In this work, dynamic mechanical analysis (DMA) was used to study the orientation relaxation of thermotropic liquid crystalline polymers (TLCPs) at temperatures up to 20 °C below their melting point. TLCPs are in general composed of rod-like aromatic monomers imparting high mechanical properties due to stearic hindrance. The motivation of this effort is based on the use of the TLCPs to reinforce filaments consisting of a matrix with a processing temperature of 30-50 °C below the melting point, Tm, of the TLCP. The composite materials are used in fused deposition modeling (FDM) and are processed below the Tm of the TLCPs. It was observed that the drop in tensile strength and modulus of the compression molded composite occurs when they are processed at temperatures near the Tm of the TLCP's. It was suspected that the drop in tensile properties is due to orientation order relaxation of TLCP's. To identify the temperature below which relaxation is minimum, DMA was carried out. It was found that the DMA tests captured the extent of orientation order relaxation within the liquid crystalline phase. DMA tests were carried out from room temperature to various temperatures up to 20 to 30 °C below Tm. After exposure to these temperatures for varying time durations, the samples were cooled to room temperature. The relaxation in orientation order that arose due to exposure to conditions at 20 °C below Tm led to a substantial drop in storage modulus relative to no thermal exposure. However, staying 30 °C below Tm did not lead to significant reduction in properties. In addition, longer exposure times at each temperature led to larger observed orientation order relaxation as the molecules had more time for relaxation to occur. It was concluded that the drop in tensile properties was due to orientation relaxation.

Symposium AT
Advanced Techniques and Methods

Organizers: Anthony Kotula and Matthew E. Helgeson

Thursday 8:40 Sandhill Crane AT10

Discretized modeling of viscoelastic liquids during centrifugal spinning

Mounica Jyothi Divvela and Yong L. Joo
Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14850, United States

Mesoscale modeling and simulation of the jetting behavior of viscoelastic liquids during centrifugal spinning is presented. We apply a discretized method to model viscoelastic flow of a Boger fluid in a rotated disk, which ejects the liquid due to centrifugal force. As opposed to conventional continuum methods this model works in a Lagrangian frame and is a combination of continuum and molecular dynamics approach. The fiber that is ejected out of the disk is described using a bead-spring model, by considering the fiber to be made of discrete beads connected with massless springs. Similar to molecular dynamic simulation, the beads are subjected to external forces, but the continuum aspect is preserved due to the connecting springs. The trajectory of the jet is obtained by solving Newton's second law of motion by formulating essential forces including viscoelastic, surface tension and drag forces for each bead. As this method does not involve differential equations as observed in continuum method, we can overcome mathematical complexity of the curvilinear computational domain due to the rotation of the disk. We simulated the flow of the liquid in the nozzle as well to incorporate shear stress effects, to provide a more reliable tool for highly viscoelastic polymers. The rheological behavior of the polymeric liquid is determined using both Oldroyd B and FENE-P models considering infinite and finite polymer chain extension, respectively. We first validated the jet profile predictions of the Newtonian fluid from discretized modeling with the continuum asymptotic theory. We then performed a parameter study to understand the effects of various properties such as viscoelasticity, surface tension on

the behavior of the viscoelastic jet and also compared the simulation results using both the rheological models with the experimental observations of polyisobutylene in polybutene Boger fluid. If time permits, discretized modeling of polymer melts during non-isothermal centrifugal spinning will be presented.

Thursday 9:05 Sandhill Crane AT11

Rheological measurement system using disk-type electromagnetically spinning technique

Taichi Hirano and Keiji Sakai

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We developed a measurement system of flow curve in a wide range of shear strain, even for lowly viscous liquids using a noncontact driving torque. The system is equipped with the electromagnetically spinning technique, which can also be applied to the direct detection of yield stress.

Lately, the electromagnetically spinning (EMS) technique was developed by our lab, and is now commercially available as EMS viscometer. In the EMS viscometer, a spherical rotor is used for balancing ease of use and operation stability. Therefore, a serious problem remains that the determination of the accurate shear strain or rate is impossible. To solve this problem and apply the EMS technique to the accurate rheological measurement, we have manufactured a rheometer named Rheology-Spectrometer.

In the newly developed system, a thin disk rotor attached to a spindle is set into a sample container, and the disk is sandwiched between the cover and the cell bottom. The liquid layers above and below the dick have the same thickness and equally contribute to the viscous torque of the sample liquid. This geometric character is supposed to be a "double" parallel-plate system, and then, the shear rate of this system is estimated precisely from the gap length and the rotational speed and the radius of the rotor. We measured the relation between the viscosity and the shear rate for the standard liquid with a non-Newtonian property, and also found a numerical procedure to obtain the "true" viscosity curve, which was consistent with that obtained from a cone-plate system.

The Rheology-Spectrometer has an advantage of unique measurement; the sample container including the rotor and the sample liquid is sealed and disposable due to the noncontact driving manner of the EMS technique. These features are outstanding when compared with the conventional viscometers or rheometers, and therefore, our measurement system would be a powerful tool for the rheological approach to volatile substances and biological specimens.

Thursday 9:30 Sandhill Crane AT12

Near-wall velocimetry on a rheometer by evanescent wave dynamic light scattering

Antonio Giuliani, Ruel McEnzie, and Benoit Loppinet

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Classical assumptions like no-slip boundary conditions and continuity in stress and flow profiles are all but universal in flow, especially when one considers complex fluids. The interplay of mechanical properties of the fluid, hydrodynamic and chemico-physical interactions with the wall may result in discontinuities and non-adhesion of the fluid to the walls. Assessing the near wall velocity profile can therefore be important in a number of situations, in particular in the context of the possible occurrence of slip at the wall. The advancement of relevant experimental techniques is then desirable. Here, we present the implementation and use of evanescent wave dynamic light scattering for near-wall velocimetry (in a range of 100 nm from surface) on a rotational rheometer. With this technique, we gain access to both a near-wall velocity as well as to the near-wall shear rate. The tool can be relatively easily implemented on commercial rheometers. We describe the principles of the technique [1] and demonstrate its use on various fluids, including simple Newtonian fluids, colloidal suspensions and polymer solutions. The technique takes advantage of the penetration depth (order of 500nm) of light at total internal reflection to resolve the velocity gradient of colloidal tracers (220nm) in the penetration depth as well as the velocity of the slowest tracers nearest to the the glass bottom plate of the rheometer. Linear no slip flows are observed for Newtonian fluids. Visco-elastic fluids were found to present near wall shear rate different from the macroscopic shear rate, and non-zero slip velocities and lengths. In particular the ability to detect the presence and onset of slip is shown in the case of Laponite dispersion.

[1]- B. Loppinet, J. K. G. Dhont, P. Lang, Eur. Phys. J. E (2012) 35: 62

Thursday 10:25 Sandhill Crane AT13

Customized 3D-printed tool geometries for rheometry of soft matter

Dimitri A. Bikos and Thomas G. Mason

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The rapid growth of three-dimensional (3D) printing has spurred interest in its use in a wide variety of scientific fields. Here, we present a method of producing customized 3D-printed polymeric geometries with accuracies and tolerances suitable for performing rheometry of soft matter. By exploiting the high in-plane resolution of consumer grade 3D printers, we have designed standard and customized 3D-printed tools, showing that standard geometries made of acrylonitrile butadiene styrene (ABS) can perform comparably well as titanium geometries for rotary oscillatory and steady-shear rheometry of concentrated oil-in-water nanoemulsions. As an example of a customized geometry, we 3D-print a raised annular parallel plate geometry that offers a more uniform strain field and higher torque response than the standard parallel plate for the same sample volume. Additionally, we show that customized tool roughness can be readily added to 3D-printed tools, thereby reducing slip of soft materials in contact with tool surfaces. Although polymeric 3D-printed tools are not anticipated to be viable replacements of metal tools in all cases, they nevertheless can offer an inexpensive and viable option for expanding the range of tool geometries for mechanical rheometers.

Thursday 10:50 Sandhill Crane AT14

Fluidized bed rheology for granular media

Joerg Laeuger[1] and Denis Schuetz[2]
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Dry granular beds are made "fluid-like" by an upstream of gas to produce gas fluidized beds. Widely used in a variety of industries they share certain similarities to suspensions, namely the combination of a viscous phase (gas) and a solid phase (particulates). A fluidized bed rheology setup consisting of a powder containing cylinder with a gas permeable bottom, through which a defined controlled gas flow is run into the powder sample, and a geometry placed in the powder. Attached to a rotational rheometer such a setup allows real rheological measurements over large ranges of shear rates and shear stresses on powder systems in a well-defined fluidization state. Being able to measure small torques in a reproducible manner enables a proper rheological study of fluidized beds similar to the rheology of complex fluids. Before the actual rheological measurement a pressure drop test reveals the fluidization behavior of a given powder and determines the minimum volumetric gas flow rate for full fluidization. A simple rotational test at a fixed speed on full fluidized samples gives the cohesion strength of the powder, which is an important measure for many powder applications and processes, such as pipe flow, dosing, or 3D-printing. To obtain absolute viscosity values a linear velocity profile is required and slip needs to be prevented. Different concentric cylinders smooth, rough and profiled surfaces were tested. Viscosity curves of a glass bead sample in the un-fluidized and the fully fluidized state measured with two profiled cylinders with different sizes are in good agreement indicating that the no slip condition is met. Results of viscosity curves in different fluidization states are presented and are compared to the behavior of liquid suspensions. While exhibiting some unique effects, the shear rate dependent behavior of a gas fluidized bed can be for the most part be linked to that of particulate suspension.

Poster Session

Symposium PO
Poster Session

Organizers: Daniel Blair and Steve Hudson

Wednesday 6:00 Foyer-Stairs/Windows PO1

Rheological investigation of nanocurcumin with carboxymethyl cellulose

Leela Rakesh[1] and Nick Ventimiglia[2]
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Curcumin has been found to have antiseptic, antioxidant, antitumor, antibacterial, antiviral, and anti-inflammatory properties, which have been used since ancient time. Curcumin has also been identified as a nuclear vitamin D receptor (VDR) ligands, and is beneficial for cancer chemo-prevention, Alzheimer's disease, Huntington etc. The impact of nanocurcumin (CUR) (natural diphenol) with Carboxymethyl cellulose(CMC) on the physcio-chemical and morphological properties have been considered in this preliminary studies. Both rheology and dissolution of nanocurcumin will be monitored to understand the critical polymeric matrix properties required to control the release rate of nanocurcumin in aqueous dispersion for better solubility. CMC and other types of cellulose /CUR dispersions could be used in the form of gel pad /injectable /fluorescent solution to transport the healing value of curcumin in a well-ordered process. The flow behavior of CMC with and without nanocurcumin will be determined using AR 2000 rheometer for different concentrations at 20-80 °C, and at shear rate between 10 -2 to 10 3 / s.

Wednesday 6:00 Foyer-Stairs/Windows PO2

Molecular dynamics investigation of temperature and pH driven drug release from carbon nanotubes with antioxidant

Leela Rakesh[1] and Sophie Bedford[2]
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There are many nanodevices, polymers, antioxidants and surfactants are being used to deliver time released drugs to site specific locations, which is crucial for the development of new drugs and drug careers. Therefore, understanding the dynamics of encapsulation and discharge of drug molecules from nano-carriers to site specific location is crucial .Here, we propose to investigate the dynamics by molecular dynamics and or coarse grain dynamics of drug career by carbon nanotube due its hydrophobicity, pH, temperature and light sensitivity that could penetrate thru' human tissues. We will assess the viability of our method by investigating the binding energy between CN, and drug molecule/s, in aqueous media with and without antioxidant. We will also compute the diffusion coefficient of the drug molecules inside CNTs at various operating conditions. Our investigation may be helpful in future in-vivo studies by medical practitioners.

Wednesday 6:00 Foyer-Stairs/Windows PO3

Kinetic modeling of the modulus change in sealants exposed to outdoor and laboratory weathering

Christopher C. White and Donald Hunston
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The thin elastic line separating the inside from outside is required to perform flawlessly for decades. It is well known that these filled elastomers or sealants change with exposure to outdoor weathering conditions. Previous work has focused on demonstrating how the time dependent stress relaxation modulus is an excellent method to follow the changes in sealant as it ages. the resulting time versus modulus curves have been previously discussed. For all but one sealant, the observed before and after stress relaxation modulus curves are identical in shape, and are vertically shifted. This work begins to explore how to kinetically model the exposure versus modulus shift data using idealized network structure.

Wednesday 6:00 Foyer-Stairs/Windows PO4

Effect of hydration on mechanical properties of anion exchange membranes for fuel cells

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Anion exchange membranes facilitate ion transport in polymer electrolyte membrane fuel cells. An AEM must have a high ionic conductivity, low fuel crossover, and be chemically and mechanically stable over the lifetime of a fuel cell. While chemical degradation is one widely studied route to membrane failure in a fuel cell, mechanical breakdown due to humidity cycling is common also. Specifically, the sorption and desorption of water can cause pin hole cracks, which lead to fuel crossover and device failure. Development of thin polymer films is critical to increase membrane function. As membrane thickness is decreased, maintaining membrane integrity becomes increasingly difficult. A modified extensional

rheometer was used to perform tensile-like testing on films 10-100 microns thick using less than 5% of material needed for a traditional tensile tester. A custom built humidity delivery system was developed for a rheometer to test films at a range of temperatures (30-100°C) and relative humidity conditions (0-95% RH). The humidity oven can be used with many rheometer accessories, including dynamic mechanical analysis. Dynamic mechanical analysis investigated moduli changes while ramping humidity at constant temperature and while ramping temperature at saturated gas conditions. These tools established metrics for a robust membrane through mechanical characterization across temperatures and humidities. Using a series of block, random, and crosslinked polymers, a relationship between mechanical stress and water stress has been proposed to predict durability of anion exchange membranes in a working device.

Wednesday 6:00 Foyer-Stairs/Windows PO5

Characterizing the effect of relative humidity on rheological properties

Bharath Rajaram, Tianhong Chen, and Aloyse J. Franck
TA Instruments, New Castle, DE 19720, United States

The rheology of a wide range of materials can be strongly influenced by environmental conditions including temperature and humidity. In polymeric materials, exposure to humid environments can lead to significant changes in the modulus and glass transition temperature depending on the amount of moisture absorbed - this behavior is often attributed to the diffusion of water inside the sample, effectively acting as a plasticizer that "lubricates" the polymer chains. Such dramatic changes in the material properties can adversely affect the performance of products such as packaging materials and has important implications on the customer perception of food stuff quality and safety. Hygroscopic materials are particularly sensitive to atmospheric water content and products like silicone sealants and adhesives that make use of specific chemistries to drive the curing reaction that could be affected by humidity. Similarly, geographic variations in environmental conditions during the transportation and storage of industrial products like paints and coatings could affect its end use properties. In this study, we report on the development of a new environmental chamber for the TA Instruments Discovery Hybrid Rheometers that is capable of simultaneous temperature and relative humidity control. The specially designed chamber provides stable, reliable control of these parameters over a wide range of operating conditions and successfully prevents condensation, a common occurrence in controlled-humidity environments which makes accurate control of relative humidity impossible. We also discuss the use of novel geometries that are designed to ensure rapid, uniform, and homogenous diffusion into the sample. Data demonstrating the effect of relative humidity and temperature on the curing of paint films, adhesives, and the tensile moduli of fuel cell membranes are presented. The results underscore the effectiveness and sensitivity of this experimental approach to explore the impact of environmental conditions on material properties.

Wednesday 6:00 Foyer-Stairs/Windows PO6

Tunable shape memory properties of lignin-rubber composites: Shape fixity and shape recovery

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Lignins are abundant as a byproduct from pulping industry and biorefineries. They are cheap, and renewable macromolecules. However, the uses of lignins are still limited. In this study, we employed lignins to tune the thermomechanical and rheological properties of nitrile-butadiene-rubber for shape memory applications. By controlling heterogeneous aromantic structures containing various side-chains and functional groups of lignins, elastomeric lignin-rubber composites exhibit variable stiffness and melt-viscosity within two order of magnitude difference. Interestingly, an increase in glass transition temperature of the composites, up to 40 °C, was achieved revealing excellent programmable shape characteristics. A wide range of trigger temperatures was able to utilize for fixing temporary shape. Repeatable cycles of reversible shape memory of the composites were investigated. In this report, the rate of strain recovery, the energy storage capacity, and the decay of shape recovery properties under the effects of lignin structures are discussed.

Wednesday 6:00 Foyer-Stairs/Windows PO7

New insights into the use of a rotational rheometer as tribometer

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A tribometer requires speed and load control as well as a force or torque measurement to acquire tribological data. An air bearing supported rotational rheometer allows the measurement of the same variables but concerning speed and torque in a broader range and with better accuracy. This fact and the intension to perform both speed and torque controlled experiments to measure Stribeck curves as well as the static friction with one single instrument led in 2006 to the idea to design a tribology attachment turning a commercial available rheometer into a high resolution tribometer based on the ball-on-three-plates principle. [Heyer P., Läuger J. (2009) Lubrication Science, 21, 253-268]. This tribometer accessory has been used extensively and a plethora of research papers have been published using the ball-on-three-plate setup. Since then the original setup has been extended into a tribometer platform including: 1. Ball-on-three-plate for a convection oven with Temperature range: -150°C - +600°C. 2. Humidity chamber with range of relative humidity: 5% to 95%. 3. Holder system for the ball-on-three-plate system with lower limit of load range of 0.03N. 4. New geometries: Pins-on-three-plates, ball-on-three-balls, rolling bearing holder, larger ball-on-three-plate geometry, holder for O-rings. 5. Pins-on-disc system with flat-on-flat, line-on-flat, point-on-flat contacts for varying surface pressures. 6. Oscillatory testing and introduction of new tribological friction moduli. The aim of this contribution is to discuss different tribological geometries and to present new results ranging from static friction measurements, Stribeck curves, and wear testing on materials as different as lubricants, bitumen, cartilage, and food under various different environmental conditions, showing the wide range of applications covered by such a type of rheo-tribometer.

Wednesday 6:00 Foyer-Stairs/Windows PO8

High-pressure linear viscoelasticity measurements of polymer solutions and gels

Kimberly A. Dennis[1], Yan Gao[2], Alhad Phatak[2], and Eric M. Furst[1]
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Oilfield fluids are used to help transport and suspend solids, reduce friction pressure and prevent fluid loss. Key to these fluid performance metrics is the fluid rheology. Depending upon the composition and flow condition, the fluid can behave as a purely viscous or viscoelastic fluid. By choosing the right composition, the flow properties can be optimized for a specific function. Mechanical rheometers are used extensively for rheological measurements of fluids. However, mechanical rheometers cannot always provide accurate measurements for all the systems. Misinterpretation of rheological data may provide underestimated or exaggerated fluid features, which may in turn lead to the failure of a specific task. In addition, many of the fluids are heterogeneous, thereof change in macrorheology does not reflect the microstructure evolution of the material. Further, high-pressure measurements can be challenging for mechanical rheometers.

To address these shortcomings, we developed a passive microrheology experiment to measure the linear viscoelasticity of complex fluids at high pressures. The apparatus incorporates a sealed steel sample chamber with dual sapphire windows into a simple diffusing-wave spectroscopy (light-scattering) setup and is capable of both transmission and backscattering geometries. The measured light intensity correlation arising from the Brownian motion of polystyrene probe particles dispersed in the sample is interpreted using the generalized Stokes-Einstein relation to determine the material creep compliance. We validate this high-pressure microrheology technique with poly(ethylene oxide) solutions and extend the measurement to stimulation fluids containing a crosslinked guar biopolymer. The apparatus enables linear viscoelastic measurements up to frequencies of 1 MHz and pressures of 30 kpsi, expanding the accessible range of experimental conditions beyond those of existing rheological measurement techniques.

Wednesday 6:00 Foyer-Stairs/Windows PO9

Fitting data is subjective: Implications for inferring structure from rheology

Piyush K. Singh and Randy H. Ewoldt
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Small-amplitude oscillatory shear (SAOS) is widely used for inferring a meaningful relaxation spectrum by fitting the G' and G" data. However, the results obtained from this fitting exercise are not unique, due to choice of data representation and how to weight the disagreement between data and the model. The SAOS data representation itself is not unique; in addition to G' and G", it can be represented instead by torque-amplitude and phase: T0 and d, complex modulus G* and tan d, dynamic viscosities: ?' and ?", dynamic compliances: J' and J", or any other two-parameter pair that describes the resulting sinusoidal waveform. Additional subjectivity comes from the choice of weighting residuals in the fitting, i.e. how to penalize disagreement between data and the model. Are any of these non-unique methods "best" in some quantifiable or objective way? We argue the answer is yes, there is a "best" method for fitting. Based on statistical arguments, the best scheme is the one where data representation has Gaussian uncertainty and residuals are weighted by experimental data uncertainty. We show that, theoretically, none of the commonly used SAOS data representations are Gaussian. Yet, some are more Gaussian than others, considering the error propagation from the primary measurement quantities of torque and displacement waveforms. Interestingly, the dominant factor in reducing subjectivity for fit parameters is to weight the residuals by the data uncertainty. When weighted by the data uncertainty, the fit parameters from various data representations are in close agreement within a small and acceptable variability. This is observed for both a real dataset on cis-1,4-polyisoprene melt (true parameter values unknown) and a synthetic dataset (true parameter values known). These findings establish best practices for fitting SAOS data and at the same time, emphasize the need for analytically estimating uncertainties for single measurement data.

Wednesday 6:00 Foyer-Stairs/Windows PO10

Human perception of viscosity: Visual and haptic discriminability

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Viscosity is one of the salient properties of liquid products that we encounter in everyday life. Through experience and some conditioning, consumers have developed preferences for viscosity ranges of products they use. Consumers would reject a shower gel if they perceived its viscosity during dispensing and use as either too low or too high. Furthermore, consumers may discontinue use of a product if the perceived viscosity changed significantly due to reformulation. Consumers' perception of viscosity differences is however limited by the performance of their perceptual system. It is therefore crucial to understand what is the minimum amount of change in viscosity that leads to a noticeable variation in the perceptual experience of a product. A quantitative assessment of such perceptual thresholds would, for example, allow reformulation of products with aesthetics that are inevitably different but still perceived the same by the consumer.

Viscosity can be perceived in many different ways. Consumers may visually assess viscosity by tilting a bottle of shampoo, or by haptic sensing during dispensing and application of a lotion or sunscreen. These different modalities of perception all contribute to the overall acceptance and continued use of a product. In this work, we attempt to separately characterize the perceptual thresholds for changes in viscosity in two modalities: visual and haptic. In the visual experiment, participants compared videos of test and reference fluids being stirred at a constant rate by a glass rod. In the haptic experiment, participants were asked to stir the test and reference fluids, Newtonian silicone oils of differing viscosity that were hidden from view, with their gloved index finger. In both experiments they were asked to indicate the stimulus that was perceived as more viscous. Using the method of constant stimuli we were able to determine perception thresholds and Weber fractions as a function of viscosity for five different reference viscosities ranging from 500 to 16,000 mPa.s.

Wednesday 6:00 Foyer-Stairs/Windows PO11

Comparison of industrial instruments yield test methods

David J. Moonay
AMETEK Brookfield, Middleboro, MA 02346, United States

This poster presents a comparison of yield test results measured with different AMETEK® Brookfield rotational Rheometers and Viscometers [and their associated software]. Yield testing is often important in industrial environments because the yield behavior may affect a material's processing and application or use. it is known that different test methods produce different results, because of the complex nature of yielding. Comparisons between methods may enable correlation between instrumentation used in R&D versus QA/QC settings. Data obtained with the DV3T Rheometer with Rheocalc T™ software are shown, along with data acquired with the RST Rheometer and its Rheo3000™ software. Results are presented for various materials, obtained through testing with different instruments, accessories and methods.

Wednesday 6:00 Foyer-Stairs/Windows PO12

Utilization of the cone partitioned plate geometry for enhanced material characterization

James P. Eickhoff[1] and Gunther Arnold[2]
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A main limitation for characterizing polymer melts at large deformations and/or high shear rates, is due to edge fracturing. This sample instability is characterized by a deformation of the sample surface at the free edges between upper and lower part of the geometry. This phenomena propagates radially as a function of both time and applied deformation. Due to this behavior the accuracy from step rate, flow curves at high shear rates, and even large-amplitude oscillatory shear (LAOS) measurements can be dramatically affected by this response. To limit the impact of edge fracture effects the use of a cone partitioned plate (CPP) has been recommended on several occasions to minimize edge fracturing from influencing rheological measurements. The aim of the following measurements is to highlight the difference in the measuring performance when using a CPP in comparison to conventional cone/plate geometries.

Wednesday 6:00 Foyer-Stairs/Windows PO13

Quality control illustrated on the industrial powder coating process using a rotational rheometer

Abhishek M. Shetty[1], Denis Schütz[2], Riedl Elke[2], Oliver Sack[3], and Katja Hartmann[3]
[1]Rheology, Anton Paar, Ashland, VA 23005, United States; [2]Rheology, Anton Paar, Graz, Austria; [3]Rheology, Anton Paar, Ostfildern, Germany

Powder coatings are a growing technology with numerous applications. Initially designed to provide greater resilience than comparable liquid applied coatings the desire for an environment friendly solvent free process has garnered a lot of attention lately and drives the development and application of this technique. The Powder Coating process is dependent on one end on pneumatic conveyance behavior, namely the transport as a dense fluidized phase of powder and on the other end on bulk polymer behavior to determine and keep constant the curing point at which the applied powder bonds and produces a smooth surface. We have successfully demonstrated the viability of a high precision air bearing rotational rheometer with different peripherals to characterize the entire process of quality control in a powder coating plant.

Wednesday 6:00 Foyer-Stairs/Windows PO14

Polymeric thickeners and surfactants: Rheology and texture in water-based cosmetics

C M. Crane and H S. Bui
R&I, L'Oreal, Clark, NJ 07066, United States

Gel eyeliners and eye shadows on the market are anhydrous systems containing silicon resins for long lastingness (wear). To develop water-based gel eyeliner systems (for sustainability) we have to control not only the wear, but also application and texture of the product; such that the product is equal to or better than the anhydrous market reference in terms of performance. This is challenging because water-based systems tend to be inferior to anhydrous systems containing silicon resins as film forming which have lower surface energy and therefore more appealing application properties.

Employing powerful tools such as a rheology and texture analysis we studied the association of water-phase polymeric thickeners with various surfactant systems to achieve the texture and application properties of anhydrous eyeliners (that typically exhibit complex moduli in the range of 10^4 -10^5 Pa with a critical yield strain less than 1%). Further association of these systems with optimal latex for wear was also investigated. The results showed that by using two thickeners and a mix of nonionic and ionic surfactants we see synergies in terms of the viscoelasticity and appealing texture. However, combination of specific ionic surfactant with the polymeric thickener gives the best application properties as perceived by cosmetologists.

Wednesday 6:00 Foyer-Stairs/Windows PO15

Deformation behavior of fast curing epoxy based carbon prepreg during compression molding process

Dong Gi Seong[1] and Daeryeong Bae[2]

[1]Composites Research Division, Korea Institute of Materials Science, Changwon, Republic of Korea; [2]University of Science and Technology, Changwon, Republic of Korea

Deformation behavior of carbon prepreg composed of fast curing epoxy resin and carbon fabrics with several kinds of texturing structure during compression molding process was investigated to set up the fabrication process of carbon fiber reinforced composite parts for automotive applications. Rheological and thermal properties of fast curing epoxy resin were measured to determine the forming temperature of the prepreg, which showed very fast increase of viscosity after gradual decrease of viscosity with increasing temperature to 110?. Non-linear mechanical properties of the carbon prepreg were measured at the determined forming temperature for several deformation modes which include tension, shear at both inter and intra laminar situations. Deformation behavior of the prepreg under compression molding process with the automotive roof-like geometry could be predicted by preforming thermoforming simulation with the input data from the measured mechanical properties of the prepreg. The predicted results were also compared with the experimental results from compression molding process with the test mold of same geometry. Several deformation behaviors such as shear angle of the woven fabric were successfully predicted, which could be expected to set up the optimum process conditions for high speed compression molding process of carbon fiber reinforced composite parts. Especially, shear deformation at the corner edge area was large and irregular, which should be of main concern to prevent defects by undesired deformation of fabric.

Wednesday 6:00 Foyer-Stairs/Windows PO16

Rheology of molten metals

Anne M. Grillet and Nicolas Argibay

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At Sandia National Laboratories, we are concerned about the response of a wide range of materials to abnormal thermal environments including fires. In these scenarios, the temperatures can get high enough to melt structural aluminum alloys. High temperature environmental chambers on modern rheometers have enabled rheology study up to 1000°C. We present measurements of the viscosity of molten metals including aluminum over a range of shear rates and temperatures. We also study aluminum alloys where the aluminum is mixed with other metals to improve strength and hardness at room temperature. Alloying can sometimes result in intermetallic inclusions which can act as particulate fillers in the molten state. Finally we look at the onset of Taylor instabilities in molten metals. The high density and low viscosity of molten metals make them prone to the onset of these centrifugal force-driven instabilities. We will compare experimental measurements critical conditions for molten aluminum to the theoretical critical Taylor number.

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Wednesday 6:00 Foyer-Stairs/Windows PO17

Fast temperature screening for viscosity determination by microfluidics

Adamska Patricia[1] and Jim Munhall[2]

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Rheological analysis is made fast and easy with a novel instrument based on a simple microfluidic flow comparator. Using only tiny amount of samples, the technology allows flow viscosity measurements of liquid products from water-like inks to thick cosmetic formulations, under a wide range of shear rates (including high values up to 105 s-1). Additionally, the user-friendly visual principle makes possible routine optical control of both samples and disposable flow cells to assess measurement quality.

Technology A sample and a viscosity standard are pushed together through a microfluidic comparator (Y-junction) at controlled flow rates. Images of the resulting laminar co-flow are acquired via an integrated optical system and the position of the interface position is measured.

The interface position is simply related to the viscosity and the flowrates ratio between the sample and the reference. Using dedicated algorithms, sample viscosity is automatically extracted over a controlled range of shear rates and temperatures.

Benefits • User-friendly, fast and simple measurement • Visual quality control • Accuracy over a wide range of viscosity (0.1 to 10000 mPa/s) and shear rates (up to 105 s-1) • Automated analysis as a function of both shear rates and temperature (4-80 °C) • Small sample volume • No user intervention (e.g. resampling) required between measurement repetitions

Applications • Inkjet (printers, flexible electronics, biochips) • Spray (cosmetics, food, paints) • Drug injection (pharma) • Blood, synovia, etc. (biomedical diagnostics) • Oil industry • Lubricants (mechanics, cutting, wire drawing)

Wednesday 6:00 Foyer-Stairs/Windows PO18

Passive microrheology: Non contact measurement of gel point of biopolymers

Roland Ramsch[1] and Jim Munhall[2]
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Passive microrheology is a non-invasive method convenient for the study of gelling systems, since the gelation process can be observed in real time and under no stress conditions.

The gelation behavior is very important for the optimization of the end product properties and quality control. Gel point determination is performed with the automatic Time- Cure-Superposition method, allowing the analysis of a wide range of applications in food, cosmetic and building industry.

Conclusions and Benefits:
- Accurate - Gel point determination
- Reliable - Measurement at rest
- Fast - 6 simultaneous measurements
- Safe - Disposable and closed measurement cells

References: µ-rheology: Mason and Weitz, Physical Review Letters 74, 7,1995. DWS: Maret et al. , Condensed Matter 65, 409, 1987. Time-Cure-Superposition: Furst et al., Physical Review Letters, 100, 14, 2008.

Wednesday 6:00 Foyer-Stairs/Windows PO19

Thermal and viscoelastic properties of miscible polymer blend with hydrogen bonding interaction: Poly(2-vinyl pyridine) / poly(2-hydroxyethyl methacrylate)

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Polymer materials with high and versatile performance have been desired in various fields. In order to control the material properties, one method is to blend several polymers with different properties. However, it is often difficult to bring out a synergistic effect in its properties which usually become the average values of the components. Introducing strong intermolecular interactions such as hydrogen bonds is known often to make the properties better. So far, some miscible blend systems with hydrogen bonding interaction have been reported to have higher glass transition temperature, Tg, than the mean value of the component polymers. However, rheological behavior of such systems has been rarely examined and thus the details of the component dynamics in such interacting blends are still unclear. We investigated the thermal and rheological properties of a hydrogen bonding polymer blend, poly(2-vinyl pyridine) / poly(2-hydroxyethyl methacrylate) to see the effect of intermolecular interaction. From DSC measurements, it was found that the composition dependence of Tg was convex upward and well described by Kwei equation which contains the intermolecular interaction term in the Gordon-Taylor equation. The interaction term in the Kwei equation can be ascribed to the formation of hydrogen bonds between the component polymers. Rheological measurements revealed that the shape of complex modulus G* in the terminal region for the blend samples were broader with longer terminal relaxation times compared to those of homopolymers. These results indicate the existence of various size of intermolecular aggregates via hydrogen bonding interaction.

Wednesday 6:00 Foyer-Stairs/Windows PO20

Nonlinear relaxation modulus via dual-frequency medium amplitude oscillatory shear (MAOS): General framework and case study for a dilute suspension of Brownian spheroids

Toni M. Bechtel and Aditya S. Khair
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

A framework for determining the first nonlinear relaxation modulus of a viscoelastic fluid from a medium-amplitude oscillatory shear (MAOS) deformation is constructed. Knowledge of this "MAOS relaxation modulus" allows one to predict the weakly nonlinear stress response of a material under an arbitrary transient deformation via a memory integral expansion. Our framework is demonstrated by explicitly determining the MAOS relaxation modulus for a dilute suspension of Brownian spheroids subject to a dual-frequency oscillatory shear flow. Specifically, we first calculate the second normal stress difference for such a deformation from a co-rotational memory integral expansion. Second, the microstructural stress response of the model system of Brownian spheroids is determined via a regular perturbation expansion of the orientation distribution function at small dimensionless strain-rate amplitude, or Weissenberg number. An analytical expression for the MAOS relaxation modulus is resolved by comparing the second normal stress difference results of the memory integral expansion and microstructural stress calculation. Finally, using the MAOS relaxation modulus, we reconstruct the stress response of the model system for the start-up and cessation of simple shear and uniaxial extension. In summary, our work offers an approach to utilizing medium (and large) amplitude oscillatory shear results to predict stress dynamics of viscoelastic fluids in other transient, nonlinear flows.

Wednesday 6:00 Foyer-Stairs/Windows PO21

Manipulating of Colloidal gels by oscillatory shear

Esmaeel Moghimi[1], Alan R. Jacob[1], Nick Koumakis[2], and George Petekidis[1]
[1]Materials Science & Technology Department, IESL-FORTH & University of Crete, Heraklion, Greece; [2]School of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom

We examine microstructural and mechanical changes which occur during oscillatory shear flow and reformation after flow cessation of an intermediate volume fraction colloidal gel using rheometry and Brownian Dynamics (BD) simulations. A model depletion colloid-polymer mixture is used, comprising of a hard sphere colloidal suspension with the addition of non-adsorbing linear polymer chains. Results reveal three distinct regimes depending on the strain amplitude of oscillatory shear. Large shear strain amplitudes fully break the structure which results into a more homogenous and stronger gel after flow cessation. Intermediate strain amplitudes densify the clusters and lead to highly heterogeneous and weak gels. Shearing the gel to even lower strain amplitudes creates a less heterogonous stronger solid. These three regimes of shearing are connected to the microscopic shear-induced structural heterogeneity. A comparison with steady shear flow reveals that the latter does not produce structural heterogeneities as large as oscillatory shear. Therefore oscillatory shear is a much more efficient way of tuning the mechanical properties of colloidal gels. Moreover, colloidal gels presheared at large strain amplitudes exhibit a distinct nonlinear response characterized largely by a single yielding process while in those presheared at lower rates a two step yield process is promoted due to the creation of highly heterogonous structures.

Wednesday 6:00 Foyer-Stairs/Windows PO22

Non-linear shear flow of model hard sphere and interpenetrable soft colloidal glasses

Alan R. Jacob[1], Andreas Poulos[2], Sunhyung Kim[3], Jan Vermant[4], and George Petekidis[1]
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Model hard sphere (PMMA spheres) and interpenetrable soft sphere (star-like micelles) colloidal suspensions in glassy states are investigated by Orthogonal Superposition Rheometry (OSR)[1]. By employing OSR we directly measure the linear viscoelastic spectra of suspensions under constant shear. The crossover frequency extracted from the linear viscoelastic spectra varies linearly with shear rate for hard spheres, and sub-linearly for the soft interpenetrable star-like micelles. A Shear Rate Orthogonal Frequency Superposition (SROFS) is achieved for both systems but deviations are observed mainly for the hard sphere colloidal glasses in short and long time scales. Horizontal Scaling factor of SROFS, the colloidal analogue to Time Temperature Sueperposition, provides insight into the timescales present under shear and the vertical scaling factor points out to the in-cage free volume of the system. Brownian Dynamics simulations show that anisotropic cage structure is responsible for the deviations in hard sphere glasses in short time scales. The long time deviations in hard sphere glasses is speculated to be due to hydro-cluster formations.

[1] A.R. Jacob, A.S. Poulos, S. Kim, J. Vermant, G. Petekidis, Convective cage release in model colloidal glasses, Phys. Rev. Lett. 115 (21) (2015) 218301.

Wednesday 6:00 Foyer-Stairs/Windows PO23

Viscoplastic adaptation of collagen networks upon repeated cycles of stress

Federica Burla and Gijsje H. Koenderink
FOM Institute AMOLF, Amsterdam, The Netherlands

The extracellular matrix plays a crucial role in regulating cell functions in tissues, including cell-cell communication, cell growth, and cell differentiation. Its main structural component is collagen, a network-forming rigid protein that confers shape, structure and mechanical rigidity to tissues. The elastic properties of collagen have been well-studied, but the inelastic response to repeated loading remains poorly understood. While earlier studies have reported a weakening of the stress-strain response of collagen when subject to a strain-controlled deformation [1], little is known about the network behavior in a stress-controlled deformation. Here, we investigate the mechanical response of model extracellular matrix networks reconstituted from purified collagen to repeated cycles of shear stress. While the network shows an instantaneous hardening response with consecutive cycles, once a waiting time is introduced between each cycle the network recovers its original response, maintaining a residual deformation. These results indicate the plastic formation of new bonds between collagen fibers together with viscous relaxation processes occurring on different length and timescales. The reported processes are likely to influence adhesion and movement of cells through the extracellular matrix. To get a direct overview of the processes governing the network behavior, we are currently investigating the mechanistic basis of the inelastic mechanics of collagen by means of a confocal rheometer.

[1] Stefan Münster et al, PNAS, 2013 110 (30) 12197-12202.

Wednesday 6:00 Foyer-Stairs/Windows PO24

Molecular mechanisms of strain-stiffening in a transient polymer network studied with experimental medium-amplitude oscillatory shear (MAOS)

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We identify the relative importance of the two hypothesized mechanisms driving nonlinear elasticity observed in a strain-stiffening transient polymer network (aqueous polyvinyl alcohol (PVA) crosslinked by sodium tetraborate (borax)). Our previous data from medium-amplitude oscillatory shear (MAOS) characterization shows nonlinear elastic stiffening for all Deborah numbers tested, 0.05 - 50; all four MAOS signatures can be fit with a strain-stiffening transient network model. The previous data set at a single composition permits two hypothesized stiffening mechanisms but cannot distinguish between them: the inherent nonlinear force-extension behavior of the polymers and the contributions of strain-induced network structuring/crosslinking. Our approach here is to measure MAOS signatures across a range of compositions for this system and to fit all data sets with the same strain-stiffening model. A single nonlinear fit parameter describes the extent of nonlinear stiffening; its dependence on the concentration of the polymer and crosslinker suggest that the mechanism of strain-induced crosslinking of the network dominates the mechanism of inherently nonlinear force-extension behavior of the PVA polymers. This study demonstrates the use of MAOS rheological signatures to infer molecular-level physics of a rheologically-complex material system.

Wednesday 6:00 Foyer-Stairs/Windows PO25

Shear-induced structural transitions in ultra-low interfacial tension microemulsions

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Injection of tuned surfactant formulations along with simultaneous brine flooding has the potential to greatly increase oil recovery during primary, secondary, and tertiary phases of oil production. The enhanced recovery is the result of surfactant adsorption at the oil/brine interface which produces an ultra-low (<0.01 mN/m) interfacial tension between the aqueous and non-aqueous phases, reducing the capillary number and clearing oil from smaller pores than possible in brine-only floods. Injecting surfactant-only solutions, however, leads to a poor sweep efficiency because of viscous fingering due to the large viscosity difference between aqueous surfactant solutions and crude oils. Improved sweep efficiency can be achieved through several methods, such as the addition of water-soluble polymers or the use of a surfactant formulation that forms worm-like micelles. Both of these methods improve sweep efficiency, but polymers present difficulties with on-site processing and can clog reservoirs, while wormlike micelle systems often undergo catastrophic phase transitions when even a very small amount of oil is introduced to the system, resulting in a complete loss of the increase to solution viscosity. Here, we present a rheological and microstructural characterization of a surfactant/brine/oil mixture that increases the viscosity of the aqueous phase, generates an ultra-low interfacial tension between the oil and aqueous phases, and is insensitive the presence of additional oil. The system consists of an industrially available extended surfactant (ethoxylated-propoxylated alkyl sulfate), brine, and small amount of a refined alkane oil mixture that undergoes a shear-induced phase transition when subjected to shear rates greater than 50 s-1. After exposure to shear above this critical value, the viscosity of the solution increases, a measurable amount of viscoelasticity develops, and the shear-induced structures require several days to fully relax.

Wednesday 6:00 Foyer-Stairs/Windows PO26

A multiscale model for the rheology of thixotropic suspensions

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Complex fluids are increasingly common in many industrial processes and consumer products. Consequently, understanding the rheology of such systems is an important undertaking, and recently, there has been a renewed interest in modeling the rheology of thixotropic suspensions based on structure kinetic models [1,2,3]. Unfortunately, while some of these models have found utility in explaining experimental data, their predictions of large amplitude oscillatory shear (LAOS) and flow reversal do not accurately represent experimentally measured rheology [3]. Ultimately, these models fail to explicitly take into account the multiscale nature of the phenomena observed in thixotropic suspensions.

Accounting for the multiple length scale and associated dynamical responses at various experimental time scales requires the formulation of truly multiscale models. This contribution describes initial efforts on how a population balance model providing information on aggregation-breakage dynamics at the more microscopic level [4], a model for aggregate deformation and a consideration of the mesoscopic dynamics of colloidal aggregates can be systematically combined to model the macroscopic rheology of a thixotropic suspension. The additional information at the latter two levels is abstracted from a conformation tensor description, making the model potentially applicable to general flows. Comparison against experimental data including LAOS will also be discussed.

[1] Larson, R. G., Journal of Rheology 59.3 (2015): 595-611. [2] Wei, Y., M. J. Solomon, and R. G. Larson., Journal of Rheology 60.6 (2016): 1301-1315. [3] Armstrong, M. J., A. N. Beris, S. A. Rogers, and N. J. Wagner, Journal of Rheology 60.3 (2016): 433-450. [4] Mwasame, P. M., A. N. Beris, R. B. Diemer, and N. J. Wagner. "A constitutive equation for thixotropic suspensions with yield stress by coarse-graining a population balance model." Accepted AIChE Journal (2016).

Wednesday 6:00 Foyer-Stairs/Windows PO27

Large amplitude oscillatory shear measurements on linear and branched polyolefins: Comparisons using parallel plate, cone and partitioned plate, and closed cavity systems

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Large amplitude oscillatory shear (LAOS) is a unique tool for the investigation of polymer melts. Recent literature studies have focused on the non-linear characterization and modeling of complex fluid and polymer materials. Instrument hardware and software advances have made fast sampling and discrete Fourier transform analysis readily available. Alternatively, default direct correlation can be used to determine magnitudes of the fundamental phase and additional harmonics up to the 9th order. Material edge fracture or slip can influence data quality at higher strain amplitudes and hinder interpretation. Thus, selection of measurement geometry is important in preventing these phenomena. This poster will utilize parallel plate, cone and partitioned plate (CPP), and a sealed cavity (or biconical die) system to compare LAOS results from linear and branched polyolefins. Data collection options from multiple instruments and the presentation of Lissajous curves and available harmonic ratio intensities will be shown.

Wednesday 6:00 Foyer-Stairs/Windows PO28

Investigating the role solid-liquid interfaces and flow on aggregate formation for the NIST IgG1 mAb

Cavan K. Kalonia
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Therapeutic proteins solutions are commonly exposed to solid-liquid interfaces under flow conditions during fill-finish processes such as batch mixing, sterile filtration, and pump-driven filling. Understanding how flow past solid-liquid interfaces can facilitate protein aggregation is a major unmet scientific need for the biopharmaceutical industry. In this work, we investigate the production of protein aggregates after exposing NIST mAb solutions to alumina or silica interfaces and to a range of flow conditions (shear rates at the solid-liquid interface up to ~20,000 s-1). Shearing studies were performed using a flow cell that can be assembled to include different solid surfaces. The rheological properties of NIST mAb adsorbed to alumina/silica surfaces were characterized using a quartz crystal microbalance with dissipation monitoring (QCM-D), and neutron reflectivity (NR) was used to investigate the structure of adsorbed protein as a function of protein concentration. Data acquired by QCM-D and NR experiments reveal that the NIST mAb forms a layer that is a few nm thick at the solid interface for all of the mAb concentrations examined (0.1 to 100 g/L) for the surface materials investigated. At high mAb concentration (>50 g/L), viscoelastic modeling of the QCM-D data suggests that a secondary softer and thicker viscoelastic layer forms and that the properties of this layer are sensitive to the solid surface material. After brief exposure to high shear rates (>20,000 s-1), large aggregates were detected by Micro Flow Imaging as a function of mAb concentration and surface material. Our working hypothesis is that shear stress may disrupt the secondary layer of the adsorbed mAb film depending upon it's thickness and mechanical strength. The data suggests that disruption of the secondary layer could cause the release of "patches" of associated mAb layers which leads to the detection of SVP in the bulk solution.

Wednesday 6:00 Foyer-Stairs/Windows PO29

The role of surface charge convection in the electrohydrodynamics and breakup of fluid drops

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The deformation of a weakly conducting leaky dielectric drop in a density matched, immiscible, weakly conducting medium under an external electric field is quantified computationally. A tangential electric stress acts along the interface, which drives both fluids into motion, causing convection of surface charge carriers along the interface. This effect is measured in terms of an electric Reynolds number. Here, using boundary integral computations, we show that the electric Reynolds number can change the breakup mode of a weakly conducting prolate drop from end-pinching to tip-streaming, if the induced flow is directed from the equator of the drop to its poles. The final state of the drop depends sensitively on the applied electric field.

Wednesday 6:00 Foyer-Stairs/Windows PO30

Visualizing nanoscopic topography, patterns, flows and instabilities in stratifying freestanding thin films

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Freely standing thin liquid films containing supramolecular structures including micelles, nanoparticles, polyelectrolyte-surfactant complexes, and smectic liquid crystals undergo drainage via stratification. The layer-by-layer removal of these supramolecular structures manifests as stepwise thinning over time and a coexistence of domains and nanostructures of discretely different thickness. The layering of supramolecular structures in confined thin films contributes additional non-DLVO, supramolecular oscillatory surface forces to disjoining pressure, thus influencing both drainage kinetics and stability of thin films. Understanding and characterizing the spontaneous creation and evolution of nanoscopic topography of stratifying, freely standing thin liquid films have been long-standing challenges due to the absence of experimental techniques with the requisite spatial (thickness <10 nm) and temporal resolution (<1 ms). Using Interferometry Digital Imaging Optical Microscopy (IDIOM) protocols developed herein, we visualize and characterize size, shape, and evolution kinetics of nanoscopic mesas, terraces, and ridges. The exquisite thickness maps created using IDIOM protocols provide much needed and unprecedented insights into the role of supramolecular oscillatory surface forces in driving growth of such nanostructures as well as in controlling properties and stability of freely standing thin films and, more generally, of colloidal dispersions like foams.

Wednesday 6:00 Foyer-Stairs/Windows PO31

Dripping-onto-substrate (DoS) rheometry of complex fluids

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Characterization of pinch-off dynamics and the response to both shear and extensional flows that influence drop formation/ deposition in microfluidic and printing applications requires bespoke instrumentation not available, or easily replicated, in most laboratories. Here we show that dripping-onto-substrate (DoS) rheometry protocols that involve visualization and analysis of capillary-driven thinning and pinch-off dynamics of

a columnar neck formed between a nozzle and a sessile drop can be used for measuring shear viscosity, power law index, extensional viscosity, relaxation time and the most relevant processing timescale for printing. We showcase the versatility of DoS rheometry by characterizing and contrasting the pinch-off dynamics of a wide spectrum of simple and complex fluids: water, printing inks, semi-dilute polymer solutions, yield stress fluids, food materials and cosmetics. We show that DoS rheometry enables characterization of low viscosity printing inks and polymer solutions that are beyond the measurable range of commercially-available capillary break-up extensional rheometer (CaBER). We show that for high viscosity fluids, DoS rheometry can be implemented relatively inexpensively using an off-the-shelf digital camera, and for many complex fluids, similar power law scaling exponent describes both neck thinning dynamics and the shear thinning response.

Wednesday 6:00 Foyer-Stairs/Windows PO32

Measurement of two-dimensional viscosity of liquid surface by electro-magnetically spinning system

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Recently developed disk-type electro- magnetically spinning (EMS) viscometer has been successfully employed also for measurements of mechanical properties of liquid surface, besides the bulk viscoity. For example, two-dimensional viscosity of the mono-molecular films adsorbed on the water surface was measured with the system. In the two-dimensional system, the hard circles freely floating in the media are considered to show contribution to the change in the viscoelastic properties, in which the modeling of the transposition of particles is much easier. In the presentation, we report the measurement of the surface viscosity of the liquid surface containing two-dimensional colloidal particles. The disk-type EMS system could detect the distribution of the surface flow due to the rotation of the probe disk. It can also obtain the excess viscous torque, which is converted to the surface viscosity as a function of the surface concentration of colloidal particles. The sample is the water surface, on which micro carbon particles are dispersed. With these samples, we carried out the measurement of the distribution of the surface flow by observing the motion of the particles. The motion was taken as movies, through which the tangential speed of the particle is obtained. As a result, we can see the rotational speed of the particle decreases with the distance from the edge of the rotating circular disk. It shows that the free surface around the probe is suffered from the steady shear distortion, which dissipate the energy and works as the shear viscosity. Next, we measured the relation between the torque applied to the probe rotor and its rotational speed, and determined the surface viscosity as a function of the density of the surface colloidal system. We can see that the surface viscosity increases with the colloid density and the relation is almost proportional. These macroscopic model of colloidal systems would be helpful for the understanding the rheological properties of the actual 3D colloidal systems.

Wednesday 6:00 Foyer-Stairs/Windows PO33

Emulsion drops spreading on liquid surfaces

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The flow behavior of surfactant solutions on a liquid surface is well established on the basis of Marangoni effect. However, the spreading behavior of an emulsion, when a second phase in a form of small droplets is present in the surfactant solution, has remained uncharacterized. Here, we studied the behavior of oil-in-water (o/w) emulsion drops at a water-air interface by using high speed photography technique. We examined emulsions stabilized with sodium dodecyl sulfate and with different droplet sizes of dispersed phase in dilute, semi-dilute, and concentrated regimes. Results showed that the spreading of the drop containing an internal phase (emulsion) on water surface differs from the ones containing only surfactant solution. It was found that the spreading behavior is affected by the internal phase droplet size and volume fraction. For drops of dilute emulsions, first a rapid bursting was observed as the emulsion drop collided the water surfaces. The bursting created a thin annular film on water surface which propagated rapidly from the contact center in the form of capillary waves. The propagation of the waves slowed down after first few milliseconds of the experiment and followed by a short relaxation closer to the water edge. At the later stage, the diffusion of surfactant across the water surface promoted destabilization and coalescence of oil droplets resulting in a formation of oil islands and crown-like edges in the film which finally retracted back to the center of contact. By increasing the volume fraction of the oil phase, two different steps of rapid bursting were observed: a rapid scattering of the emulsion outer layer at the time of collision followed by a secondary bursting of the remained emulsion during the slow propagation stage of the first bursting. Two-step bursting phenomena was shifted to higher volume fractions as the droplet size of oil phase was decreased, indicating the presence of different kinetic of surfactant adsorption at water surface.

Wednesday 6:00 Foyer-Stairs/Windows PO34

Modeling of stable emulsions using a diffuse interface model with a surfactant phase and interfacial viscosity

Sean A. Colbert-Kelly[1], Trevor Keller[2], Geoffrey McFadden[1], and Frederick R. Phelan, Jr.[2]
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An outstanding problem in emulsion science is modeling of binary emulsions stabilized by surfactants. Surfactants migrate to the fluid interface in a binary mixture due to the amphiphilic nature of these molecules. This alters the interfacial tension and interfacial viscosity between the two phases leading to greater emulsion stability. They further play a profound role on the drop size distribution that emerges from processing. To first order, drop size is controlled by the surface tension between the two phases, but the rise of gradients in the surfactant concentration on the drop surface introduces Marangoni stresses that alters drop shape, breakup and coalescence dynamics, and leads to flow induced migration. While surfactants are very low in overall composition, their dominant effect at the interface makes accounting for them in modeling a very important

and challenging problem. In this study we formulate a diffuse interface model to investigate binary emulsions with a ternary surfactant component. First, we compare a number of models for the Gibbs free energy for binary systems stabilized by a surfactant phase, including a Langmuir isotherm model and a modified ternary Ginzburg-Landau formulation. The properties of these various models are compared by means of phase diagrams to derive a model that best represents the phase behavior. Then, we examine a number of models for concentration dependent interfacial viscosity. This is accomplished by studying the effects of these different models on emulsion stability looking at growth rates and growth to stable drop size. Finally, we compare droplet dynamics in some simple flow fields, looking at the effect of the models on drop size distributions.

Wednesday 6:00 Foyer-Stairs/Windows PO35

Experimental observation of generalized plasma skimming effect in microvascular networks

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In the design of drug carriers, the delivering efficiency is highly related to their pathway in microcirculation through complex vessel geometry. Even though the concept of drug carrier is simple, it is difficult to predict how cells and drug carriers move in the microvasculature. A key parameter for unveiling the journey of drug carriers in microvascular networks is "plasma skimming of blood" at each bifurcating vessels. By the redistribution of blood cells, the fate of drug carriers in the microvasculature will be determined. Recently, a generalized plasma skimming model is suggested to mathematically predict the redistribution of cells and drug carriers at the same in the entire microvasculature. In this talk, the generalized plasma skimming model is compared with microchannel experiments including whole blood and drug carriers. In addition, the drug carrier distribution by the generalized plasma skimming model is predicted in microvascular-network level by coupling the channel experiments with computational models.

Wednesday 6:00 Foyer-Stairs/Windows PO36

Migration of an elastic capsule in microfluidic channels

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The study of the motion and deformation of capsules and biological cells in microfluidic channels is motivated by a wide range of applications including drug delivery, cell sorting and cell characterization devices of microparticles and microcapsules with desirable properties, determination of membrane properties and of course its similarity to blood flow in vascular capillaries. In this work, we investigate computationally the deformation and motion of a strain-hardening elastic capsule in different microfluidic channels. Our interest in concentrated on the lateral migration of the capsule. In the talk, we will present the effects of the flow rate, the size and the initial position of the capsule.

Wednesday 6:00 Foyer-Stairs/Windows PO37

Deviations from Einstein viscosity in polymer nanocomposites

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Polymer nanocomposites have been shown to display improved thermal, mechanical and electrical properties over polymer matrices even at low loadings. Dispersion has proven to be a key factor in property enhancement for these materials. One method of achieving good dispersion is to densely graft a short brush to prevent enthalpic attraction and a sparsely grafted long brush to provide entanglements with the matrix. Effectively processing these materials is challenging. Currently there are equations to predict the viscosity of colloidal suspensions. These equations don't work well for polymer grafted nanoparticles, which are necessary to achieve good dispersion in high molecular weight polymer matrices. The complex rheology of these materials needs to be understood to effectively process them. Towards this end, the viscosity of a model system has been measured. The model system consists of SiO2 nanoparticles grafted with two populations of polystyrene brushes: one short brush and one long brush. These were dispersed into two homopolymer matrices (96 kg/mol and 190 kg/mol) at different loadings. The composite viscosity was measured for each sample using oscillatory rheology. It was found that the composites have significantly different glass transition temperatures. To normalize this effect the viscosities were shifted to an isohomologous temperature. The shifted data deviated from the Einstein viscosity in both cases. The largest deviation was found for the smallest matrix. It is hypothesized that the matrix-grafted brush penetration is larger for the smaller matrix since the grafted chains and matrix chains are of a similar size. Future work will test this by measuring composite viscosity of fillers with different grafted chain molecular weight and matrix brush molecular weight.

Wednesday 6:00 Foyer-Stairs/Windows PO38

Gelation of polymer-grafted silica nanoparticles studied with X-ray photon correlation spectroscopy (XPCS) and rheology

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We report a combined XPCS study of particle dynamics and rheological study of moderately concentrated suspensions of silica colloids and their binary mixtures that form a gel on cooling. The suspensions are comprised of silica colloids (32nm, 86nm and 185 nm) coated with octadecyl-hydrocarbon chains and suspended in decalin at colloidal volume fractions (?) ranging from 0.2 to 0.4. Different scaling relationships are explored to predict the elastic modulus and the limit of linearity. Gel temperatures of the different size particles and the elastic moduli, though different, collapse onto a single curve when scaled as G'D3/?kT and plotted versus (1/T - 1/Tgel), where G' is the elastic modulus and Tgel is the gel temperature. This scaling is in line with predictions of mode coupling theory which emphasizes the importance of local structure (localization length) over longer-range correlations in determining the dynamical and mechanical properties of such gels. The dynamics nanoparticles during of the gelation process is measured using X-ray Photon Correlation Spectroscopy (XPCS) at Argonne National Labs. Using a newly developed ultrafast frame rate (11.8 kHz) pixel-array-detector, we have, for the first time, captured the complete transition of the dynamics of the suspension from tens of seconds in the gel state to hundreds of µs in the liquid state. The transition is triggered when the gel is slowly heated. Our nanoscale measurements of the colloid dynamics as a function of temperature and particle size can be compared to macroscopic viscoelastic properties probed by rheology under the same conditions and suggest that smaller colloids form stronger networks when they gel. This is in line with the measurements of the gel boundary with smaller particles gelling at higher temperatures. Efforts to extend the scaling relationships of elastic modulus to smaller particle sizes and their mixtures and limitations of the theories in predicting the mechanical properties will also be discussed.

Wednesday 6:00 Foyer-Stairs/Windows PO39

Effect of particle roughness on hydrodynamic diffusion in steady shear

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We measured and simulated the dynamics of non-Brownian and neutrally buoyant spheres suspended in a viscous shear flow to investigate hydrodynamic diffusion. Measurements were performed for a range of volume fractions between 0.25 and 0.35 of monodisperse spheres with different values of particle roughness. Two regimes of dependence of the diffusion coefficient on roughness were found. The diffusion coefficient increases with particle roughness for small volume fractions. However, at high volume fractions, the diffusion coefficient decreases as particle roughness is increased. These trends were confirmed by simulations of a minimal model that solely includes normal lubrication interactions and a frictionless contact force. We found that particle organization into layers, as promoted by increasing the particle roughness, alters the expected trend of a positive correlation between particle diffusion and roughness as the volume fraction increases.

Wednesday 6:00 Foyer-Stairs/Windows PO40

The onset of the collective motion of active fluids

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Few things seem to capture our imagination more reliably than the collective motion of flocking birds, schooling fish or swarming insects. Such a collective behavior represents a universal feature of active fluids, which has profound influences on their rheological properties. While the collective motion of active fluids in steady states has been extensively studied in recent years, the kinetic route to this striking behavior is still largely unknown. Here, we study the transition kinetics of the collective motion of active fluids by using an engineered light-controlled E. coli strain, whose locomotion can be reversibly switched between swimming and tumbling using a blue light. We investigate the emergence of bacterial collective motion, particularly the formation of coherent vortex structures, when bacteria are switched from tumbling to swimming. Velocity correlations, energy spectrum and vortex statistics are measured for quantifying the kinetics of this non-equilibrium "phase transition". We map the phase diagram of active bacterial suspensions by systematically varying bacterial concentrations and the ratio of tumblers and swimmers. The transition kinetics are also explored based on the dynamics of single bacteria.

Wednesday 6:00 Foyer-Stairs/Windows PO41

Determining the role of TIMPs in matrix remodeling during 3D hMSC motility

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Cells locally remodel and degrade their microenvironment. During the wound healing process, cells must migrate out of the native extracellular matrix (ECM) to reach an injury. There is a lack of understanding of these cell-material interactions; key missing information slowing the design of implantable materials that enhance wound healing. But, the native ECM is complex and not completely understood; therefore, we characterize scaffold remodeling prior to and during motility. To do this, we encapsulate human mesenchymal stem cells (hMSCs) in 3D in a well-defined synthetic scaffold. The chemically cross-linked scaffold is composed of poly(ethylene glycol) end functionalized with norbornene cross-linked with a matrix metalloproteinases (MMPs) degradable peptide that is degraded by cell-secreted enzymes. Multiple particle tracking microrheology (MPT) is used to measure temporal matrix remodeling and degradation. In MPT, the Brownian motion of fluorescent probe particles embedded inside the hydrogel is measured. Before cell encapsulation enzymatic degradation of the scaffold is measured using collagenase, a mixture of enzymes including MMPs. Using time-cure superposition, the superposition of viscoelastic functions at different extents of reaction, we calculate the critical relaxation exponent, $n = 0.25 \pm 0.05$. This value pinpoints the gel-sol transition, identifying the state of the hydrogel in the area around each cell. Before cell migration, directly under the cell there is no scaffold degradation enabling spreading and attachment. The greatest degradation is measured in the region farthest from the cells, 160 µm away. We hypothesize that MMPs are inhibited by a second cell-secreted enzyme, tissue inhibitors of metalloproteinases (TIMPs). Next, we study the effect of neutralizing TIMPs on matrix degradation and motility. We anticipate that TIMP inhibition will result in more aggressive cell-mediated degradation and migration to stiffer regions, enhancing delivery of cells to wounded areas.

Wednesday 6:00 Foyer-Stairs/Windows PO43

Active microrheology in a colloidal glass

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Microrheology is a tool to access viscoelastic properties of complex fluids on a local scale by monitoring a microscopic probe in the sample under test. While passive probes provide only information on the linear response, external driving of the probe particle allows to probe nonlinear phenomena. Soft solids, e.g. colloidal glasses, melt under macroscopic shear. The same phenomenon appears on the microscopic scale: the probe particle can delocalize, when the force is large enough [1]. Our model system is a colloidal glass of hard spheres with an immersed probe particle, which is subject to a constant force. Using a refined mode-coupling theory (MCT) approach [2], we study the self-intermediate scattering function, from which we can obtain the spatial probability distribution of the probe particle as well as mean and mean squared displacements.

We find highly nonlinear effects like force thinning or diffusion enhancement, where the corresponding coefficients change by several orders of magnitudes. Furthermore, the spatial probability distribution of the probe shows pronounced exponential tails in direction of the external force but also perpendicular to it. To support these MCT predictions, we compare the results with molecular dynamic computer simulations.

[1] I. Gazuz, A. M. Puertas, T. Voigtmann and M. Fuchs, Phys. Rev. Lett. 102, 248302 (2009). [2] M. Gruber, G. C. Abade, A. M. Puertas, and M. Fuchs, Physical Review E 94, 042602 (2016).

Wednesday 6:00 Foyer-Stairs/Windows PO44

Rheology of pendular networks in particle-containing polymer blends

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We report on the rheology of blends of two immiscible polymers, polyisobutylene (PIB) and polyethylene oxide (PEO), with addition of 20 vol% of silica particles that are fully-wetted by the PEO. At compositions when PEO is in a minority, the PEO binds the particles into aggregates. These aggregates may form a percolating network with strongly non-Newtonian flow behavior.

We show that the rheological properties (examined by Large Amplitude Oscillatory Shear, LAOS) of such mixtures depends on composition as well as on flow rate. Flow visualization experiments suggest that the aggregates undergo reversible breakdown, and the changes in rheology are correlated with such breakdown. Knowing the detailed behavior of the pairwise meniscus force between two particles, we develop a scaling model according to which the breakdown strain scales with the 1/3 power of the wetting fluid fraction. The model is qualitatively in agreement with the results, but quantitatively, the model greatly overpredicts the breakdown strain.

Wednesday 6:00 Foyer-Stairs/Windows PO45

Normal stress differences of model attractive colloids: Towards tests of theories for shear-induced migration

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Confined flows of colloids abound both in nature and in technological applications. In the body, blood is a complex suspension that flows through confined arterioles [1]. In 3D printing of microelectronic devices [2], suspensions of metallic colloids flow through nozzles and tubing. Confined flow, however, can cause particles to move across streamlines to become concentrated at the center or the walls of the channels through a phenomenon known as shear-induced migration, which can eventually lead to jamming or cause unfavorable properties in final products. Theoretical studies have proposed that normal stress differences [3] or shear stress gradients [4] may drive cross-streamline movement of particles. In earlier work, we showed that inducing an attractive interaction between the colloids reduces shear-induced migration [5]. To investigate the mechanism by which attractive interactions reduce shear-induced migrations, we measured the changes in normal stress differences of model colloidal suspensions with systematically varied attraction strengths. We synthesized particles made of copolymers of 2,2,2-trifluoroethyl methacrylate and t-butyl methacrylate [6], which were nearly density- and refractive-index-matched to a solution of glycerol and water. The high viscosity background solvent was chosen to increase the normal stress signal to measurable values on commercial rheometers. The suspensions for rheology measurements had particle volume fraction of 0.4 with various concentrations of poly(acrylic acid) added as the depletant, resulting in various attraction strengths between the particles.

[1] Kumar, A. and M.D. Graham, Soft Matter 8, 10536-10548 (2012). [2] Fuller, S.B., et al., J. Microelectromechanical Syst. 11, 54-60 (2002). [3] Nott, P. and J. Brady, J. Fluid Mech. 275, 157-199 (1994). [4] Leighton, D. and A. Acrivos, J. Fluid Mech. 181, 415-439 (1987). [5] Pandey, R. and J.C. Conrad, Soft Matter 8, 10695-10703 (2012). [6] Kodger, T.E., et al., Sci. Rep. 5, 14635 (2015).

Wednesday 6:00 Foyer-Stairs/Windows PO46

Rigidity percolation for anisotropic thermoreversible colloidal gels and glasses composed of adhesive hard rods

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Particle technologies ranging from cements to protein therapeutics benefit from anisotropic colloids due to their unique rheological properties and orientation-dependent interactions. While the particle geometry is known to affect the rheological and thermodynamic properties, a comprehensive understanding is lacking for how the coupled effects of shape anisotropy and interparticle attractions influence rigidity percolation or dynamical arrest transitions, such as gel and glass formation. To quantify and map these coupled effects, a tunable model system of adhesive hard rods (AHR) was developed with convenient control of the aspect ratio and thermoreversible, short-range attractions. The AHR system serves as a chemically consistent extension of the well-studied adhesive hard sphere system (AHS) composed of octadecyl-coated silica. Measurements of the fluid-like and solid-like rheology, microstructure, and particle dynamics were mapped and compared as a function of aspect ratio (L/D 3-7), volume fraction (0.1-0.5), and temperature-dependent attraction strength (15-40 C). SAOS measurements, X-ray and neutron scattering, and dynamic light scattering methods identified spatial and temporal effects of shape anisotropy on the rigidity percolation transition. In general, quantitatively distinct yet qualitatively similar signatures of dynamic arrest were observed for AHR, as compared to AHS. By systematically mapping these transitions, it is proposed that a connected rigidity percolation surface exists for quasi one-dimensional hard particles with short-range attractions. It is reasoned that the percolation surface becomes bounded by a hard rod glass line at high volume fractions (excluded volume-driven) and is intersected by phase-separation at low volume fractions (attraction-driven). Although many questions remain open, the AHR system enables an adaptable experimental framework for future explorations on the coupling between attraction strength, concentration, and particle shape anisotropy.

Wednesday 6:00 Foyer-Stairs/Windows PO47

Structure and dynamics of nanoparticles and polymer in model polymer solutions with particle-particle interactions

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The bulk rheology of polymer nanocomposites deviate significantly from that for pure polymer melts due to competing relaxations of both particles and the surrounding polymer. We investigate these competing relaxations with a model system of charged silica nanoparticles (50 nm in diameter) dispersed in semidilute solutions of high molecular weight polystyrene (of radius of gyration 30 nm). We probe the structure of the silica nanoparticles using static x-ray and of the polymer using small angle neutron scattering. The particles are well dispersed and the polystyrene chains are Gaussian with a correlation length of 4 nm that agrees with polymer scaling laws. We then use dynamic scattering methods to independently quantify the dynamics of polymers and particles. Using neutron spin echo spectroscopy, we show that the polymer chains relax according to the Zimm model, with hydrodynamic coupling over the correlation length. The polymer dynamics are unchanged in the presence of particles; the polymer chains do not hydrodynamically couple to the particle. Using x-ray photon correlation spectroscopy, we show that the nanoparticle dynamics are subdiffusive with stretched exponential decays. The subdiffusive dynamics derive from a coupling between the particle dynamics and the polymer relaxations over the particle surface. Over the interparticle distance, the particle dynamics are suppressed and inversely correlated to the structure factor, as observed in many homogeneous materials with diffusive dynamics. Notably, the de Gennes narrowing of the particle dynamics persists despite the coupling of particle and polymer dynamics on shorter length scales and the resulting subdiffusive particle dynamics. Exploiting contrast variation in x-rays and neutrons, we separated changes in the particle dynamics from those of the polymer. Thus, we developed a nanoscale understanding of the complex, competing relaxations present in composite materials.

Wednesday 6:00 Foyer-Stairs/Windows PO48

Rheological characterization of biomass granular suspensions for renewable fuels

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A compelling vision for the future of combustible engines is to rely on renewable sources of fuel, such as cellulosic ethanol from biomass. A common biomass feedstock with high cellulosic content is corn pericarp, a byproduct of corn fractionation in typical fermentation processes. A major shortcoming of utilizing corn pericarp is the inability to fully characterize the fluid mechanics during enzymatic hydrolysis (liquefaction) due to the complex structure of corn pericarp suspensions. This project utilizes rheometry as a powerful tool to characterize corn pericarp to develop an understanding of the dominating flow regimes and identify fluid instabilities. In this study simple shear rheology was used to obtain stress-strain curves to characterize the flow mechanics of corn pericarp suspensions. At low shear rates (0.01 1/s - 0.05 1/s) the rheological data shows the suspensions to be unstable. However, as the enzymes in the suspension digest the pericarp, causing the interstitial fluid to become more viscous and non-Newtonian, the shear stress reduces and stable conditions within the same shear rate range occur. Further, it was found that a viscous reduction of the suspension occurred within three hours of liquefaction. This suggests that a flow regime change occurs between frictional and lubrication interactions and that lubrication may dominate over the frictional between the granular particulates. To mimic the conditions of the liquefaction process, larger shear rate ranges of 0.01 1/s - 500 1/s were applied, resulting in suspected shear banding and visible particle migration instabilities. In order to fully characterize flow of opaque materials, an Ultrasonic Speckle Velocimetry (USV) system is currently being constructed in order to image complex materials and will be applied to the pericarp. Once completed, this analysis will be able to identify and quantify the rheological instabilities due to liquefaction of corn pericarp, allowing for more efficient processing of corn and other biomass into ethanol.

Wednesday 6:00 Foyer-Stairs/Windows PO49

Effect of interaction type and nanoparticles ratio of modified CNT-graphene hybrids on rheological and electrical properties of SEBS nanocomposites

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Novel nanocomposites based on poly(styrene-b-(ethylene-co-butylene)-b-styrene) triblock copolymer with hexagonally packed cylindrical (HEX) microdomains, and Graphene-CNT hybrids had made it possible to achieve stretchable electrically conductive materials at very low loadings of nanoadditives. organophilic graphene nanosheets had been functionalized through reacting graphene oxide nanosheets with octadecylamine. Chemical modification of MWCNTs was performed via sidewall carboxylic acid functionalization and further modification using octadecylamine. Effective functionalization of nanoparticles was characterized by means of FTIR ,XRD,FE-SEM and TGA. Nanocomposites were prepared by solution mixing. Appropriate surface modification of hybrid components results in well dispersion of nanoadditives in SEBS. Rheological data indicated that the storage modulus increased considerably with addition of hybrids of nanoparticles, due to formation of 3-Dimensional network of nanoadditives. Rheological measurements were also used to determine the effect of hybrid nanoparticles on micro phase separated structures, orientation and recovery of cylindrical PS domains. Electrical conductivity measurements using CNT and Graphene simultaneously, demonstrates synergistic transport effect due to Graphene-CNT-Graphene physically interconnected conductive network structure formed throughout the matrix.

Wednesday 6:00 Foyer-Stairs/Windows PO50

Functionalized graphene nanosheets-induced electrical conductivity in a dynamically asymmetric LCST polymer blend

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Demixing in a dynamically asymmetric polymer blend of polystyrene/ poly (vinyl methyl ether), PS/PVME, a well-known phase separating model of viscoelastic phase separation (VPS), in the presence of nanoparticles having significant affinity to a specific phase, can lead to slowing down or even arresting the transient and thermodynamically unstable network-like structure, which needs to be stabilized for designing a heterogeneous structure with desired mechanical and electrical applications. For this purpose, hydrophobic graphene nanosheets, which self-assemble in the bulk of PS-rich phase (slower dynamics), had been functionalized through reacting graphene oxide nanosheets with octadecylamine and were used to control the kinetics of phase separation and also induce high electrical conductivity through double percolation event at a very low volume fraction.

Wednesday 6:00 Foyer-Stairs/Windows PO51

State transitions in shear thickening suspensions

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Shear thickening fluids are known to have an effective viscosity that diverges as the packing fraction φ approaches the jamming transition, φ_j. We find that the transient relaxation viscosity of suspensions of cornstarch and water start to deviate from the steady state viscosity as the packing fraction increases above $\varphi_c<\varphi_j$ and goes to zero at φ_j. Further, we find the ratio of the normal stress to shear stress changes from negative to positive at $\varphi_N<\varphi_c$. We also identify a quantitative critical φ_t such that $\varphi_N<\varphi_t<\varphi_j$ where the shear thickening behavior transitions from continuous to discontinuous. This transition happens at φ consistent with the φ at which the compressive modulus of these fluids, measured under impact, increases to $\approx 10^6$ Pa. By locating these different state transitions with respect to φ_j, we can quantitatively identify critical φ values for other environments.

Wednesday 6:00 Foyer-Stairs/Windows PO52

Microstructure, rheology and heterogeneity in colloidal gels

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

Wednesday 6:00 Foyer-Stairs/Windows PO53

Jammed micro-organogels for 3D printing with oily soft matter

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3D printing methods generally rely on the rapid solidification of fluid inks to prevent instabilities driven by surface tension and gravity. Recently, these instabilities have been overcome in soft matter 3D printing through the use of a jammed microgel support medium; localized yielding at low stress and rapid reflow after yielding trap injected fluid structures in space. Traditional methods of microgel manufacturing produce materials that are predominately swollen in aqueous solvents, severely limiting their applicability in 3D printing oil-based soft materials due to interfacial instabilities. Here we present a new method for the manufacturing of a microgel system in an organic solvent through the self-assembly of block copolymers. We explore the tunability of these micro-organogels in search of rheological properties favorable for 3D printing silicone structures.

Wednesday 6:00 Foyer-Stairs/Windows PO54

Polymer physics scaling laws in yielding of jammed microgels

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Granular-scale microgel particles are a critical ingredient in most personal care products like hand sanitizers and lotions, which must be able to transition between fluid and solid states under shear. These "liquid-like solids" show promise for emerging technologies; they have recently been exploited in 3D printing objects made from a variety of soft matter materials including colloids, hydrogels, elastomers, and living cells. By leveraging the jamming/unjamming transition, complex large aspect ratio objects, thin closed shells, and hierarchically branched tubular networks have been 3D printed within jammed microgels. Yielding and fluidization in granular matter is known as the jamming transition and has been studied extensively within the rheology and soft matter communities. However, the underlying polymer physics that set the system yield stress is not known. In this study, we explore how the connection between polymer mesh-size, relaxation times, and microgel elasticity set the yield stress in granular liquid-like solids that controls the jamming transition.

Wednesday 6:00 Foyer-Stairs/Windows PO55

Rheological aspects of film formation from suspensions of montmorillonite clay (MMT) in dilute poly(vinyl alcohol) solutions

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Composite films can be made by simple dip-coating of a suitable substrate into a dilute suspension of montmorillonite clay (MMT) in a poly(vinyl alcohol) solution. The resulting thin films have unusually favorable mechanical, flame-retarding and oxygen-barrier properties. To optimize the processing and properties of these coatings we are examining factors that do, or might, control the ordering of the clay nanoplates that are responsible for the properties mentioned above. Among these factors are (1) the shear-stress magnitude and history during the coating process and (2) the interaction of the clay with the substrate, each other and the polymer "glue." This presentation considers aspects of both of these. For example, we show that at normal coating concentrations (1.5% solids), the suspension does not gel, in contrast to some reports in the literature. However, as drying proceeds, gelation is observed at about 5% solids. The lack of gelation is undoubtedly favorable for orderly placement of the nanoplates into a nacre-like structure.

Wednesday 6:00 Foyer-Stairs/Windows PO56

Role of chain scission in cross-slot flow

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Recently, there has been intense experimental investigations about the development of an asymmetric instability in the flow of viscoelastic liquids in a cross-slot. The instability has been observed in both polymer and wormlike micellar solutions. Unlike polymer chains, wormlike micelles (WLMs) continuously break and reform. This behavior causes a major difference in the extensional rheology of polymer and wormlike micellar solutions. Despite these differences, the observed elastic instability has been characterized the same. Unlike for polymer solutions, a lip vortex has been observed in the cross-slot flow of WLMs. Could this flow phenomenon, as well as the asymmetric instability, be a result of chain scission?

To examine the role of chain scission, we investigate the pressure-driven flow of the VCM constitutive model (Vasquez, McKinley and Cook (2007)) through a cross-slot device using the open-source CFD library OpenFOAM developed by OpenCFD Ltd. The VCM model is a two species, microstructural network model, which incorporates breakage and reforming of two micellar chains (a long chain 'A' and a shorter chain 'B'), developed to describe entangled solutions of wormlike micelles. In order to isolate the role of chain scission on the flow, parameters are chosen

such that the VCM predictions under homogeneous shear and planar extensional flows follow those of the Oldroyd-B (OB) model. The two-species model cross-slot predictions are compared and contrasted with the corresponding predictions of the single-species OB model. Both models predict the formation of an asymmetric elastic instability. However, unlike the OB model, the VCM model predicts the formation of recirculation zones near where the inlet and outlet channels meet. As a result, the computational results can also compared with experimental observations of the flow of wormlike micellar solutions through a microfluidic-based cross-slot geometry.

Wednesday 6:00 Foyer-Stairs/Windows PO57

Determination of characteristic lengths and times for wormlike micellar solutions from rheology using a mesoscopic simulation method

Weizhong Zou[1], Xueming Tang[1], Mike Weaver[2], Peter Koenig[3], and Ronald G. Larson[1]
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We apply our recently developed mesoscopic simulation method for wormlike micelle (WLM) solutions to extract multiple micellar characteristic lengths and time constants: i.e., average micelle length, breakage rate, and entanglement and persistence lengths, from linear rheological measurements on commercial surfactant solutions over a wide range of added salt and perfume raw materials (PRMs). Measurements include both mechanical rheometry and diffusing wave spectroscopy (DWS), the latter providing the high-frequency data needed to determine micelle persistence accurately. The effects of entanglements and branching on the viscoelastic behaviors of WLM solutions are obtained as well as the dependence of micellar properties on added salts and PRMs. By fitting the experimental data (G' and G") across the entire frequency range, the method is of practical use in characterizing and designing surfactant solutions for different applications, which are difficult to achieve through other theoretical or experimental methods.

Wednesday 6:00 Foyer-Stairs/Windows PO58

Understanding steady and dynamic shear banding in a model wormlike micellar solution

Michelle A. Calabrese[1], Simon A. Rogers[2], Lionel Porcar[3], and Norman J. Wagner[1]
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Shear banding under steady and dynamic deformation is examined in a model wormlike micellar solution to experimentally validate predictions of the Vasquez-Cook-McKinley (VCM) model, which explicitly accounts for breakage and reformation events leading to shear banding (Zhou, et al., JNNFM 2010). Shear banding is confirmed using a combination of rheology and flow-small angle neutron scattering (flow-SANS) measurements, where startup rheology and flow-SANS reveal long transients during shear band formation (Calabrese, et al., JOR 2016). Spatially- and temporally-resolved flow-SANS measurements probe the microstructure during steady and dynamic shear banding. Under large amplitude oscillatory shear (LAOS) deformation, shear banding is dependent on the Deborah and Weissenberg numbers, validating the VCM model predictions. Micelle segmental alignment in the flow-gradient plane during LAOS is a complex function of cycle time, radial position, frequency and shear rate. The maximum segmental alignment under LAOS often exceeds that of the corresponding shear rate under steady shear, termed "over-orientation." Guidelines for LAOS shear banding are developed based on LAOS rheological features and degree of over-orientation. The results of this study present new methods for identifying shear banding under steady and dynamic deformation, while providing an extensive data set for the development and further improvement of constitutive models.

Wednesday 6:00 Foyer-Stairs/Windows PO59

Flow-visualization study of a worm-like micellar system

Eduard A. Caicedo-Casso and Kendra A. Erk
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The application of visualization techniques to flow studies lead to quantitative and qualitative understanding of the theoretical models. The ability to observe the flow behavior helps to elucidate certain transient phenomena that are overseen in a regular rheological test. Time-resolved visualization is a useful tool that could lead to new discoveries in the analysis of worm micelles viscoelasticity. At present, the effect of an external factor such as temperature over the viscoelastic behavior of a worm-like micellar system is studied. An ionic commercial shampoo with translucent characteristics is selected as the experimental sample. A customized flow-visualization set up coupled with a state of the art shear rheometer with glass cell are used to elucidate the most important parameters of this study. Shear start up at different shear rates are used to induce the particle motion. Particle tracking is carried out using a license-free PTV software based on Matlab. Concentric cylinder geometries are used to perform flow curves, viscosity curves, amplitude sweeps, and frequency sweeps to enlighten the effect of temperature over the most important parameters of the Maxwell model. Increasing temperature reduces the relaxation time of the commercial shampoo. It is believed that the effective entanglements are reduced with increasing temperature. Above a critical temperature of 30 oC, the viscoelastic response of the commercial shampoo and the probability to have a worm-like micellar system is greatly compromised. From flow visualization techniques analysis, strong evidence of flow instability formation has not been observed at the investigated shear rates. Linear velocity profiles corresponding to simple shear behavior has been observed at shear rates of 0.1 s-1 and 1 s-1 at different temperatures. However, it is expected that current experiments at higher shear rates provide more exciting results.

Wednesday 6:00 Foyer-Stairs/Windows PO60

Shear induced orientation effects in optical active samples characterized with polarized light imaging

Loredana Völker-Pop, Gunther Arnold, Tobias Nill, and Joerg Laeuger
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While the classical rheology gives information about the macroscopical behavior of a material under certain conditions, this behavior is strongly determined by the underlying microstructure of the material itself. Thus, the combination of optical techniques with rheological measurements might be of interest in order to correlate microstructural properties with the rheological behavior of the material. One of these techniques is polarized light imaging which allows e.g. the observation of flow induced crystallization processes of polymers or the characterization of the orientation of polymer chains in polymer solutions and melts under shear [1-3]. The method is based on the phase difference of light passing through optical active materials and provides information on optical path boundaries between optical isotropic and anisotropic structures. The phase differences can be analyzed by an optical setup consisting of light source, collimating lens, polarizer, analyzer and CCD camera. This contribution will present a polarized light imaging setup mounted on a Modular Compact Rheometer (Anton Paar) and highlight applications which indicate the usability of this technique in order to correlate microstructural changes with the rheological behavior of different samples. Different polymer solutions were investigated with cone-and-plate and parallel-plate geometries in order to visualize possible effects of non-constant shear rate on the shear induced orientation within the sample. Additionally the impact of shear on the behavior of liquid crystals was determined at different temperatures in order to evaluate the crystals' transition from the isotropic to the anisotropic state. The results indicate the suitability of the combination of polarized light imaging and rheology to monitor shear induced transformations in complex fluids.

Wednesday 6:00 Foyer-Stairs/Windows PO61

Flexible molecules in viscoelastic solutions undergoing planar extensional flow

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We present experimental results of weakly viscoelastic dilute DNA suspensions undergoing planar extensional flow in cross-slot microfluidic devices. We characterize flow fields and single molecule dynamics near the central stagnation point and we find that low-molecular weight (MW) DNA suspensions behave similar to a Newtonian fluid while high-MW DNA suspensions exhibit a symmetry-breaking flow instability similar to a viscoelastic fluid. High-speed visualization shows that high MW DNA approach the central stagnation point significantly pre-stretched and are aligned with the flow direction. At high strain rates, hydrodynamic forces near the central stagnation point (i) compress pre-stretched molecules producing high curvature along the DNA backbone followed by (ii) elongation of coiled molecules producing highly-stretched DNA and molecular scission.

Wednesday 6:00 Foyer-Stairs/Windows PO62

Constitutive model that predicts stress overshoot and shear thinning for entangled melts

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We review constitutive modeling of melts of linear polymers, focusing on changes in bulk rheological response in startup shear flow. The time dependent rheological anomalies are captured by constitutive equations, originate from the MLD model and Rolie-Poly equation for entangled melts. According to these models and supporting experimental data, for melts, the shear viscosity decrease dramatically by increasing the shear rate as the entanglement density increases. However the shear stress growth and first normal stress coefficients do not increase monotonically but pass through a maximum with increasing time or strain at sufficiently high shear rates. The stress overshoot which occurs at rates between the reciprocal of the Rouse time and of the reptation time have been attributed to CCR and alignment of the primitive chain. In particular this initial stress overshoot is basically due to chain retraction after affine deformation rather than chain orientation.

Wednesday 6:00 Foyer-Stairs/Windows PO63

Entanglements in glassy polymer crazing: Crosslinks or tubes?

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Using molecular dynamics simulations and topological analyses, we examine the evolution of entanglements during crazing in model polymer glasses. By tracking individual topological constraints (TCs) over the course of deformation, we show how the evolution of their statistical properties can be used in conjunction with characterization of the complex, nonaffine lateral displacements that occur during fibrillation to provide insights not available from previous studies. Our findings directly contradict the conventional assumptions that entanglements act like chemical crosslinks and that therefore a large fraction must be lost during interfibril void formation and expansion. Instead, the number of TCs remains nearly constant throughout the craze drawing process, but about 1/3 of TCs are ultimately replaced by other TCs associated with the same rheological tubes. By combining this key result with extensive measurements of the distributions of entanglement spacings and stretches, the evolution of these during deformation, and end-constrained melt-dynamics simulations that relate processes in crazes to processes familiar from tube theory, we formulate a new molecular-scale picture of entanglement evolution during crazing.

Wednesday 6:00 Foyer-Stairs/Windows PO64

Nonlinear uniaxial extension behavior of polyisoprene melts: Polymer melts and mixtures

Jianning Liu[1], Yi Feng[1], Konstantinos Misichronis[2], Konstantinos Ntetsikas[3], Jimmy Mays[2], Apostolos Avgeropoulos[3], and Shi-Qing Wang[1]

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Based on linear polyisoprene (PI) melts of different molecular weights and their mixtures, we explore nonlinear responses to melt stretching including startup and step extension, as a function of molecular weight and mixture composition. For example, we show in the limit of no chain stretching, i.e., Rouse-Weissenberg number WiR << 1, homogeneous extension is terminated by tensile decohesion, contrary to the literature assertion that such entangled melts and melts can attain steady flow. By comparison between mixtures and monodisperse melts we indicate how the entanglement structure influences the characteristics such as yielding and melt rupture.

This work is supported, in part, by National Science Foundation (DMR-1105135).

Wednesday 6:00 Foyer-Stairs/Windows PO65

Extensional rheology and final morphology of LDPE fibers

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Properties of polymeric fibers are highly dependent on the molecular conformation induced during processing[1]. In this study we investigate the influence of non-linear extensional flow on the molecular conformation of branched semi-crystalline polymers. Such materials show a stress overshoot when stretched at a constant extensional rate[2]. The common explanation is, that at first the backbone stretches until the stress maximum is reached. This is followed by a collapse of the branches causing backbone retraction and thus the decrease in stress[3]. Consequently, one would expect the greatest molecular orientation in fibers quenched at the stress maximum. Indeed we find that this is true and also a more general observation that the final orientation scales with stress at quench in the melt.

[1] Schrauwen B. et al, Macromol. 37 (23), 8618 (2004). [2] Rasmussen, H.K. et al. J. Rheol. 49 (2), 369 (2005). [3] Hawke, L.G.D. et al., J. Rheol. 59 (4), 995 (2015).

Wednesday 6:00 Foyer-Stairs/Windows PO66

Molecular dynamic simulation on rupture-like failure in startup uniaxial extension

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Experimental data show that when Weissenberg number W_i is high, uniaxial extension exhibit strain hardening and suffer a sharp rupture-like failure. In this work, molecular dynamic simulation is carried out to show that instead of steady flow after partial yielding, non-Gaussian chain stretching leads to monotonic increase of engineering stress until the system runs out of entanglement and undergoes breakup. When a bond breaking mechanism is introduced, the melt rupture can take place much earlier, at more reasonable stretching ratios.

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Wednesday 6:00 Foyer-Stairs/Windows PO67

Elastic yielding of melt-stretched glassy polymers below glass transition temperature

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We have recently carried out mechanical and in situ IR-thermal-imaging based temperature measurements of SBR melts during uniaxial extension to demonstrate the nature of mechanical responses. We concluded there was monotonic increase of internal energy during adiabatic melt stretching until the point of inhomogeneous extension. We will present supporting evidence that melt extension of PS and PMMA indeed leads to an intrachain stress that is sufficiently high to produce elastic yielding [1] in the glassy state. This work systematically investigates how characteristics of this elastic yielding, e.g., induction time and magnitude of the tensile stress, change as a function of the temperature at which melt stretching is carried out, the degree of melt stretching, the annealing temperature where elastic yielding is observed.

[1] Cheng S, Wang SQ. Elastic Yielding in Cold Drawn Polymer Glasses Well below the Glass Transition Temperature. Physical review letters. 2013 Feb 7;110(6):065506.

Wednesday 6:00 Foyer-Stairs/Windows PO68

Exploring the nature of mechanical stress of polymers in melt and glassy states

Xiaoxiao Li, Mesfin Tsige, and Shi-Qing Wang
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The components of stress building up during deformation of a polymer with high molecular weight is a basic topic that has been studied for decades. The microscopic nature of stress remains elusive in both melt and glassy states. In this work, molecular dynamics simulation is carried out based on a coarse-grained model for polystyrene, aiming to examine how chain networking plays a role in the yielding and ductile deformation of polymer glasses in comparison to the proposed picture in literature [1]. The MD simulation is also shown to provide insightful information concerning the question of whether fast melt deformation leads to a buildup of internal energy that would be intrasegmental in origin. This work is supported, in part, by a NSF grant (DMR-1444859 and DMR-1609977).

[1] S.-Q. Wang, S. Cheng, P. Lin, and X. Li, The Journal of chemical physics 141, 094905 (2014).

Wednesday 6:00 Foyer-Stairs/Windows PO69

Instability growth in 2D array of confined cylinders and its role on oil displacement

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Flow of viscoelastic fluids around cylinders in a microchannel resembles to inertia elastic instabilities that occur atcreate flow instabilities at critical Mach number (Ma) that result in both downstream and upstream phenomenon; it is believed that similar phenomenon likely aids in the displacement of oil from porous material in enhanced oil recovery techniques. In this work, oil displacement in porous medium implementing by viscoelastic instabilities is studied using microfluidic channelsy at low Reynold's number is presented. The efficiency of the oil displacement is investigated. Using 2D arrays of cylinders in a microchannel of with varryingvaryingdifferent pore size geometries, the oil is displaced using low viscosity Boger solutions and comparblaecomparable . A comparison between Newtonian glycerol solutions. with the same viscosity as the Boger fluids at the same flow rate is also investigated. Efficacy of displacement is evaluated byevaluated by examining the displaced volume of oil, as well as by examining flow visualization and excess pressure drop. Once the base flow approaches to ?Ma?_crit ~ 0.12, the onset of the instability occurs. Above a critical flow rate when instabilities are known to occur, Boger solutions has better ability to displace trapped oil than in comparison tothe glycerol solutions. Based on analysis of flow and pressure drops, it appears that this is due to the change in flow patterns caused by viscoelastic instabilities and not due to excess pressure drop. We present initial results on this phenomenon and suggest future work in order to better understand this problem.Also the work has been expanded to different flow rate with different geometries; such as, hexagonal array and fracture array, to study the efficiency of the displacement. Flow resistance is also characterized by examining excess pressure drop which is affected by the instabilities. This work will apply to many problems of improved oil recovery techniques which is one of the on ongoing research in microfluidics.

Wednesday 6:00 Foyer-Stairs/Windows PO70

Solution rheology of a methyl methacrylate based resin system

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Free radical polymerization of methacrylate based resins is well established for industrial scale casting of acrylic sheets. However, fundamental characterization of the solution properties of PMMA/MMA solutions within the framework of overlap concentration scaling is lacking in the literature. This study investigates the steady state shear rheology of PMMA dissolved in MMA over various molecular weights. The initial study of this system characterizes the viscosity of four different molecular weight solutions over five concentrations at each molecular weight. The viscosity of these solutions is measured as a function of shear rate over a combined range from 1 1/s to 1,000 1/s. Additionally, the temperature dependence of the viscosity is measured for each system in the Newtonian region over a temperature range from 0 to 70 °C. The zero shear viscosity of these systems is correlated as a function of the concentration of polymer normalized by the overlap concentration (c/c*). Data from this sample set are used to fit the shear dependent Carreau-Yasuda viscosity model. This model proves useful for describing the cure kinetics and chemorheology of a methacrylate based resin system when casting acrylic sheets.

Wednesday 6:00 Foyer-Stairs/Windows PO71

DMA, sound damping and application properties of acrylic polymers for liquid applied sound damping (LASD) materials

Catheryn L. Jackson[1] and Justin Gimbal[2]
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Over the last decade, damping materials have contributed major improvements to automobile passenger comfort, and Noise, Vibration and Harshness (NVH) engineers have targeted key properties that improve vehicle performance. The specified sound damping material is applied to the formed surfaces of the vehicle body, typically with incumbent asphaltic damper materials cut from sheets and baked-on to the metal surfaces. More recently, liquid applied sound damping (LASD) coatings based on acrylic emulsion polymers that can be sprayed-on and are water-based, offer advantages of application flexibility on curved or difficult to reach surfaces. These liquid damper formulations have advanced to give coatings

which meet increased performance requirements through improved loss modulus of the final dried coating. Data generated by dynamic mechanical analysis (DMA) show that the coating viscoelastic behavior is what drives the performance in damping materials. Through the correlation of loss moduli to damping performance of Oberst bar tests, and the composite loss factor (CLF) equation, the mechanism can be further quantified and explained. Various types of LASD polymers will be compared as the technology has evolved and improved. In addition to the increase in damping efficiency, formulation of acrylic liquid dampers can offer improved resistance to blister formation when cured between 120 - 180 C°, increased tensile properties, and increased water resistance.

Wednesday 6:00 Foyer-Stairs/Windows PO72

Formulation and validation of an efficient computational model for a dilute, settling suspension undergoing rotational mixing

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Designing processing equipment for the mixing of settling suspensions is a challenging problem. Achieving low-cost mixing is especially difficult for the application of slowly reacting suspended solids because the cost of impeller power consumption becomes quite high due to the long reaction times (batch mode) or due to large-volume reactors (continuous mode). Further, the usual scale-up metrics for mixing, e.g., constant tip speed and constant power per volume, do not apply well for mixing of suspensions. As an alternative, computational fluid dynamics (CFD) can be useful for analyzing mixing at multiple scales and determining appropriate mixer designs and operating parameters.

We developed a mixture model to describe the hydrodynamics of a settling cellulose suspension. The suspension motion is represented as a single velocity field in a computationally efficient Eulerian framework. The solids are represented by a scalar volume-fraction field that undergoes transport due to particle diffusion, settling, fluid advection, and shear stress. A settling model and a viscosity model, both functions of volume fraction, were selected to fit experimental settling and viscosity data, respectively. Simulations were performed with the open-source Nek5000 CFD program, which is based on the high-order spectral-finite-element method.

Simulations were performed for the cellulose suspension undergoing mixing in a laboratory-scale vane mixer. The settled-bed heights predicted by the simulations were in semi-quantitative agreement with experimental observations. Further, the simulation results were in quantitative agreement with experimentally obtained torque and mixing-rate data, including a characteristic torque bifurcation. In future work, we plan to couple this CFD model with a reaction-kinetics model for the enzymatic digestion of cellulose, allowing us to predict enzymatic digestion performance for various mixing intensities and novel reactor designs.

Wednesday 6:00 Foyer-Stairs/Windows PO73

Sinking bubbles

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Intuition tells us that bubbles will rise and steel objects will sink in liquids, though here we describe the opposite. With experimental demonstration and theoretical rationale, we describe how the motion of containers of liquid with immersed solid objects and air bubbles can cause curious behaviors: sinking bubbles and rising high-density particles. Bubbles and solid spheres of diameter on the order of a few millimeters are introduced into dramatically shear-thinning fluids with an effective yield stress (aqueous Carbopol microgel particle suspensions). Imposed motion of the rigid container allows for control of the trajectories of the immersed particles -- without the container imparting direct shearing motion on the fluid. Results demonstrate the necessary conditions to prevent or produce net motion of the bubbles and heavy particles, both with and against gravitational expectations.

Wednesday 6:00 Foyer-Stairs/Windows PO74

Characterizing relaxation behavior of weak gels under steady shear using Orthogonal Superposition

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Orthogonal Superposition (OSP) is a novel technique for characterizing viscoelastic properties of dispersions and weak gels under shear. OSP applies a small amplitude oscillation in the axial direction, orthogonal to a rotational steady shear. This technique allows viscoelastic properties to be measured under shear, without the practical disadvantages of Parallel Superposition. The relaxation time of dispersions and weak gels is demonstrated to decrease under increasing shear. G'(?) and G"(?) measured orthogonal to a range of shear rates can be shifted with respect to frequency to superimpose, generating a Master Curve, similar to Time Temperature Superposition. This technique of "Time-Shear-Superposition" expands the frequency range beyond the limitations of direct measurement, and provides an insight into the relaxations of these systems under shear. This study will show the Time-Shear-Superposition of multiple shear-thinning systems to investigate the potential applications of the technique. The orthogonal measurements will be presented in conjunction with other rheological measurements, including flow curves, SAOS and LAOS.

Wednesday 6:00 Foyer-Stairs/Windows PO76

Continuous sheathless separation of normal and drug-treated Cryptococcus neoformans in viscoelastic fluid flow through a straight rectangular microchannel

Di Li[1], Preston Walker[2], Josh Sparks[2], Lukasz Kozubowski[2], and Xiangchun Xuan[1]
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Meningitis is the most common central nervous system infection caused by Cryptococcus neoformans, an encapsulated yeast. Current treatments for cryptococcal infections are still inadequate due partly to the drug resistance of C. neoformans. Recent results indicate that drug treatment changes C. neoformans from round unbudded cells or cells with a single bud to "multimeras" that are enlarged consisting of multiple cells. We present in this work a continuous sheath-free separation of normal and drug treated C. neoformans cells by shape and size in viscoelastic fluids through straight rectangular microchannels. This label-free separation is realized by using a combination of elastic and inertial lift forces to push cells to shape-and size-dependent equilibrium positions. Multiple experimental parameters that can significantly affect the distribution of equilibrium positions are investigated.

Wednesday 6:00 Foyer-Stairs/Windows PO77

Continuous separation of micron and submicron particles via elasto-inertial pinched flow fractionation

Qi Chen[1], Di Li[2], Jianhan Lin[3], Maohua Wang[3], and Xiangchun Xuan[2]
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Rapid and efficient separation of micron (e.g., bacteria) and submicron (or nano, e.g., magnetic beads for cell labeling) particles using a microfluidic system offers promising improvements in the detection of pathogenic microorganisms in clinical or food samples. We present in this work a continuous-flow separation of 2.2 µm- and 0.53µm-diameter polystyrene particles in a viscoelastic polymer solution through a rectangular microchannel. This separation is based on our recently developed technique that we termed as elasto-inertial pinched flow fractionation (eiPFF). It utilizes the flow-induced intrinsic elastic and inertial lift forces to deflect micron particles away from the sheath flow-focused particle stream. The submicron particles are, however, restrained within the stream due to the strong size dependence of the elasto-inertial lift.

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Plenary Lectures and Award Presentation

Monday, February 13 *8:30 AM, Audubon DEF*	**Microrheology's place in the rheologist's toolbox** Eric M. Furst *Chemical & Biomolecular Engineering, University of Delaware*
Tuesday, February 14 *Bingham Lecture* *8:30 AM, Audubon DEF*	**Frictional rheology of very dense suspensions** Mike Cates *Applied Mathematics and Theoretical Physics, University of Cambridge*
Wednesday, February 15 *8:30 AM, Audubon DEF*	**Spontaneous flows in soft active matter** Zvonimir Dogic *Martin A. Fisher School of Physics, Brandeis University*
Thursday, February 16 *Metzner Award Presentation* *8:00 AM, Audubon DEF*	**From simple polymers to supramolecular assemblies: Understanding and predicting the rheology of complex polymeric structures** Evelyne Van Ruymbeke *Bio and Soft Matter, Inst. on Cond. Matter and Nano-science, Université catholique de Louvain*

Social Program

Sunday, February 12	**Student-Industry Forum:** ***Careers in Rheology*** 4:00 PM – 6:00 PM *Sponsored by American Institute of Physics and The Dow Chemical Company*	White Ibis
	Welcoming Reception 6:30 PM – 8:30 PM *Hosted by TA Instruments*	Audubon DEF
Tuesday, February 14	**Society Business Meeting** 12:05 PM – 1:30 PM	Audubon DEF
	Awards Reception 7:00 PM – 8:00 PM *Sponsored by Malvern Instruments*	Foyer-Stairs/Windows
	Awards Banquet 8:00 PM	Audubon BC
Wednesday, February 15	**Poster Session and Reception** 6:05 PM – 8:00 PM *Sponsored by Anton-Paar USA*	Foyer-Stairs/Windows

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