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THE SOCIETY OF RHEOLOGY

91ST ANNUAL MEETING
PROGRAM AND ABSTRACTS

Raleigh Convention Center
Raleigh, North Carolina
October 20 - 24, 2019

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Meeting Schedule

Monday, October 21, 2019

	305A	*304*	*201*	*305B*	*306A*	*306B*	*306C*
8:30	C. F. Schmidt (PL1) - *306*						
9:20	Coffee Break						
9:50	TM1	SC1	SM1	IN1	SF1	BB1	GG1
10:15	TM2	SC2	SM2	IN2	SF2	BB2	GG2
10:40	TM3	SC3	SM3	IN3	SF3	BB3	GG3
11:05	TM4	SC4	SM4	IN4	SF4	BB4	GG4
11:30	TM5	SC5	SM5	IN5	SF5	BB5	GG5
11:55	Lunch Break / Student-Industry Forum						
1:30	TM6	SC6	SM6	IN6	SF6	BB6	GG6
1:55	TM7	SC7	SM7	IN7	SF7	BB7	GG7
2:20	TM8	SC8	SM8	IN8	SF8	BB8	GG8
2:45	TM9	SC9	SM9	IN9	SF9	BB9	GG9
3:10	Coffee Break						
3:45	TM10	SC10	SM10	IN10	SF10	BB10	GG10
4:10	TM11	SC11	SM11	IN11	SF11	BB11	GG11
4:35	TM12	SC12	SM12	IN12	SF12	BB12	GG12
5:00	TM13	SC13	SM13	IN13	SF13	BB13	GG13
5:25	TM14	SC14	SM14	IN14	SF14	BB14	GG14
5:50	End						
6:30	Monday Evening Reception						

Tuesday, October 22, 2019

	305A	*304*	*201*	*305B*	*306A*	*306B*	*306C*
8:30	D. Vlassopoulos (PL2) - *306*						
9:20	Coffee Break						
9:50	TM15	SC15	SM15	IN15	SF15	BB15	GG15
10:15	TM16	SC16	SM16	IN16	SF16	BB16	GG16
10:40	TM17	SC17	SM17	IN17	SF17	BB17	GG17
11:05	TM18	SC18	SM18	IN18	SF18	BB18	GG18
11:30	TM19	SC19	SM19	IN19	SF19	BB19	GG19
11:55	Lunch Break / Society Business Meeting						
1:30	TM20	SC20	SM20	IN20	SF20	BB20	GG20
1:55	TM21	SC21	SM21	IN21	SF21	BB21	GG21
2:20	TM22	SC22	SM22	IN22	SF22	BB22	GG22
2:45	TM23	SC23	SM23	IN23	SF23	BB23	GG23
3:10	Coffee Break						
3:45	TM24	SC24	SM24	IN24	SF24	BB24	GG24
4:10	TM25	SC25	SM25	IN25	SF25	BB25	GG25
4:35	TM26	SC26	SM26	IN26	SF26	BB26	GG26
5:00	TM29	SC27	SM27	IN27	SF27	BB27	GG27
5:25	TM28	SC28	SM28	IN28	SF28	BB28	GG28
5:50	End						
7:00	Awards Reception						
8:00	Awards Banquet						

Wednesday, October 23, 2019

	305A	*304*	*201*	*305B*	*306A*	*306B*	*306C*
8:30	E. Del Gado (PL3) - *306*						
9:20	Coffee Break						
9:50	AM1	SC29	SM29	IN29	MC1	AR1	GG29
10:15	AM2	SC30	SM30	IN30	MC2	AR2	GG30
10:40	AM3	SC31	SM31	IN31	MC3	AR3	GG31
11:05	AM4	SC33	SM32	IN32	MC4	AR4	GG32
11:30	AM5		SM33	IN33	MC5	AR5	GG33
11:55	Lunch Break						
1:30	AM6	SC34	SM35	IN34	AD1	TM27	IR1
1:55	AM7	SC35	SM34	IN35	AD2	TM30	IR2
2:20	AM8	SC36	SM36	IN36	AD3	TM31	IR3
2:45	AM9	SC37	SM37	IN37	AD4	TM32	IR4
3:10	Coffee Break						
3:45	AM10	SC38	SM38	MC6	AD5	AR6	IR5
4:10	AM11	SC39	SM39	MC7	AD6	AR7	IR6
4:35	AM12	SC40	SM40	MC8	AD7	AR8	IR7
5:00	AM13	SC41	SM41	MC9	AD8	AR9	IR8
5:25	AM14	SC42	SM43	MC10	AD9	AR10	IR9
5:50	End						
6:30	Poster Session & Reception						
6:30	Gallery of Rheology Contest						

Thursday, October 24, 2019

	305A	*304*	*201*	*305B*	*306A*	*306B*	*306C*
8:00	X. Cheng (AP1) - *304*						
8:40	AM15	SC43	SM44	IN38	AD10	MC11	IR10
9:05		SC44	SM45	IN39	AD11	MC12	IR12
9:30	AM17	SC45	SM46		AD12	MC13	IR11
9:55	Coffee Break						
10:25	AM18	SC46	SM47	IN41	AD13	AR11	IR13
10:50	AM19	SC47	SM48	IN42	AD14	AR12	IR14
11:15	AM20	SC48	SM42	IN43	AD15	AR13	IR15
11:40		SC49	SM49	IN44	AD16	AR14	IR16
12:05	End						

Session and Room Codes

AD = Active and Directed Systems
AM = Additive Manufacturing and Composites
AP = Award Presentations
AR = Applied Rheology for Pharmaceuticals, Food, and Consumer Products
BB = Biomaterials and Biofluid Dynamics
GG = Out of Equilibrium Systems: Gels and Glasses
GR = Gallery of Rheology Contest
IN = Flow Induced Instabilities and Non-Newtonian Fluids
IR = Interfacial Rheology
MC = Microfluidic and Confined Flows

PL = Plenary Lectures
SC = Suspensions, Colloids, and Granular Materials
SF = Surfactants, Foams, and Emulsions
SM = Polymers Solutions, Melts and Blends
TM = Rheometry: Advanced Techniques and Methods
Shaded = Keynote

201 = Room 201
304 = Room 304
305A = Room 305A
305B = Room 305B
306 = Room 306
306A = Room 306A
306B = Room 306B
306C = Room 306C
BR4 = Ballroom on 4th floor
ML3 = Main Lobby on 3rd floor
Meeting Prep: Room 202, Room 307

Contents

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Room 306 PL1

Statistical physics of active biological matter

Christoph F. Schmidt[1], Kengo Nishi[2], Chris Battle[2], Nikta Fakhri[3], Chase P. Broedersz[4], and Fred C. MacKintosh[5]

[1]Physics, Duke University, Durham, NC 27708, United States; [2]Third Institute of Physics, Biophysics, University of Göttingen, Göttingen, Germany; [3]Physics, Massachusetts Institute of Technology, Cambridge, MA, United States; [4]Arnold-Sommerfeld-Center for Theoretical Physics and Center, Ludwig-Maximilians-Universitat Munchen, Munchen, Germany; [5]Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77030, United States

Thermodynamic non-equilibrium is a defining feature of living systems on all levels of organization. Cells and tissues are built of "active matter", dynamic materials with built-in force generators. Such materials self-organize in biological systems into well-ordered dynamic steady states, sustained by the dissipation of metabolic energy. The materials show striking collective phenomena on a mesoscopic scale. We use advanced light microscopy as well as microscopic motion and force-sensing techniques to characterize the complex mechanical properties of and the motion and stress patterns in biological active matter, in particular the actin cortex, both in reconstituted model systems and in cells. I will also introduce methods to detect and quantitate thermodynamic non-equilibrium using fundamental concepts of statistical physics such as the fluctuation-dissipation theorem and the principle of detailed balance.

Symposium TM
Rheometry: Advanced Techniques and Methods

Organizers: Joseph Samaniuk and Michelle Calabrese

Monday 9:50 Room 305A TM1

Development of µRheoSANS and investigating the structure and rheology of complex fluids at high shear rate

Katie M. Weigandt[1], Steven Hudson[2], Javen Weston[3], and Ryan Murphy[1]

[1]NIST Center for Neutron Research, Gaithersburg, MD 20899, United States; [2]NIST, Gaithersburg, MD 20899, United States; [3]Chemical Engineering, University of Tulsa, Tulsa, OK 74104, United States

We are developing slit rheometers compatible with simultaneous small angle neutron scattering (SANS) measurements to directly correlate structure and rheology over a broad range of conditions. Eventually we hope to probe sample structure in Poiseuille flow at high shear rates, under high pressure head, and relatively high temperatures. This builds upon an existing suite of Couette rheoSANS and flowSANS devices at the NIST Center for Neutron Research that are accessible to the scientific community through a peer reviewed proposal system. Industrial applications, such as lubrication, mixing, spraying and injection, involve the flow of complex fluids at high deformation rates. Clogging, fluid degradation, and other processing challenges can arise in these extreme contexts and are often driven by structural changes in the fluid. To date, we have developed a prototype slit rheometer capable of simultaneously measuring structure and rheology of relatively low viscosity or shear thinning fluids (?8 < 5 mPa·s) at shear rates up to 100,000 s-1 and a capillary rheoSANS instrument capable of simultaneously measuring structure and rheology at rates up to 106 s-1. Our initial investigations have focused on measuring wormlike micelle solutions at low to moderate shear rates and comparing the results with Couette rheoSANS measurements. In this talk we will discuss the ongoing development of µRheoSANS measurements including our existing low-pressure apparatus, the capillary device and our newly built high pressure µRheoSANS device, designed to withstand pressure drops or pressure heads up to 350 bar. This device will enable us to measure SANS at shear rates up to 106 in samples with ?8 ~ 100 mPa·s. Furthermore, we will discuss the results of a series of experiments aimed at understanding the rheological response of wormlike micelle solutions at relatively high shear rates.

Monday 10:15 Room 305A TM2

Rheological NMR to study polymer dynamics and protein aggregation

Benjamin Kohn[1], Vincent Köber[1], Enno Stündel[1], Kenji Sugase[2], Erik Walinda[2], Daichi Morimoto[2], Petrik Galvosas[3], and Ulrich Scheler[1]

[1]Leibniz-Institut für Polymerforschung Dresden e.V, Dresden, Germany; [2]Kyoto University, Kyoto, Japan; [3]Victoria University of Wellington, Wellington, New Zealand

Rheo NMR [1] has been applied to investigate the effect of external shear on the aggregation of proteins [2, 3] and on the chain dynamics of polymers [4], where shear-enhanced polymer dynamics is observed. Rheo NMR is able to provide insight into the molecular response to external shear. In the mean time NMR imaging enables measuring flow profiles while studying molecular parameters in the same system. The knowledge on local shear fields may be crucial for the interpretation of shear effects in more complex shear environments. To gain further insight two modified Taylor Couette geometries have been developed and used where (i) the rotating part in the Couette cell is placed off center and (ii) oscillating rotation is applied instead of continuous rotation [5].

Experiments have been performed on a 300 MHz Bruker AvanceIII spectrometer with a Micro2.5 microimaging accessory and an in-house built Rheo NMR system based on a servo motor, avoiding any vibrations. For the oscillatory shear a crank mechanism has been designed and introduced between the motor and the drive of the Couette rotor.

Recording, quantifying and understanding the emerging flow profiles is crucial for the shear geometries and protocols listed above. In particular for low-viscosity liquids like dilute solutions or lower molecular weight polymers flow pattern appearing under oscillatory shear show peculiar features. Counterflows are created locally at shear rates larger than the averaged shear rate applied across the gap when the angular velocity is at its peak value. Likewise, for the geometry where the rotor is off the center a counter rotating flow is seen in the wider part of the cell. Both experimental approaches may aid the study of complex flows in complex fluids.

[1] Callaghan, Rep. Prog. Phys. 62, 599-670 (1999).
[2] Ohgo et.al., JACS 130, 4182-4186 (2008).
[3] Morimoto et. al., Anal. Chem. 89, 7286-7290 (2017).
[4] Kohn et. al., Polymers 10, 1231 (2018).
[5] Kuczera et. al., Langmuir 34, 8314-8325 (2018).

Monday 10:40 Room 305A TM3

Simultaneous Raman and rheology measurements for reaction and stress monitoring

Christine Roberts, Ashley M. Maes, Anne M. Grillet, and Rekha R. Rao
Engineering Sciences Division, Sandia National Laboratories, Albuquerque, NM 87185-0346, United States

Monitoring the rheology, polymerization, and stress generation of polymeric systems is essential for properly understanding polymeric encapsulation processes for electronics components and other phase-changing systems. Using simultaneous Raman spectroscopy and rheological measurements, the evolving rheology of complex fluids can be linked to chemical or conformational changes that occur during processing such as melting, crystallization, curing, or gelation. Simultaneous measurements streamline the creation of material models that link the extent of reaction of curing polymer systems to the viscosity of the material. Here, we will discuss examples of our research including monitoring the crystallinity and modulus of ethylene vinyl acetate for photovoltaic photovoltaic module encapsulants, measuring curing kinetics of EPON 828 epoxy using Jeffamine, and solidification of paraffin wax which is used as a phase change material in thermal energy storage devices. We will also discuss efforts to measure stress in materials using Raman spectroscopy using carbon nanotube tracer materials.

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Monday 11:05 Room 305A TM4

Simultaneous rheo-Raman spectroscopy to identify the chemical origins of rheological response

Bharath Rajaram[1], Amit Ahuja[1], and Jennifer Ramirez[2]
[1]TA Instruments, New Castle, DE 19720, United States; [2]Thermo Fisher Scientific, Madison, WI, United States

Access to chemical structure characterization during rheological experiments provides valuable information that elucidates the impact of intermolecular interactions on the bulk rheology. Here, we introduce and present the details of a new rheo-Raman setup that permits in situ chemical structure characterization during rheological measurements. Raman spectroscopy provides critical information about the molecular structure and bonding in a material and tracks its evolution in response to shear deformation and changes in environmental conditions. The turnkey system described in this study integrates a commercially available rheometer (Discovery Series HR-3, TA Instruments) with a Raman spectrometer (iXR, Thermo Fisher Scientific). We demonstrate the effectiveness of combining these two techniques by simultaneously studying the temperature-induced rheological and chemical changes in a commercially available personal care product. Specifically, the temperature dependent changes in the viscosity are coincident with corresponding changes in the conformational order of the one of the main components in the sample. The results from the rheo-Raman analysis are complemented through Differential Scanning Calorimetry data, further establishing the link between the changes in chemical structure and viscoelastic behavior.

Monday 11:30 Room 305A TM5

New rheological tools for Rheo-SAXS and Rheo-SANS

Joerg Laeuger
Anton Paar Germany, Ostfildern, Germany

The mechanical material properties as well as the flow behavior of complex fluids are strongly determined by their microstructure. In order to understand and customize the behavior of such of systems under flow conditions it is necessary to pay special attention to the structural changes that occur at the microstructural level. Therefore combined rheology small angle scattering techniques with light, neutron and x-rays have emerged as valuable tool over the last decades. The use of a commercial rheometer allows the application of more complex flow conditions and offers an "in situ" correlation between rheological behavior and the corresponding structural changes. A modular design of a scattering cell for a rheometer makes it possible to use the same basic unit for Rheo-SAXS and Rheo-SANS experiments. A high temperature system will be introduced as well as different new geometries and measurement options including a "dent" geometry for high viscous materials such as polymer melts. An extensional flow tool attached to the rheometer has been employed in Rheo-SANS investigations for copolymer-polystyrene blends and in Rheo-SAXS for observation of polymer crystallization during flow at small times and high elongation rates. Geometries for Rheo-GISANS are used to measure the reflectivity during flow and reveal information in thin sample layers during flow. Electrically isolated geometries can be used to obtain dielectric spectroscopy data during the simultaneous application of a flow field and the acquisition of SANS or SAXS data and provide additional information on the electrical conductivity during flow. For combined Rheo-SAXS measurement in a laboratory environment a rheometer measuring head has been attached to laboratory SAXS instrument. First results of this setup will be presented as well.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Monday 9:50 Room 304 SC1

Time-dependent shear bands in a thixotropic yield-stress fluid under transient shear

Yufei Wei, Michael J. Solomon, and Ronald G. Larson
Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

We find that thixotropic fumed silica suspension under transient shear exhibits not only viscoelasticity, yielding, kinematic hardening, and thixotropy, but also shear bands when the apparent shear rate is below a critical value between 0.1 and 0.25 s-1. Through multiple shear startup tests and flow reversal tests, we find that thixotropy promotes bands while kinematic hardening suppresses them. We propose a simple thixo-plastic constitutive equation that can qualitatively predict the important features of the rheological response and banding dynamics in shear startup tests and flow reversal tests. Under very long periods of shearing at constant apparent shear rates, shear bands eventually travel periodically through the field of view , which causes noticable velocimetry oscillation. We find that the period of these traveling waves is set by the rotational speed of the cone or plate, and evidently provoked by a very slight mis-alignment of geometry, within the specifications of the instrument, and too small to produce more than tiny oscillations in the stress of Newtonian fluids. The results show that these fluids are not only sensitive to banding, but that the band dynamics are highly sensitive to geometry, including slight geometric imperfections. These results are of significance for processing flows of thixotropic yield stress fluids.

Monday 10:15 Room 304 SC2

Generic elastoplastic behavior of yield stress fluids in their solid regime

Elie Ngouamba, Julie Goyon, and Philippe Coussot
Université Paris Est, Laboratoire Navier, Champs sur Marne 77420, France

The transition from a solid state to an apparently liquid state for yield stress fluids is intriguing, all the more when one considers that it is reversible after some appropriate relaxation, whereas for standard solids, breakage or irreversible plastic deformations occur. It has even been suggested that the liquid regime would in fact be in the continuity of the solid regime just with continuous plastic deformation [1], but the solid regime of these materials has not been much explored so far. Here we follow the structure state of various yield stress fluids (emulsion, gel, thixotropic suspensions) during their solid-liquid transition in creep tests by superimposing small oscillations in order to measure simultaneously the elastic and loss moduli. Subsequently, recovery tests are performed to get further information on the elastic and plastic components in the solid regime. Thus we show that the solid state of the materials is associated with the persistence of an elastic network of constant elastic modulus up to yielding, while progressively larger plastic events occur. The solid-liquid transition can then be strictly associated with the collapse of this structure. Moreover, the additional elastic component (for larger deformations) and the plastic component appear to be equal and increase as a square of the stress imposed. These observations allow to model the rheological behavior of all these systems by a basic elastic network plus a continuous series of elasto-plastic blocks with a linear probability density, which is in perfect agreement with the data for the different systems.

[1] Coussot P (2018) slow flow of yield stress fluid: yielding liquid or flowing solid. Rheol Acta 57:1-14

Monday 10:40 Room 304 SC3

A new effort in determining the viscoelastic properties from micro-rheological measurements

Qi Li[1], J. Galen Wang[2], Dongjie Chen[1], Xiaoguang Peng[1], Roseanna N. Zia[2], and Gregory B. McKenna[1]
[1]Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79404, United States; [2]Department of Chemical Engineering, Stanford University, Stanford, CA, United States

Probe micro-rheology has proven to be a powerful tool in measuring viscoelastic properties for both polymer and colloidal systems [1,2]. However, its accuracy is limited by the probe size effect from the Stokes-Einstein continuum assumption, as well as the validity of the generalized Stokes-Einstein relationship (GSER) in some concentrated systems. Also, the introduction of probes into the sample can sometimes bring extra variables to the experiments, for example, surfactant absorption differences [3]. Here we investigate a straightforward method inspired from the generalized Langevin equation relating the mean squared displacements (MSD) with compliance [4]: J(t)=[3pa/(Nk_B T)], together with the basic viscoelastic spectral interconversions, in calculating the viscoelastic properties of a model soft PNIPAM-based colloidal system, polyethylene oxide (PEO) polymer solutions with different concentrations, and dynamic simulations. The results show that this new effort gives good estimations of the viscoelastic properties in probe-free conditions for both semi-dilute polymer solutions and concentrated soft colloidal systems. Therefore, this Stokes-Einstein-independent method can have a wider range of applications covering the range from low concentration to concentrated systems.

[1] J. Liu, M. L. Gardel, K. Kroy, E. Frey, B. D. Hoffman, J. C. Crocker, A. R. Bausch, and D. A. Weitz. Phys. Rev. Lett. 96, 118104 (2006). [2] W. Brown. Dynamic Light Scattering: The Method and Some Applications. Oxford Univ. Press, Oxford. 1993 [3] A. Raudsepp, P. Callaghan, and Y. Hemar. J. Rheol. 52, 1113 (2008). [4] T. M. Squires, and T. G. Mason. Ann. Rev. Flu. Mech. 42, 1 (2010).

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Monday 11:05 Room 304 SC4

Constitutive model selection using neural networks

Brendan C. Blackwell and Paulo E. Arratia
Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States

In this work we apply the tools of machine learning to improve the process of constitutive model selection. Choosing a model to characterize empirical data is a nuanced process. A complex model with many parameters will always provide the closest fit to the data, while a simple model with fewer parameters is often more valuable to understanding the underlying physics that are at play. A good approach is to start with the simplest model possible and gradually add complexity until the fit is sufficient for the given purpose, but for many models this is a high-dimensional problem with several choices for where and how to add complexity. Beginning with experimental data of a colloidal suspension (shear rheology of aqueous kaolinite clay) that shows an unusual signature, we set out to find a model that captures the unique signature without having so many parameters as to become unwieldy. We begin with a simple, structure parameter thixotropic model, and show that the simplest version does not capture key aspects of the data. Faced with a choice of where in the model to add additional parameters, we turn to machine learning to make a complicated task computational feasible. After writing a 'master' model with fifteen parameters, each of which can be interpreted to have a physical meaning, we use a neural network to determine what subset of the parameters is optimal. A Bayesian inference criterion is used to penalize the number of parameters, preventing an overly complex result. The technique of the neural network allows us to evaluate all possible combinations and subsets of parameters, a task that would otherwise be computationally infeasible.

Monday 11:30 Room 304 *Keynote* SC5

Microstructure design in consumer products

Marco Caggioni[1], Veronique Trappe[2], and Patrik T. Spicer[3]
[1]Complex Fluids Microctructures, Procter and Gamble, West Chester, OH 45069, United States; [2]Department of Physics, University of Fribourg, Fribourg 1700, Switzerland; [3]Complex Fluids Group, UNSW Syndey, Sydney, Australia

In the last 20 years, consumer products evolved from simple solutions to multi-phase complex fluids in which surfactants, polymers, solid particles, encapsulated materials and emulsion droplets coexist in a delicate equilibrium. Such evolution enabled the addition and fine-tuning of multiple functions but also increased the complexity of the liquid microstructure and required the development of fluid structuring strategies that closely relate to colloidal gels and glasses. The product formulation effort changed significantly from independent selection of ingredients and subsequent optimization of production processes, to a much more interdependent selection of formulation and processing strategies. In this talk, we will review some of the challenges we face in characterizing and designing the mechanical properties of liquid formulated products and we describe the development and validation of a micromechanical model for structured fluids that enables a direct link between bulk material properties and specific microstructure components.

Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Monday 9:50 Room 201 SM1

Mobility of polymer-tethered nanoparticles in entangled polymer melts

Ting Ge and Michael Rubinstein
Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, United States

A scaling theory is developed for the motion of a polymer-tethered nanoparticle (NP) in an entangled polymer melt. The mobility of a NP tethered with a single polymer chain (tail) is determined by the competition between the bare particle and the tail, and is dominated by either the particle or the tail, depending on the particle diameter d and the tail size R_{tail}. If d is smaller than the tube diameter a of the melt, the particle is not directly affected by the entanglement network, but can be dragged to follow the tail in the confining tube for time t above a crossover time τ^* in a tail-dominated regime. If d is moderately larger than a, the particle is confined by the entanglement network until the hopping diffusion time τ_{hop}, but can then participate in the entangled dynamics of the tail for $t > \tau^*$ in a tail-dominated regime. If d is sufficiently larger than a, hopping diffusion is suppressed, and a single-tail NP has to wait for the terminal relaxation of the entangled melt to freely diffuse. The mobility of a NP tethered with multiple polymer chains (tails) is studied by comparing the dynamics of the bare particle and that of the branch point of a corresponding entangled star polymer. We propose that the diffusion mechanism for the branch point of an entangled star is pulling by the majority of retracted arms through a gate surrounding the entanglement cell confining the branch point. The time τ_s for one such diffusion step over a distance $\approx a$ is

longer than the arm retraction time τ_{arm} by a combinatorial factor. The mobility of a multi-tail NP is approximated as the lower of the mobilities of the bare NP and the branch point of the star polymer.

Monday 10:15 Room 201 SM2

Amine functionalised polycyclooctenes, polynorbornenes and their copolymers: Transition from liquid- to solid-like

Tanja Tomkovic[1], Nirmalendu Kuanr[2], Damon J. Gilmour[2], Laurel L. Schafer[2], and Savvas G. Hatzikiriakos[1]
[1]Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC V6T-1Z3, Canada; [2]Chemistry, The University of British Columbia, Vancouver, BC V6T-1Z1, Canada

Amine functionalised polycyclooctenes and polynorbornenes with secondary aryl-amine functionalities, as well as several copolymers were synthesized using ring-opening metathesis polymerization combined with hydroaminoalkylation reaction. The resulting polymers were characterized by means of 1H NMR and IR spectroscopies, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and melt rheology. A plethora of distinctively different rheological behavior was obtained by controlling the molecular weight, by introducing various functionalities that exhibit different hydrogen bonding strengths and copolymer composition. These novel materials reveal an evident tunable transition from liquid- to solid-like behavior through gel formation. The detailed rheological study demonstrates the formation of the 3D network formed by physical crosslinking of hydrogen bonds.

Monday 10:40 Room 201 SM3

Dynamics of entangled liquid coacervates made from oppositely charged polyelectrolytes

Christian Aponte-Rivera and Michael Rubinstein
Mechanical Engineering and Materials Science, Duke University, Durham, NC 27705, United States

Mixtures of oppositely charged polyelectrolytes can phase separate to form a polymer rich phase, called a coacervate, and a polymer depleted phase. Much effort has been devoted to understanding the charge-driven phase separation of coacervates made from oppositely charged polyelectrolytes, leading to models that are able to predict the coacervate phase diagram and structure. However, development of models to predict the dynamic properties of coacervates and how these depend on experimentally controllable parameters lags behind. We develop a scaling theory to predict viscoelasticity of and diffusion in entangled charge asymmetric liquid coacervates made from oppositely charged polyelectrolyte solutions. In this work, charge asymmetry results from making a coacervate from polyanions and polycations that have a different line density of charges along their backbones, e.g. a high charge density polyanion and a low charge density polycation. The resulting coacervate has a double-semidilute structure with two correlations lengths - one of the polycation and another of the polyanion. Coacervates can have entangled either only the polyanions, only the polycations or they can have entangled both types of chains. We model entangled coacervates by considering reptation of polymer chains along confining tubes. In unentangled asymmetric coacervates, the different correlation lengths result in a dynamic coupling between the polycation and polyanion, which alters viscosity and diffusion. We predict this dynamic coupling also alters viscosity and diffusion in entangled asymmetric coacervates. Furthermore, we find that the concentration dependence of viscosity and diffusion changes depending on whether the polymer chains are confined to tubes formed by chains of equal or opposite charge in the entangled asymmetric coacervate.

Monday 11:05 Room 201 SM4

Dielectric relaxation of type-A chains undergoing head-to-tail association/dissociation: Difference from head-to-head case and correlation with viscoelastic relaxation

Hiroshi Watanabe[1], Yumi Matsumiya[1], and Youngdon Kwon[2]
[1]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan; [2]School of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

Dielectric relaxation of type-A chains reflects global motion of the chains but is also affected by the relative alignment of the dipoles along the chain backbone, namely, by the dipole inversion. Head-to-head association of type-A unimer gives a symmetrically dipole-inverted dimer, and the association/dissociation equilibrium of the unimer and dimer results in motional coupling of those chains thereby affecting the dielectric behavior. In fact, for this head-to-head case, eigenmode analysis has been conducted to reveal that the motional coupling results in moderate retardation and acceleration of the dielectric relaxation of the unimer and dimer obeying the reptation dynamics whereas the coupling has no effect on the dielectric relaxation of Rouse unimer and dimer. Namely, the effect of motional coupling on the dielectric relaxation changes with the type of chain dynamics. Nevertheless, the effect was not clarified for head-to-tail associating unimers and their dimer having no dipole inversion. Thus, for completeness, this study makes the eigenmode analysis of the dielectric relaxation for this case of head-to-tail reaction. For the unimer and dimer obeying either Rouse or reptation dynamics, the analysis indicates that the retardation and acceleration of the dielectric relaxation of the unimer and dimer are much more significant for the head-to-tail case than for the head-to-head case irrespective of the chain dynamics and that the dielectric relaxation function for the head-to-tail case exactly coincides with the viscoelastic relaxation function if the unimer and dimer obey the reptation dynamics. This result suggests an interesting method of resolving some detail of the chain dynamics under the reaction through comparison of dielectric and viscoelastic responses of the associative type-A chains.

Monday 11:30 Room 201 SM5

Controlling the viscoelastic properties of entangled telechelic star polymers by combining stickers of different lifetimes

Evelyne van Ruymbeke, Yanzhao Li, and Flanco Zhuge

Bio and Soft Matter - IMCN, Univeriste catholique de Louvain, Louvain-La-Neuve 1348, Belgium

These last years, several works have shown that combining supramolecular and disentanglement dynamics within the same polymer systems can lead to very interesting viscoelastic properties. In particular, if the disentanglement time of the building blocks is long compared to the average time during which a supramolecular sticker stays unassociated, these two dynamics can have a synergistic effect, and the terminal relaxation of the corresponding system can be much longer than the sticker lifetime. In the present work, we study the dynamics of entangled metallo-supramolecular polymer networks composed of telechelic entangled star polymers, and model their viscoelastic properties with the help of our TMA tube model. We first investigate the influence of the nature of the ion as well as their amount on the dynamics of the network. Then, we investigate how their relaxation properties can be tuned if two different metal ions are used within the same sample, i.e. if the star molecules are associated via metal-ligand complexes characterized by two different lifetimes. The obtained results reveal that the dynamics of the complexes and stickers exchange are very fast compared to the motion of the star molecules.

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Monday 9:50 Room 305B IN1

Characterizing the extensional rheology of weakly elastic fluids using capillary breakup technique: An experimental and numerical study

Jianyi Du[1], Hiroko Ohtani[2], Kevin Ellwood[2], and Gareth H. McKinley[1]

[1]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; [2]Vehicle Manufacturing and Additive Manufacturing-Metals, Ford Motor Company, Dearborn, MI 48121, United States

Many commercial fluid materials appear close to Newtonian in shear rheometry but can be subtly distinguished by the weakly viscoelastic properties exhibited in strong extensional flows. Typical examples include automotive lubricants and commercial paints. This weak elasticity can profoundly alter the final stages of filament breakup processes due to the large accumulated strains and strain rates, hence it is of practical importance to understanding industrial processes such as jetting, painting and fragmentation. Rheological characterization of such weakly elastic fluids can be achieved using capillary breakup extensional rheometry (CaBER). The experimental results obtained with two commercial motor oils are shown to be broadly consistent with the predictions of the Second Order Fluid model, and the normal stress differences arising from both the viscous (first order) and elastic (second order) terms are found to be comparable in magnitude. Because of the additional elastic stress, the slender self-similar profile expected for a viscous Newtonian fluid filament is no longer valid. In order to understand the evolution of the measured filament profile R(z,t), we solve numerically the axisymmetric one-dimensional Cauchy momentum equation for the Second Order Fluid model using a fully implicit formulation. Very close to pinch-off, the mid-plane radius is found to asymptotically thin quadratically with the time to breakup, and the resulting filament profiles become slenderer than for a Newtonian fluid of the same viscosity. The midplane curvature ratios in the radial and axial directions exhibit new power-law relationships in time, suggesting self-similar dynamics. Careful analysis of the simulation results shows that modification is required in the numerical coefficients that enter the self-similar solutions used for analyzing the thinning profile, if accurate values for the viscosity and other material coefficients are to be obtained for weakly elastic fluid filaments undergoing thinning and breakup.

Monday 10:15 Room 305B IN2

Inkjet printing of viscoelastic fluids: Examining the effect of concentration and polymer architecture on jetting

Kashyap Sundara Rajan, Samrat Sur, and Jonathan P. Rothstein

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

The addition of polymers to inkjet fluids can have both beneficial and detrimental effects on the jetting process. In this experimental study, we systematically compare four different polymer binders in order to better understand the influence of polymer properties including polymer chemistry, molecular weight, backbone rigidity and concentration on the jettability of industrially-relevant inkjet formulations. As the breakup of jets into drops is an extensional flow, the extensional viscosity of each polymer solution was first characterized using drip onto substrate capillary breakup extensional rheology. With increasing concentration, CaBER-DoS showed a transition from inertia-capillary to visco-capillary and finally to elasto-capillary breakup dynamics. The effect of changes in extensional rheology on jetting were probed by imposing a strong perturbation at the most unstable wavelengths to the fluid jet and then using high speed imaging techniques to accurately capture the drop formation and pinch off dynamics. With increasing concentration, molecular weight or backbone flexibility, the jet breakup dynamics transition from being dominated by inertial effects to being governed by elastic effects. This transition was quantified by measuring satellite drop size and relative velocity, droplet breakup time and breakup distance, and the persistence of the fluid threads connecting primary drops. Through this study we establish the effectiveness and impact of a broad range of polymers commonly used in inkjet printing.

Monday 10:40 Room 305B IN3

Pinch-off dynamics, extensional rheology and printability of polyelectrolyte solutions

Leidy N. Jimenez[1], Jelena Dinic[2], and Vivek Sharma[1]

[1]Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States; [2]Institute for Molecular Engineering, University of Chicago, Chicago, IL, United States

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

Monday 11:05 Room 305B IN4

Macromolecular relaxation, strain, and extensibility determine elastocapillary thinning and extensional viscosity of polymer solutions

Jelena Dinic[1] and Vivek Sharma[2]

[1]Institute for Molecular Engineering, University of Chicago, Chicago, IL, United States; [2]Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States

Delayed capillary break-up of viscoelastic filaments presents scientific and technical challenges relevant for drop formation, dispensing, and adhesion in industrial and biological applications. The flow kinematics are primarily dictated by the viscoelastic stresses contributed by the polymers that are stretched and oriented in a strong extensional flow field resulting from the streamwise gradients created by the capillarity-driven squeeze flow. After an initial inertiocapillary (IC) or viscocapillary (VC) regime, where elastic effects seem to play no role, the interplay of capillarity and viscoelasticity can lead to an elastocapillary (EC) response characterized by exponentially-slow thinning of neck radius (extensional relaxation time is determined from the delay constant). Less frequently, a terminal visco-elastocapillary (TVEC) response with linear decay in radius can be observed and used for measuring terminal, steady extensional viscosity. However, both IC/VC-EC and EC-TVEC transitions are inaccessible in devices that create stretched necks by applying a step strain to a liquid bridge (e.g., capillary breakup extensional rheometer). In this study, we use dripping-onto-substrate rheometry to obtain radius evolution data for unentangled polymer solutions. We deduce that the plots of transient extensional viscosity vs. Hencky strain (scaled by the respective values at the EC-TVEC transition) emulate the functional form of the birefringence-macromolecular strain relationship based on Peterlin's theory. We quantify the duration and strain between the IC/VC-EC and the EC-TVEC transitions using measures we term elastocapillary span and elastocapillary strain increment and find both measures as well as filament lifespan show values directly correlated with the corresponding variation in extensional relaxation time.

Monday 11:30 Room 305B IN5

Rheological behavior of mesophase pitches for carbon fiber processing

Heedong Yoon[1], Zachary R. Hinton[1], Stuart E. Smith[2], Clarence E. Chase[2], and Nicolas J. Alvarez[1]

[1]Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States; [2]ExxonMobil Research and Engineering Company, Annandale, PA 08001, United States

Pitch-based carbon fibers in particular have received much attention in recent decades because of their excellent material performance and simple manufacturing process compared with other precursor materials. To develop cost-efficient and high-performance carbon fibers, it is essential to understand the rheological behavior of mesophase pitches in the processing regime. In the current work, we use shear and extensional rheology to investigate the rheological behavior of mesophase pitches to determine the optimum processing conditions for pitch-based carbon fibers. Shear and extensional rheological measurements were performed on pitches with varying amounts of mesophase (0.5 - 60 %) to understand how mesophase affects the linear viscoelasticity of pitches. To determine the optimum processing conditions for pitch-based carbon fibers, the effect of strain rate on stress evolution for mesophase pitches as examined by extensional rheology. Failure behavior for pitch fiber precursors was also investigated through extensional rheological measurements. The rheological behavior and failure strength for mesophase pitches will be presented and discussed in terms of processing condition.

Symposium SF
Surfactants, Foams, and Emulsions

Organizers: Reza Foudazi and Nick Alvarez

Monday 9:50 Room 306A SF1

Mimicking coalescence using a dynamic thin film balance technique

Emmanouil Chatzigiannakis and Jan Vermant
Materials Department, ETH Zurich, Zürich CH-8093, Switzerland

Thin liquid film (TLF) dynamics is considered to be an important (if not deciding) factor when it comes to foam and emulsion stability. When two bubbles/droplets come into close proximity a TLF is usually formed between them, which gradually drains until it ruptures. The role of the interfacial properties on the hydrodynamic drainage process of various systems under a constant driving force has received some attention [1,2]. However, there are no experimental studies regarding how the rheological properties of the bulk liquid (e.g. viscoelasticity, shear thinning) affect the overall drainage process, especially under dynamic pressure conditions. Such experiments will provide significant information related to flow-induced coalescence processes, as well as to the behavior of foams and emulsions under oscillatory shear. In this study, the drainage dynamics of liquid-air films of polymer solutions were examined using a variation of the thin film balance technique which allows us to vary the Capillary number [3]. A standard thin film balance was modified to perform hydrodynamic studies. Constant, as well as dynamic pressure was applied in order to mimick both head-on and glancing collisions. The effect of three parameters on drainage was studied, namely that of driving force, polymer concentration and molecular weight. All parameters were found to influence non-trivially the drainage of the thin liquid films, giving rise to a multitude of phenomena, both with respect to flow instabilities (symmetric-to-asymmetric drainage transitions, cyclic dimpling and vortices), as well as with respect to confinement effects on structure and possibly rheology.

References: [1] Hermans, E. et al. (2015), Soft Matter, 11(41): 8048. [2] Kannan, A. et al. (2018), Langmuir, 34(2): 630. [3] Beltramo, P.J. et al. (2016), Soft Matter, 12(19): 4324.

Monday 10:15 Room 306A SF2

The interfacial tension of the water-diluted bitumen interface at high bitumen concentrations measured using a microfluidic technique

Sachin Goel[1], Niyati Joshi[1], Muhammad Uddin[1], Samson Ng[2], Edgar Acosta[1], and Arun Ramachandran[1]
[1]Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S3E5, Canada; [2]Syncrude Canada Inc, Edmonton, Canada

After the froth treatment section in the processing of oil sands, the product - diluted bitumen or dilbit, still contains about 2 to 5 % by weight of water. The difficulty in removing the residual water originates from the extremely fine sizes of the water droplets (less than 10 microns). The interfacial tension (IFT) is a critical parameter to inform our understanding of drop breakup and droplet-droplet coalescence, which together govern the drop size distribution in sheared water-in-dilbit emulsions. A microfluidic extensional flow device (MEFD) was used to determine the IFT of the dilbit - water emulsion system for bitumen concentrations of 33%, 50% and 67% (solvent to bitumen ratio (S/B) = 2, 1 and 0.5, respectively) and two different pH values of water: 8.3 and 9.9. IFT was observed to increase with the bitumen concentration, and decrease significantly upon lowering the water pH. The time scale for achieving the steady state IFT increased with bitumen concentration, and was less sensitive to the water pH. A key feature of our measurements is that the IFTs reported here are significantly smaller than the values reported in the literature. After eliminating the obvious doubt of flow-induced segregation of surfactants leading to the lower IFTs, we recognized two other important differences from prior studies: measurement of the IFT water drops in dilbit as opposed to dilbit drops in water in earlier studies, and time scales of measurement of IFT that ranged from hundreds of milliseconds to a few seconds, as compared to a minute or longer in past investigations. These differences were examined carefully, but neither was found to explain the low IFTs measured in our studies. Our work leads ultimately to the following hypothesis: the mechanical properties of a sheared water-bitumen interface can be significantly different from a stagnant one.

Monday 10:40 Room 306A SF3

Asphaltene adsorption and spontaneous emulsification at water/oil interfaces

Mariana Rodriguez-Hakim, Simone Bochner de Araujo, and Gerald G. Fuller
Chemical Engineering, Stanford University, Stanford, CA 94305-4125, United States

Asphaltenes are a class of high molecular weight aromatic compounds found in crude oil defined by their good solubility in toluene. When an asphaltene-toluene solution is brought into contact with water, asphaltenes adsorb onto the oil-water interface and induce the formation of a micron-sized water-in-oil emulsion (Bochner de Araujo et al, 2017). This process, known as spontaneous emulsification, differs from traditional emulsification because the transition from a phase-separated state to an emulsified state requires no external input of energy. In this work, we aim to understand which interfacial properties affect the rate and extent of spontaneous emulsification. Specifically, we perform experiments to measure the interfacial tension and rigidity of asphaltene-laden toluene/water interfaces by conducting step-strain measurements using a Langmuir trough and a pendant drop apparatus connected to a pressure transducer. We find that rigidity increases with the age of the interface, and is correlated to the propensity of the system to spontaneously emulsify. In addition, we study the effect of the addition of poly(styrene-alt-octadecyl maleimide) (SNODMI), a co-polymer found to increase crude oil flowability (Cao et al, 2016). We find that the SNODMI molecules competitively adsorb onto the toluene-water interface, lowering the interfacial energy, increasing the interfacial rigidity, and inhibiting spontaneous emulsification.

Monday 11:05 Room 306A SF4

Humidity affects the rheology of supramolecular organogels

Emmanouil Vereroudakis and Dimitris Vlassopoulos
Institute of Electronic Structure & Laser, FORTH, Heraklion 70013, Greece

Supramolecular organogelators have been known for more than 30 years, however the surprisingly extraordinary sensitivity of their self-assembly and viscoelastic properties to humidity have been ignored until recently[1,2]. It turns out that organic oils typically contain tiny quantities of water (0.01% by weight) which can influence the self-assembly as well as the flow properties of supramolecular gelators they contain[1,2]. Here we explore the properties of biphenyl tricarboxamides (BPTA) in dodecane which exhibit structural transitions with varying temperature. The driving force behind these transitions is the fact that the humidity content of the supramolecular polymer changes with temperature. The present system is investigated using shear rheology under controlled humidity conditions in both humid (~60% relative humidity) and dry (~5% relative humidity) conditions. We observe that in a humid environment the linear and non-linear rheological properties are affected by the temperature. Equivalently, the humidity content in the supramolecular polymer tunes its rheology at constant temperature. At temperatures where the system does not interact with water,we observe the higher plateau modulus, slower relaxation time and substantial strain-hardening under shear. On the other hand, at temperatures where the systems strongly interacts with water the plateau modulus is lower, the relaxation faster and there is absolutely no sign of strain hardening behavior. These findings suggest that humidity effects cannot be dismissed when working with oily environments. They also provide new insights into tailoring the flow properties of organogels.

Work in collaboration with N. J. Van Zee, E. W. Meijer (Techonological University of Eindhoven).

References

1. N.J. Van Zee et al., Nature, 558, 100-103 (2018)
2. A. Louhichi et al., J. Rheol. 61, 1173-1182 (2017)

Monday 11:30 Room 306A SF5

Rheological behavior of amphiphilic block copolymers in oil water mixtures

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

Self-assembly of block copolymers in the presence of solvents forms ordered mesophase structures, also known as lyotropic liquid crystals (LLCs). Rheological properties of Plurnic block copolymer/water/oil mesophases with lamellar and hexagonal structures are studied. Flow behavior of lamellar and hexagonal mesophases indicates that they have yield stress and the shear banding is possibly present due to the presence of plateau stress in the flow curve of these systems, originated from shear-induced alignment/transition. Applying high strains on these LLCs, induces two relaxation times after cessation of flow, decreases the storage modulus in the whole frequency regime, and decreases the loss modulus in small frequencies with negligible effect at high frequencies. We suggest that at relatively low frequencies, grain boundaries and defects control the rheological behavior of LLCs, while at high frequencies micelles are playing a more important role in the observed rheological behavior. The decrease in moduli is reversible and the system relaxes back to its original elastic modulus at rest. The observed behavior can be attributed to the mesophase alignment, defect formation and/or alignment of defects. Oscillatory experiments show that mesophases have solid-like behavior and exhibit type III non-linear behavior. Mesophases elastic modulus is fitted with a model developed previously by the authors.

Symposium BB
Biomaterials and Biofluid Dynamics

Organizers: Xiang F. Cheng and Amanda Marciel

Monday 9:50 Room 306B BB1

Modeling and simulation of blood flow syneresis and pulsatile pipe flow effects

Tim van de Vyver, Jeffrey S. Horner, Norman J. Wagner, and Antony N. Beris
Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Blood flow simulations are used for various applications ranging from drug delivery to bypass surgery. However, due to the inherent complexity of the system, modern methods for simulating blood flow are typically oversimplified. This is particularly notable regarding the rheology of blood. Rheologically, blood is a complex fluid that exhibits pseudoplasticity, viscoelasticity, and thixotropy. Coupled with these effects is the potential for blood to separate into a pure plasma region near the walls and a concentrated red blood cell region near the center when subjected to flow, a phenomenon referred to as syneresis. Here, we present a new model that can be used to predict these inhomogeneous effects. In the model, the plasma layer thickness is connected to a structure kinetics model for the transient rheology of the blood, which enables insight into how the transient microstructure within the blood gives rise to this complex syneresis effect. Integrating the model into CFD flow simulations, we develop a robust and accurate numerical method for studying the flow of blood in arterial, pulsatile flow. The model simulation can help to understand the underlying physics and to make realistic predictions for other flow parameters under microfluidic conditions. An efficient code based on spectral collocation method has been designed to take advantage of the mathematical form of the flow conditions and the cylindrical geometry. Orthogonal

Fourier and Chebyshev polynomials represent the time and axial dependence of the solution. This allows for machine-accurate solutions to be obtained for smooth problems. The numerical method was successfully validated for the calculation of Newtonian fluids, elastic solid, viscoelastic Maxwellian fluids, and power law fluids, where analytical results were available. It has then been used in conjunction with the thixotropic structure kinetics model. In doing so, we provide an accurate, robust, and computationally inexpensive technique to simulate transient and inhomogeneous blood flow.

Monday 10:15 Room 306B BB2

Metabolic rates in red blood cells under shear studied by Rheo-NMR

Johanna Milius[1], Philip W. Kuchel[2], Dmitry Shishmarev[3], Sarah J. Stevenson[1], Timothy I. Brox[1], and Petrik Galvosas[1]
[1]Victoria University of Wellington, Wellington, New Zealand; [2]University of Sydney, Sydney, Australia; [3]Australian National University, Canberra, Australia

Red blood cells (RBCs) are responsible for the oxygen transport in living organisms including humans. While circulating, RBCs experience different flow rates and shear stress in different parts of the cardiovascular system with shear rates of up to 2000/s in healthy humans[1]. It has been shown that mechanical deformation modifies the conversion rate from glucose to lactate in the main metabolic pathway of RBCs[2]. Static compression of RBCs in gel, thus distorting the cell shape, resulted in an enhancement of the metabolic rate by ~80% [2].

Here we use Rheo-NMR[3] and study metabolic rates as a stress response at physiological shear rates. We use a cylindrical Taylor-Couette cell adapted for the use in a high resolution 400MHz NMR Bruker Avance spectrometer. The RBC samples were prepared from fresh human blood, under Human Ethics Clearances, as in [2]. Time series of ^{13}C NMR spectra were continuously recorded over 12h while applying a shear rate of 1005.3/s. After 12h, the shear was stopped while recording spectra continued for another 4h.

The rate of conversion from glucose to lactate in the RBCs was estimated from the temporal evolution of the spectra. Without shear the rate was 0.8±0.1 mmol/[liter RBC]/h while the metabolic activity was 2.5 times larger under shear, confirming that the cells respond to mechanical stress imposed by shear flow. The detected difference in the metabolic rate is consistent with the operation of the mechanosensitive non-selective cation channel PIEZO1 while enhancement factors are higher due to shear induced alignment. The experimental set-up paves the way for further studies and improved understanding of the fundamental biophysics of shape and volume regulation by cells in normal and disease states.

[1] Sakariassen, Future Sci. OA 1 (2015). [2] Kuchel, Sci. Adv. 3, eaao1016 (2017). [3] Callaghan, Rep. Prog. Phys. 62 , 599-670 (1999).

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Monday 10:40 Room 306B BB3

Characterization and rheology of platelet rich plasma and platelet poor plasma

Prathap Jayaram[1], Harsa Mitra[2], Andrew T. Bratsman[1], Trevor Gabel[3], and Kamran Alba[3]
[1]Department of Orthopedic Surgery, Baylor College of Medicine, Houston, TX, United States; [2]Mechanical Engineering, University of Houston, Houston, TX 77025, United States; [3]Mechanical Engineering Technology, University of Houston, Houston, TX 77025, United States

During the past several years, various papers have been written about a blood-based preparation called platelet-rich plasma (PRP) which has potential effectiveness as being used in the treatment of various injuries. PRP is a type of plasma with more platelets as compared to blood, which have proteins called growth factors which can heal injuries. Hence the concentration of growth factors also can be richer than usual being a remedy for arthritis, sprained knees, and other chronic tendon injuries are what makes it so lucrative, especially to athletes. Despite the effectiveness and publicity of PRP in the medicine domain, there are still unanswered questions about it from a biological and rheological standpoint. Rheology has been receiving increasing attention in the medical field, especially blood and its products (hemorheology), over the past few decades. We utilize shear rheology to test the mechanical properties of the PRP and Platelet Poor Plasma (PPP). We follow the meticulous protocol for both flow sweep and frequency sweep tests to characterize the apparent viscosity, evaluating possible non-Newtonian effects associated with the samples caused from the interaction of cells within blood products which can cause elastic behavior. All tests are performed at 25°C and 37°C to study the effect of temperature (room and core-body temperature). The PRP samples exhibit shear-thinning which appears to be of the Carreau model where there, we also discuss the limits that one needs to be aware of in interpreting the results. The frequency sweep tests are furthermore carried at out in a triplicate manner at different shear rates to reduce particle settling effects and evaluate the viscoelastic response of samples. Over the acceptable range of angular velocity, the majority of the samples, the loss modulus, dominates the storage modulus. Similar to flow sweep test, the rheological measurements in frequency sweep case are not immune to artifacts and need to be interpreted very carefully.

Monday 11:05 Room 306B BB4

Design of a microfluidic platform for high-sensitivity diagnosis of blood cell disorder

Amir Saadat[1], Diego A. Huyke[2], Juan G. Santiago[2], and Eric S. G. Shaqfeh[1]
[1]Stanford University, Stanford, CA 94305, United States; [2]Mechanical Engineering, Stanford University, Stanford, CA 94305, United States

Changes in red blood cell (RBC) deformability in patients with blood cell disorders can affect the hemodynamics in the microcirculation and, in turn, affect the oxygen transport efficiency. We are developing microfluidic devices to control and observe the flow mechanics of RBCs. We have developed high-fidelity computational simulations of RBC flow mechanics in various microfluidic platforms to guide the design of such devices. One goal of this work is to develop detailed models of the hemodynamic flows including relatively small changes in RBC deformability and spatiotemporal evolution of RBC shape. A second goal is to develop a microfluidic platform and supporting computational tools which can be used to diagnose blood cell disorders. In the current study, we have applied the computational simulation platform that we recently developed to achieve two goals: 1) The optimal microfluidic design within a class of simple, single channel designs, for a personalized diagnosis of a red blood cell disorder; and 2) Determining the appropriate deformability figure(s) of merit which allows us to quantify RBC stiffness (elastic resistance) based on a steady shape measure. Our computational tool that has previously been published allows the study of deformable objects and membranes in complex flows and any user-specified geometry, making it suitable for studying complex blood suspensions in microfluidic devices. We have also developed experiments to track individual RBCs flowing within confined microchannels to quantitively measure RBC shape as a function of a capillary number based on surface shear modulus. For this purpose, we have used soft lithography to fabricate microchannels with a square cross-section (order 7x7 µm2 cross-section) and developed a mechanism to control applied pressure in a variety of microchannel designs. Furthermore, we created a custom imaging setup and image processing code which uses morphological image analysis and thresholding techniques to track and quantify the shape of individual cells.

Monday 11:30 Room 306B BB5

Large amplitude oscillatory shear (LAOS) flow as a metric of comparison for contemporary human blood rheological models

Matthew J. Armstrong[1], Jeffrey S. Horner[2], Michael Deegan[3], Norman J. Wagner[2], and Antony N. Beris[2]

[1]United States Military Academy, West Point, NY 10996, United States; [2]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [3]Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States

Recent work modeling the rheological behavior of human blood indicates that blood has all of the hallmark features of a complex material, including shear-thinning, viscoelastic behavior, a yield stress and thixotropy. After decades of modeling steady state blood data, and the development of steady state models, like the Casson, Carreau-Yasuda, Herschel-Bulkley, etc. the advancement and evolution of blood modeling to transient flow conditions now has a renewed interest [1,2,5,11]. Using recently collected human blood rheological data we show and compare modeling efforts with several new models including the new modified Horner-Armstrong-Wagner-Beris (mHAWB), the viscoelastic enhanced Modified Delaware Thixotropic Model (MDTM), and more. We will compare the new approaches by ability to predict smalland large amplitude oscillatory shear flow as well as uni-directional oscillatory shear flow. This effort is followed with a discussion of novel transient flow rheological experiments applied to human blood including for model fitting purposes including step-up/step-down, and triangle ramp experiments [7-10]. The family of models that can handle these transient flows involve modifications to the recently published Modified Delaware Thixotropic Model (MDTM), the mHAWB model and the Bautista-Monero-Puig Model (BMP) [1-11]. We fist discuss the development of the scalar, structure parameter evolution models and we compare fitting results with our newly acquired transient blood data to the models [5,11]. We also highlight our novel model fitting procedure by first fitting to steady state, and while keeping the steady state parameters constant fitting the remaining model transient parameters to a series of step up/down in shear rate experiments. With the full set of parameters determined with a global, stochastic optimization algorithm the SAOS, LAOS and unidirectional oscillatory shear flow is predicted and compared to the data. Model efficacy is then compared.

Symposium GG
Out of Equilibrium Systems: Gels and Glasses

Organizers: Suzanne Fielding, Ran Tao and Rosanna Zia

Monday 9:50 Room 306C *Keynote* GG1

Reversible and irreversible stress induced rheological changes in complex fluids

William H. Hartt[1], Marco Caggioni[2], Conor Harris[3], Setareh Shahsavari[4], and Emilio Tozzi[4]

[1]Corporate Engineering Technologies Lab, The Procter & Gamble Co, West Chester, OH 45069, United States; [2]Complex Fluids Microctructures, Procter and Gamble, West Chester, OH 45069, United States; [3]Chemical Engineering, The University of Michigan, West Chester, OH 45069, United States; [4]The Procter & Gamble Co, West Chester, OH 45069, United States

Complex fluids exhibit a variety of flow or stress induced changes in rheological properties. Some of these changes are transient and temporary, such as viscoelastic and thixotropic. Some flow induced changes in rheological properties are permanent, or irreversible. We focus here on changes in the yield stress of structured fluids after flow. Three case studies showing reversible and irreversible changes in the yield stress are presented. We demonstrate rheological measurements that enable distinction between reversible and irreversible rheological changes. We also demonstrate models for irreversible changes in the yield stress. Utilization of these models to simulate irreversible rheological changes in complex flows are shown. Finally, we integrate machine learning and feature engineering into rheological measurements to elucidate complex fluid behavior.

Monday 10:15 Room 306C GG2

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

Gavin J. Donley[1], Jun Dong Park[1], Matthew A. Wade[1], Suresh Naranayan[2], Robert L. Leheny[3], James L. Harden[4], and Simon A. Rogers[1]

[1]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]X-ray Sciences Divison, Argonne National Laboratory, Argonne, IL 60439, United States; [3]Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218, United States; [4]Department of Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

We probe the microstructural yielding dynamics of a concentrated colloidal system by performing creep/recovery and shear/recovery tests with simultaneous collection of scattering data via X-ray Photon Correlation Spectroscopy (XPCS). The combination of rheology and dynamics from scattering allows for time-resolved observations of the microstructure as yielding occurs, which can be linked back to the applied rheological deformation. To more accurately track the non-equilibrium processes which occur under yielding, we make use of two-time correlation functions, which provide additional time-resolved information that is inaccessible via more typical one-time correlations. The data suggest that yielding in these materials is triggered by a limitation in the acquisition of recoverable strain. In cases below the yield point, the scattering response recorrelates with its pre-deformed state, indicating that the microstructure recovers nearly-completely. By investigating the nature and extent of these recorrelations we can track the progress of the yielding transition. Examination of the correlation in the flow direction shows that larger creep stresses increase the speed of the dynamics, both during the application of creep and recovery intervals.

Monday 10:40 Room 306C GG3

Effect of attractive forces on slow dynamics in dense colloidal suspensions

Kenneth S. Schweizer[1] and Ashesh Ghosh[2]

[1]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Department of Chemistry, University of Illinois at Urbana-Champaign, Champaign, IL 61820, United States

How strong short-range attractive interactions can massively modify the dynamics and viscoelasticity of dense suspensions of spherical colloids remains a topic of enduring interest. Existing microscopic theories based on local cage scale physics typically assume dynamical constraints are fully quantified by equilibrium pair correlation functions. Despite some successes, these approaches qualitatively fail to explain a number of aspects of activated dynamics in dense attractive colloidal suspensions and supercooled thermal liquids. We construct a new microscopic theory for attractive colloidal suspensions formulated directly in terms of the real Newtonian forces within the framework of the Elastically Collective Nonlinear Langevin Equation (ECNLE) approach which treats activated relaxation as a coupled local-nonlocal event involving large amplitude cage hopping and a longer range facilitating elastic fluctuation. A rich interplay between physical bond breaking and cage escape processes is found. The theory appears to properly capture the key physics including a non-monotonic variation of the relaxation time and diffusion constant with attraction strength, the re-entrant repulsive glass to fluid to attractive glass transition behavior, and the crossover to dense-gel-like dynamics upon moderately lowering volume fraction. Moreover, the theoretical results for the variation of the bond-breaking and de-caging time scales with attraction strength and volume fraction are consistent with simulation. In contrast, even theories that go beyond the ideal mode coupling description which include activated hopping do not properly capture multiple dynamical phenomena if attractive forces are assumed to only modify local structure. An additional consequence of the new formulation is activated dynamics can be strongly dependent upon the functional form of the microscopic attractive forces (e.g., LJ versus exponential).

Monday 11:05 Room 306C GG4

Frictional dynamics of sticky colloids

Gerald J. Wang and James Swan

Chemical Engineering, MIT, Cambridge, MA 02139, United States

When two particles in a suspension approach contact, there is the possibility of a non-negligible (and perhaps even substantial) inter-particle frictional force. As a consequence, frictional forces can play a significant role in the structural and transport properties of systems that contain an appreciable number of particle-particle contacts, as is the case for suspensions at high particle volume fraction or with inter-particle attractions. Elucidating the relationship between microscopic frictional contact and macroscopic suspension properties is critical for understanding numerous rheological phenomena, most notably discontinuous shear thickening. Here, we present computational and theoretical modeling of frictional colloidal suspensions, in which friction is incorporated straightforwardly as a hydrodynamic resistance to sliding between nearly touching particles. Our simulations reveal that even a small amount of friction can dramatically decrease the diffusivity of both particles and particle clusters; more specifically, we observe a power-law scaling between the diffusivity suppression and the friction coefficient. This result is supported by a spectral model accounting for the effect of friction on the near-field components of the hydrodynamic resistance tensor. We also present evidence that friction gives rise to non-Gaussian particle displacement statistics, consistent with stick-slip dynamics. Moreover, we demonstrate that a combination of graph theory and classical rigidity theory can be applied to frictionally arrested particle clusters, in order to shed light on the conditions under which friction is especially important; in particular, we discuss the significance of system-spanning frictional clusters. We conclude by drawing comparisons between our work and experimental results from the literature, and by proposing fruitful avenues for joint computational-experimental work.

Monday 11:30 Room 306C GG5

Realistic multi-body finite element models for the linear elastic response of compressed micro-gel suspensions.

Ahmed Elgailani and Craig E. Maloney
Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States

Suspensions of micro-gel particles exhibit a non-zero zero-frequency shear modulus while compressed osmotically. Recent experiments have shown the shear modulus of the packing to be of the same order of magnitude as a monolithic gel at the same density of crosslinks. This result is puzzling as one would expect the breakup of a monolith into individual constituent particles to result in a reduction of the modulus, as interfaces between the particles should be free to slip past each other with no deformation of the elastic network. Here, we perform a multi-body finite element model simulation where the deformation of the gel network is assumed to be perfectly described by the Flory-Rehner model for gel elasticity. We show that, at large osmotic pressure, the modulus is indeed reduced by strong sliding at inter particle facets and compare our results to experimental data.

Monday Afternoon

Symposium TM
Rheometry: Advanced Techniques and Methods

Organizers: Joseph Samaniuk and Michelle Calabrese

Monday 1:30 Room 305A TM6

Gaining physical insights into LAOS experiments: Stress decomposition in LAOS of dense suspensions

Edward Yong Xi Ong, Meera Ramaswamy, and Itai Cohen
Applied Engineering and Physics, Cornell University, Ithaca, NY 14850, United States

Large amplitude oscillatory shear (LAOS) has emerged as the most used characterization methods for large, non-linear perturbation due to the ease of implementation and because it allows for independent probes of the time and length scales by tuning the frequency and amplitude of oscillation. The complex non-linear interactions that are the results of a LAOS experiment, however, are difficult to understand. Attempts to quantify LAOS behavior through techniques like Chebyshev polynomials and a Sequence of Physical Processes give insights into the shape of the LAOS curve and predicts thickening, thinning, stiffening and softening behaviors but provide limited understanding for the dynamics and interplay of the stresses involved. Here, we present an intuitive way of understanding the rich interactions present in the LAOS of shear-thickening suspensions by experimentally decomposing the stresses involved. The decomposition allows us to extract the hydrodynamic, contact and Brownian contributions across the Lissajous curve to map out the different stress dynamics across an oscillation cycle. Access to the time evolution of each stress component provides us with valuable insights on the potential microscopic details of the system, such as the time scales for the buildup and relaxation of the force chains during oscillation, the corresponding type of contact mechanism and the microstructure during the transition from low to high Péclet number and vice-versa. While we have chosen to demonstrate this experimental method on colloidal suspensions, the generality of the method also allows it to be used to investigate other non-linear systems such as gels and polymers.

Monday 1:55 Room 305A TM7

Understanding molecular changes in three wheat flour doughs during aging through their LAOS behavior

Secil Turksoy, Merve Yildirim, and Jozef Kokini
Food Science, Purdue University, West Lafayette, IN 47907, United States

The effect of different aging times on the non-linear LAOS rheological properties of 3 wheat flour doughs were investigated. Hard, soft and semolina flours were mixed with a constant amount of water using a Brabender Farinograph. The dough samples were aged at room temperature (25°C) for 5 days. Starting from t=0, dough samples were analyzed every six hours. LAOS experiments were carried out using a DHR-3 Rheometer with parallel plate geometry. The strain sweep tests were conducted between the strain values of 0.01% and 200% at a constant angular frequency (10 rad/s). The frequency sweep experiments in the linear region (0.05%) were carried out using frequencies between 0.01-100 rad/s. LAOS parameters (G'M, G'L, ?'L, ?'M, e3/e1, v3/v1, S, T) were used to characterize the nonlinear rheological properties of dough samples during aging process. The LAOS behavior of all dough samples showed that dough networks displayed non-linear behavior as strain increased after a characteristic linear region, which was a function of the type of dough and the strength of the gluten network. Semolina dough has the strongest gluten network compared to other dough samples, followed by hard and soft samples. In the linear region, all dough samples exhibited strong elastic behavior (G'? G"). As strain amplitude increased beyond a critical strain, both G' and G" moduli (no longer having a fundamental meaning in the non-linear region) for each dough sample decreased significantly. Due to higher protein content and higher glutenin content of semolina dough which forms a stronger network, it has a larger G' and lower tangent delta than hard and soft flour dough. Semolina dough was the most resistant against increasing aging time as well due to its higher protein network and intermolecular disulfide cross-linkages which are not susceptible to enzymatic action. Prolonged aging time had a reducing effect on LAOS parameters which is attributed to molecular breakdown cause by enzymatic action of intrinsic enzymes of the protein network.

Monday 2:20 Room 305A TM8

Medium amplitude parallel superposition (MAPS) rheology

James Swan[1], Gareth H. McKinley[2], and Kyle Lennon[1]
[1]Chemical Engineering, MIT, Cambridge, MA 02139, United States; [2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

A mathematical representation for nonlinear viscoelasticity based on Volterra series expansion of the shear stress as a functional of the shear strain is presented. In this work, we develop a new theoretical and experimental framework based on this Volterra series representation, which we call medium amplitude parallel superposition (MAPS) rheology. The framework reveals a new material property, the third order complex modulus, that describes completely the weak, time-dependent nonlinearities of the shear stress within a homogeneously-sheared viscoelastic material. This nonlinear modulus is a unifying super-set of the response functions measured in medium amplitude oscillatory shear (MAOS) and parallel superposition (PS) experiments. Unlike the MAOS and PS transfer functions, the third order complex modulus can be used to construct the weakly nonlinear shear stress in response to an arbitrary shear history. This material function offers a new data-rich approach for completely characterizing the nonlinear viscoelasticity of unknown materials at third order in the magnitude of the deformation. For some simple constitutive models, the third order complex modulus possess startlingly complex and distinctive features. An experimental protocol is presented that allows for direct measurement of the third order complex modulus using existing commercial rheometers and their associated control software. We demonstrate this experimental protocol through measurement of the nonlinear viscoelastic response in a polymer hydrogel that possesses an ultra-narrow distribution of equilibrium relaxation times.

Monday 2:45 Room 305A TM9

Calibration of a commercial rheometer for orthogonal superposition measurements

Ran Tao and Aaron M. Forster
Material Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, United States

The technique of orthogonal superposition (OSP) rheology involves superimposing a small amplitude oscillation on a primary steady shear flow, which allows for probing structural changes in complex fluids under nonlinear flow conditions. The OSP functionality has been integrated in a commercial strain-controlled ARES-G2 rheometer utilizing a double wall concentric cylinder geometry. The normal force rebalance transducer is modified to operate as a stress-controlled rheometer, allowing the shaft to apply axial deformation and measure the axial oscillation force. The axial motion is imposed simultaneously with the motion of the rotary motor, which performs either an oscillatory or continuous shear in the angular direction. While the availability of the commercial instrument promoted more experimental OSP research in recent years, understanding the correction factors due to non-idealized flow field in this geometry is important for proper use of the instrument and obtaining correct results. This work focuses on end-effect factor calibration measurements on the commercial rotational shear rheometer using different viscosity standards that range from 0.01 to 300 Pa·s. The results from the study should inform other OSP users with better operational knowledge to calibrate the instrument and evaluate the experiment data. This work also aims to provide flow field information (i.e., velocity, pressure, shear rate) during measurement for Newtonian fluids, which is achieved by computational fluid dynamics simulation using a finite element method software package.

Monday 3:45 Room 305A *Keynote* TM10

Injectability screening for concentrated biologics by microfluidic quartz resonator

Zehra Parlak
Qatch Technologies, Durham, NC 27701, United States

QATCH is developing a microfluidic viscometer based on microfluidic quartz resonator (MQR) technology. This technology harnesses semiconductor fabrication principles to rigidly couple micro-channels of ~10 nanoliters of volume to the quartz resonator surface. The quartz resonators intrinsically operate at very high shear rates (>5,000,000 1/s), and the shifts in the MQR resonance spectrum can be used to directly determine the high shear-rate viscosity of liquid inside the channels. Concurrently, the MQR channels also function as an acoustic capillary viscometer, measuring the low shear rate viscosities (at 20-2,000 1/s) by observing fluid flow. This is accomplished by detecting the position of the fluid flow via tracking resonance frequency shifts. QATCH is using MQR technology to address the growing needs of the biopharmaceutical industry in characterization of concentrated protein formulations. High concentration protein formulations are typically created for subcutaneous injections and exhibit a complex shear-thinning behavior with low and high shear-rate plateaus. Injectability testing of these formulations by rheometry requires understanding of their rheological behavior at both low and high shear-rates. However, the sample volume available in early development stages are not sufficient for a wide range characterization with the existing instrumentation. QATCH's MQR-based microfluidic viscometers require only a small drop of sample (~5 microliters, while only a few nanoliters of this drop is used) and provides viscosity information from 20-2,000 1/s and >5,000,000 1/s in under 2 minutes. Having this critical rheological data available at an early development stage can de-risk candidate selection process and reduce the process development cost.

Monday 4:10 Room 305A TM11

High frequency rheometry with the quartz crystal microbalance

Kenneth R. Shull, Qifeng Wang, and David E. Delgado
Department of Materials Science and Engineering, Northwestern University, Evanson, IL 60208-3109, United States

The quartz crystal microbalance (QCM) consists of a piezoelectric quartz disk with electrodes deposited on either side of the crystal. The crystals are cut so that an electric field applied across the electrodes results in a shear displacement of the crystal surfaces. Details of the crystal resonance depend on the thickness and rheological properties of a film deposited on one of the electrode surfaces, enabling the QCM to be used as a fixed frequency rheometer, in our case operating at 15 MHz. While this has been known for many years, our focus has been on the development of the technique to provide quantitative rheometric information, with uncertainties comparable to uncertainties obtained from more traditional rheological methods. This sort of accuracy can indeed be obtained, but only with film thicknesses in an appropriate regime, typically in the micron range for polymeric materials. The focus on this talk is on the validation of the approach with a variety of glassy and rubbery polymers, and on a discussion of the sorts of problems for which the technique is well suited.

Monday 4:35 Room 305A TM12

Single and multi-particle tracking to study transport properties and viscoelasticity of biopolymer solutions

Parveen Kumar, Joshua Tamayo, and Arvind Gopinath

University of California Merced, Merced, CA 95343, United States

Passive microrheology using single-particle and multi-particle techniques are often used to assess the local transport properties, mechanical properties and network properties of cells and biological fluids. We present single particle tracking (SPT) and multiple particle tracking (MPT) to probe the displacements of tracer particles ranging from 0.1 to 10 microns in size in complex, viscoelastic biopolymer fluids. The trajectory of individual particles are imaged through a microscope and recorded with a digital camera at frame rates ranging from a few Hz up to a few hundred Hz. Sub-micron particles are recorded using fluorescence, while brightfield and phase contrast microscopy is used to record micron-sized particles. Particle tracking and linking algorithms are implemented in MATLAB and Python to construct 2-dimensional trajectories from a scrambled list of particle coordinates determined in consecutive video frames. Limited spatial resolution and statistical uncertainty are the primary limiting factors that affect the analysis and interpretation of tracking data; here, recorded trajectories are corrected for drift, and subject to careful filtering techniques based on parameters such as track length, three-dimensional effects, local inhomogeneities in the fluid and particle displacement. The corrected data is used to calculate the distributions of displacements and velocities, ensemble averaged mean square displacement and two-particle velocity autocorrelations from which we extract diffusion coefficients of the particles and viscoelastic properties of the fluidic medium. We first validate our methods by comparing measured diffusivities of spherical tracers in water to known to theoretically predicted values from the Stokes-Einstein relation, and then investigate the rheological properties of CMC (Carboxy Methylcellulose) and mucin solutions ranging in concentration from 0.2 wt% to 5 wt%.

Monday 5:00 Room 305A TM13

Artificial thermal noise to probe local viscoelastic properties of complex fluids

Shalaka K. Kale and Joseph R. Samaniuk

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

Passive microrheology can play a key role in characterizing the variations in mechanical response of materials at micron and sub-micron length scales. Combined with video microscopy it can infer viscoelastic properties by simply tracking the Brownian motion of the probe particles. However, passive particle tracking microrheology is generally limited to low modulus materials ($G^*\sim10^0$Pa) due to limits in spatial resolution. In higher modulus materials ($G^*>10^1$Pa), the probe particle experiences restricted Brownian motion that is beyond the spatial resolution of a typical optical microscope (~10nm), putting passive microrheology at its upper limit. To overcome this, we have developed a form of active microrheology using electromagnetic tweezers that induces an artificial thermal noise on a superparamagnetic particle. By driving the particle in the presence of an artificial noise signal we are effectively amplifying its restricted Brownian motion to reach beyond the limit of the microscope's spatial resolution. We simulate and supply a white noise current signal to the electromagnetic coils to create magnetic fields that vary in direction and intensity randomly in a way that we can drive a probe with average energies greater than kT. Our method provides two main advantages. First, the induced random motion of the particle allows one to obtain rheological material functions via hydrodynamic models, just like passive microrheology, without needing knowledge of a defined strain field. Second, unlike conventional active microrheological techniques that require large forces to drag a micron-scale particle through a sample, the use of small amplitude artificial thermal noise for the same sample requires relatively small forces. We validate our approach by using Newtonian calibration fluids with viscosities up to 100 Pas. We will also discuss our efforts to extend the technique to viscoelastic fluids, and the use of the Langevin equation to quantify the excess energy we apply to the probe.

Monday 5:25 Room 305A TM14

Bi-disperse multiple particle tracking to characterize evolving gels

Matthew D. Wehrman[1], Seth Lindberg[2], and Kelly M. Schultz[1]

[1]Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; [2]Corporate Engineering, The Procter & Gamble Company, West Chester, OH 45069, United States

Synthetic gels are being designed with unprecedented complexity from bulk material properties down to the scaffold microstructure. This complexity grows out of the vast array of applications and high demand on gel versatility. Gels are part of everyday life from personal, fabric and home care products to biomaterials that mimic the extracellular matrix (ECM). Due to this complexity, new measurement techniques are needed to fully characterize the evolution of these materials. This work develops a new technique to measure several length scales in a single sample using multiple particle tracking microrheology (MPT). Traditionally, MPT uses a single particle size to characterize rheological properties. But in complex systems, MPT measurements with a single size particle can characterize distinct properties that are linked to the materials length scale dependent structure. By varying probe size, MPT can measure material properties associated with different length scales. We develop a technique to simultaneously track a bi-disperse population of particles. 0.5 and 2 micron particles are embedded in the same sample and these particle populations are tracked separately using a brightness-based squared radius of gyration. Bi- disperse MPT is validated by measuring the viscosity of glycerol at varying concentrations. This technique characterizes a homogeneous PEG-acrylate: PEG-dithiol gelation that includes polymeric interaction. These measurements are not dependent on the length scale. Finally, degradation of a heterogeneous hydrogenated castor oil colloidal gel is characterized. The two particle sizes measure different structures in the material. Analysis of material heterogeneity shows the maximum is dependent on probe size indicating that each particle is measuring rheological evolution of a length scale dependent structure. Bi-disperse MPT increases the information gained in a single measurement, enabling more complete characterization of complex systems that range from consumer care products to biological materials.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Monday 1:30 Room 304 SC6

Force network structure development in discontinuous shear thickening

Jeffrey F. Morris[1], Omer Sedes[1], and Singh Abhinendra[2]

[1]Levich Institute, CUNY City College of New York, New York, NY 10031, United States; [2]Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637, United States

Using numerical simulations inclusive of lubrication hydrodynamics, repulsive forces and contact with friction, we consider the force network development of dense suspensions. The focus is on the behavior of systems at the boundary between continuous (CST) and discontinuous shear thickening (DST), where the system displays behavior suggestive of a non-equilibrium phase transition. For solid fraction below the critical value (~ 0.55), the suspension exhibits CST, with a finite rate of viscosity increase. At the critical volume fraction, as the shear rate is increased, the system reaches a critical point at which the viscosity (or stress) has infinite slope, but remains continuous (as would the density at a gas-liquid critical point) and at which correlations in stress fluctuations simultaneously grow. The underlying basis for this behavior in terms of the force network is analyzed by various measures: contact number, percolation, and k-core analyses will be presented.

Monday 1:55 Room 304 SC7

Towards a tribological perspective on dense suspension rheology

Lilian C. Hsiao

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

The importance of microscopic and macroscopic friction between closely packed particles is becoming increasingly recognized in fields as diverse as geosciences, consumer products, and slurry processing. Particles encountered in these real-life scenarios often possess rough or bumpy surfaces, which generate significant tangential forces when pushed into near contact at high shear stresses. These frictional forces may arise from either hydrodynamic or contact origins depending on particle relative velocities. We report our experimental findings on the linear viscoelasticity and shear thickening behavior of a series of increasingly rough colloids suspended at high volume fractions in squalene. The volume fraction is experimentally determined from confocal laser scanning microscopy and independently validated using the divergence of low-shear viscosity. To define contact between the sterically-stabilized poly(methyl methacrylate) colloids, we measure the mean coordination number as a function of particle separation obtained from 3D confocal laser scanning micrographs. The results support the idea that rheological phenomena can be understood as a function of the distance from jamming, a parameter that is both material- and process-dependent. We further investigate the role of particle volume fraction and roughness using a tribology accessory mounted on a stress-controlled rheometer. Preliminary results suggest that it may be possible to link the macroscopic rheology and tribology of dense suspensions using the dimensionless Sommerfeld number.

Monday 2:20 Room 304 SC8

Role of rolling friction in the flow of dense frictional suspension

Abhinendra Singh[1], Juan J. de Pablo[2], and Heinrich M. Jaeger[1]

[1]James Franck Institute, University of Chicago, Chicago, IL 60637, United States; [2]Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637, United States

Concentrated suspensions of rigid neutrally buoyant spheres can exhibit various non-Newtonian features such as shear thickening, normal stress differences, and shear jamming. The viscosity of such suspensions is often found to undergo an abrupt increase making a transition from a low-viscosity to a high-viscosity state, termed as discontinuous shear thickening (DST). The observed behavior has recently been linked to a transition from "lubricated" rheology, where close interactions between suspended particles take place through a thin liquid film, to a "frictional" rheology, where particles make unlubricated frictional contacts. So far the role of sliding mode of friction has been discussed. Interlocking due to asperities or roughness and adhesion due to forces such as hydrogen bonding which can also hinder the rolling between particles has not been studied. We explore the role of rolling friction between particles. We show that using rolling friction together with sliding friction can dramatically decrease the volume fraction for the onset of DST. We find that using short-ranged attraction together with rolling friction can also change the onset stress for thickening as well as the extent and abruptness of shear thickening. A flow-state diagram encompassing these results will be presented.

Monday 2:45 Room 304 SC9

Experimental tests of frictional contact models for suspensions

Yu-Fan Lee[1], Yimin Luo[1], Chiao-Peng Hsu[2], Scott C. Brown[3], Kimberly A. Dennis[1], Lucio Isa[2], Eric M. Furst[1], and Norman J. Wagner[1]

[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]Department of Materials, ETH Zurich, Zurich 8093, Switzerland; [3]The Chemours Company, Wilmington, DE 19805, United States

The shear-thickening of dense colloidal suspensions is an active topic of research to understand the non-linear flow response. Efforts in theoretical models and simulations have been made to examine the essential physics thought to be controlled by nanometer scale inter-particle forces,

including lubrication hydrodynamics and frictional contact forces. At high stresses and concentrations, the particles are in close enough proximity and form transient structures called hydroclusters, which manifests in shear-thickening. Recently, there has been significant effort in exploring the possible role of contact friction in shear thickening. Wyart and Cates propose an increase in fraction of frictional contact with increasing stress as the source of the shear thickening viscosity. Further work by Morris and co-workers suggest that the jamming volume fraction, where the suspension ceases to flow, depends on the friction at particle-particle contact. These authors performed simulations by varying contact friction coefficients to correlate with the jamming volume fraction. What is lacking, however, are experiments on model suspensions with known levels of contact friction where the full rheological stress tensor under shear is measured. Recent characterization of coated colloidal particles provides a reference for a system with low surface friction, while estimates of surface friction for the uncoated particles provides a reference for a suspension with higher friction. Further research of this work studies the relationship between contact friction, jamming volume fraction, and shear thickening rheology by studying model suspensions with known surface properties of systematically varying contact friction coefficients, as typically measured by particle atomic force microscopy. The shear rheology of suspensions of particles with varying surface chemistry that exhibit a variation in jamming fractions and contact friction coefficients is characterized to understand the mechanistic role of frictional contact in shear thickening.

Monday 3:45 Room 304 SC10

Cellular Stokesian dynamics: The colloidal hydrodynamics of intracellular transport

Roseanna N. Zia[1], Akshay Maheshwari[2], Emma Gonzalez[1], Alp Sunol[1], and Drew Endy[2]
[1]Department of Chemical Engineering, Stanford University, Stanford, CA, United States; [2]Bioengineering, Stanford University, Stanford, CA 94305, United States

Many representations of intra-cellular behavior rely on abstractions that do not account for how macromolecules are organized and move inside the crowded, watery cell milieu. For example, linear algebra- and differential equation-based models typically do not represent biomolecules or their spatial positioning and motion. For many questions in biology and medicine these simpler models have been sufficient. However, fundamental gaps in understanding of many cell functions persist; physics may provide a bridge to close such gaps. I will discuss our progress in developing computational and theoretical tools to model spherically confined colloidal suspensions, as a simple model cell, so that biomolecules and their interactions can be physically represented, individually and explicitly. By developing a more robust and fundamentally well-grounded physics model for how macromolecules interact within cells we can contribute to a more physically complete representation of living matter. A primary challenge in models of confined colloidal suspensions is the accurate and efficient representation of many-body hydrodynamic interactions, Brownian motion, and the enclosure itself. To this end, we developed a new "Cellular Stokesian dynamics" framework that accounts for spherically confined many-body hydrodynamic and lubrication interactions, Brownian motion, and active transport. Utilizing this model, we studied diffusion, cooperative motion, and self-organization with confinement and crowding levels representative of a cell interior. I will discuss the qualitative influence of hydrodynamics, confinement and crowding on transport behavior, as well as the consequences of neglecting such influences. Connections to underlying structure are made, and implications for cellular function are discussed.

Monday 4:10 Room 304 SC11

Dynamics and rheology of suspensions of particles with arbitrary shapes

Mingyang Tan, Joshua Adeniran, and Travis W. Walker
Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, SD, United States

Suspensions of particles in fluids are common in both nature, such as proteins, bacteria, and viruses in biological media, and in engineering fields, such as manufacture of composite materials, dispersion of pigments in paint, and mixture of emulsion polymers. While the rheological properties of suspensions of spherical particles have been widely studied, suspensions of aspherical particles create new questions and phenomena that still need to be explained. The rheological properties require an accurate knowledge of the interactions among particles, i.e., hydrodynamic interaction and/or other interactions that are induced by external fields. The hydrodynamic interactions depend on the configuration of the suspension, which makes itself formidable to calculate for an aspherical suspension caused by the complex geometry. In this study, we decomposed the aspherical particles into constitutive spheres and constrained them in rigid-body assemblies. We use the accelerated Stokesian dynamics to model and study the dynamics of the rheology of the suspension and apply this method to any arbitrarily -shaped particles.

Monday 4:35 Room 304 SC12

Relationship between rheology and microstructure in thermosensitive micellar copolymer polycrystals with embedded colloidal nanoparticles

Imane Boucenna, Florent Carn, and Ahmed Mourchid
Matière et Systèmes Complexes, CNRS and Université Paris Diderot, Paris 75013, France

We studied the rheological properties of copolymer-nanoparticle aqueous solutions and their relationship to the structure at both nano and microscales. The samples are formed of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer micellar solutions with embedded spherical silica nanoparticles. The concentrated micellar solutions exhibit a phase transition from fluid to crystal induced by temperature. Addition of nanoparticles is found to trigger the formation of polycrystallized micellar micrograins, above the transition temperature, instead of a cubic monocrystal. This transition is associated with the confinement of the nanoparticles, which play the role of impurities, in interstices between the micrograins, in the weak concentration regime, while above a concentration threshold inefficient nanoparticle segregation is observed. This behavior is associated with a non-monotonous variation of the onset of transition seen in the evolution of viscoelastic moduli. The analysis and comparison of the experimental data show that the increase of nanoparticle concentration has the effect to increase both the yield

stress and storage modulus and simultaneously to decrease the size of the polycrystalline micrograins observed by optical microscopy. We use the Hall Petch relation to account for the observed rheological reinforcement and micrograin size decrease in these micellar solutions. These data will be compared and discussed with the results of copolymer- anisotropic laponite nanoparticles for which the high adsorption rate largely influences the macroscopic properties.

Monday 5:00 Room 304 SC13

Simulation of nanocrystalline cellulose suspensions

Jing-Yao Chen[1], Zhouhan Li[2], Izabela Szlufarska[2], and Daniel J. Klingenberg[1]
[1]Chemical and biological engineering, University of Wisconsin-Madison, Madison, WI 53706, United States; [2]Material science engineering, University of Wisconsin-Madison, Madison, WI 53706, United States

Cellulose nanocrystals are rigid particles with diameters on the order of a few nanometers and lengths up to one hundred nanometers. In suspension, these materials can exist in a variety of liquid crystalline phases depending on the interactions between the particles. We model the crystals as spherocylinders that interact via short-range repulsive and various attractive forces. Brownian dynamics simulations are used to study the dependence of the microstructure, dynamics, and rheology of these suspensions on the nanocrystal diameter, length, and parameters of both the repulsive and attractive particle interactions. Simulations indeed show isotropic, nematic, and smectic phases under different conditions, with a wide range of rheological properties in simple shear flow.

Monday 5:25 Room 304 SC14

Elucidating powder rheology via Discrete Element simulations and mechanically stirred powder rheometry

Jeremy B. Lechman, Dan S. Bolintineanu, and Anne M. Grillet
Engineering Sciences Division, Sandia National Laboratories, Albuquerque, NM 87185-0346, United States

Bulk solids composed of many discrete particles, i.e., grains and powders, are present in numerous engineering applications from mining to materials processing to energy storage to consumer products to food. In addition, particles are often added to materials to enhance their properties and subsequent performance in some fashion. Although particulate materials are ubiquitous, there remains a general lack of predictive understanding of their behavior; leading to a deficiency in effective, efficient control of the processing of such materials. At the core of this poor understanding is a shaky fundamental explanation of how the dynamics of individual particles, in ensemble, lead to the complicated dilative, yield stress, pressure dependent rheological behaviors of the bulk material. This challenge is particularly acute at low confining stresses for small, mildly cohesive particles. In this paper, we will present work to simulate, via the Discrete Element Method (DEM), the dynamics of individual particles of metal powders in a mechanically stirred powder rheometer. Our aim is to elucidate the connection between particle dynamics and powder rheology. In addition, we will assess the use of powder rheometry as a means of validating DEM models.

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Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Monday 1:30 Room 201 *Keynote* SM6

Using rheology, colloid force microscopy and mathematical modeling for understanding the role of associative polymers in lubrication

Eugene Pashkovski[1], Reid Patterson[1], Timothy Murdoch[2], Daeyeon Lee[3], Robert Carpick[2], and Ilya Kudish[4]
[1]R&D, The Lubrizol Corporation, Wickliffe, OH 44092, United States; [2]Mechanical Engineering, The University of Pennsylvania, Philadelphia, PA 19104, United States; [3]Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States; [4]ILRIMA Consulting, Inc., Millersburg, MI 49759, United States

Polymers are widely used for rheology control in lubricating and hydraulic fluids. Traditionally, these fluids are described in terms of empirical rheological models, which account for shear thinning but do not include elastic (normal) stresses originating from polymer chains stretched under flow. We have shown through mathematical modeling of hydrodynamic friction that the Trouton ratio (the ratio of extensional to shear viscosity) of lubricants controls viscous energy losses in the tribological contact zone. The visco-elastic properties of polymer solutions depend on chemical nature of polymers. Associative polymers with randomly distributed functional groups (stickers) represent an interesting class of polymers with quite rich rheological behavior. These industrially-important polymers have relatively low molecular weight, which makes it difficult to measure elastic polymer stresses using shear rheology in dilute regime. However, using transient elastocapillary flow in capillary breakup extensional rheometer (CaBER), it is possible to measure extensional viscosity and relaxation time of lubricants. In bulk solutions, the chains dynamics in extensional flow were found to depend on chemical nature of stickers. In addition, these stickers promote adsorption of macromolecules onto metal surfaces, forming thick concentrated polymer layers. We use colloidal force microscopy for characterizing the mechanics of adsorbed layers and their effect on friction. Lateral force measurements show that the adsorbed layers can significantly reduce frictional forces between moving

surfaces. Dynamic force-distance curves obtained at range of velocities provide addition insight into the structure of adsorbed polymer networks and its interaction with solvent. This allows be further analysis using classical rheology in the linear viscoelastic regime.

Monday 1:55 Room 201 SM7

Electrostatics in semidilute polyelectrolyte solutions

Guang Chen, Antonio Perazzo, and Howard A. Stone
Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, United States

Polyelectrolyte (PE) solutions, which are charged polymers that dissociate in aqueous electrolyte solution, are common in nature and essential to life. The electrostatic interactions among charged systems depend on the charge strength, separation distance and salt-screening effects. Therefore, when the electrostatic energy dominates the chain conformation of a PE solution, the corresponding rheology is responsive to the environmental changes such as polymer concentration C and salt concentration Cs. In this work, we present a theoretical model based on a self-consistent mean-field approach to study the electrostatics of semidilute PE solutions and its contribution to the viscosity. By probing the electrostatic potential and ion distributions at various C and Cs using the Poisson-Boltzmann equation, we document four different scaling regimes for the electrostatic energy density F within and beyond the Debye-Hückel approximation, which are consistent with numerical solutions. Accordingly, we propose four different scaling laws, depending on solution conditions, for the viscosity η of unentangled semidilute PE solution with Rouse dynamics: For PE solutions with added salt, F ~ C^2 Cs^{-1} and η ~ C^{1.25} Cs^{-0.75} for weak PEs, while F ~ C^{3/2} Cs^{-1/2} and η ~ C^{0.875} Cs^{-0.375} for strongly charged PEs; for "salt-free" PE solutions, F ~ C and η ~ C^{0.5} when salt contamination is proportional to C, while F ~ C^{5/4} and η ~ C^{0.6875} when salt contamination is negligible. The new scaling law η ~ C^{0.6875} captures the unexplained observation of a recent experiment, where η ~ C^{0.68} was reported for "salt-free" PE solutions [1]. Therefore, our model can provide more fundamental understanding of the electrostatics and dynamics of semidilute PE solutions.

Reference: [1] C. G. Lopez, R. H. Colby, P. Graham and J. T. Cabral, Viscosity and scaling of semiflexible polyelectrolyte NaCMC in aqueous salt solutions, Macromolecules, 50, 332 (2017)

Monday 2:20 Room 201 SM8

Solution rheology of dry native cellulose in ionic liquids: Weakly associating polymers?

Nyalaliska Utomo, Behzad Nazari, and Ralph Colby
Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, United States

We report solution rheology of six dry native cellulose samples of different molecular weight in three different ionic liquids; 1-ethyl-3-methylimidazolium acetate [EMIm]Ac, 1-butyl-3-methyl imidazolium chloride [BMIm]Cl and 1-ethyl-3-methylimidazolium methylphosphonate [EMIm][P(OCH3)(H)O2]. These solutions do not crystallize, making it possible to measure the glass transition using oscillatory shear rheology. Trace amounts of water impart a yield stress to these solutions so they experience 20 min at 80 C in the rheometer after loading to remove water. Concentration dependences of specific viscosity and relaxation time make each solution appear to be a 'normal' polymer solution, with dilute, semidilute unentangled and entangled regimes of concentration. However, the same cellulose sample in different solvents at the same concentration has a different width of the rubbery plateau and there is a strange failure of the Cox-Merz rule (shear viscosity larger than linear complex viscosity in the shear-thinning region) for cellulose solutions in ionic liquids. Both of those observations suggest that native cellulose is not a simple flexible polymer in solution and that it instead has some inter-chain hydrogen bonds between cellulose chains. Urea is known to compete for hydrogen bonds and adding urea to these solutions lowers the viscosity, most dramatically for the solutions with the widest rubbery plateau. An additional complication with these solutions is that cellulose seems to adsorb to the air interface to create a viscoelastic film and the consequences of that adsorption on literature for the temperature dependence of intrinsic viscosity of cellulose in [EMIm]Ac will be discussed.

Monday 2:45 Room 201 SM9

The impact of association strength on performance and processing of entangled ionomers

Zachary R. Hinton and Nicolas J. Alvarez
Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States

Associating polymers are highly valued for their unique performance characteristics including improved mechanical, optical, and chemical properties over the base polymer. While much is understood about the linear rheology of associating polymers, fast non-linear flows are critical to further understanding polymer melt processability and ultimate performance. In this work, we use a filament stretching rheometer to measure the non-linear flow behavior of poly(ethylene-co-methacrylic acid) and its ionomer under constant rate of extension. We show that the processing limits of these polymers are highly dependent on the strength of the associating groups. Furthermore, we show that the presence of entanglements increases the processing window of strong ionomers over their unentangled counterparts. We measure the self-healing properties of associating polymers and quantify recovery as a function of intrinsic relaxation times. Overall, we show that the timescales which govern associating bond lifetime are directly responsible for changes in processability and self-healing. Overall, it is evident that there is a trade-off between associating polymers which exhibit high-performance (i.e., good mechanical properties) and are highly processable.

Monday 3:45 Room 201 SM10

Rapid relaxation by internal slip – rheology and ordering of diblock bottlebrush polymers

Benjamin M. Yavitt[1], Huafeng Fei[2], Gayathri K. Kopanati[2], James J. Watkins[2], and H. Henning Winter[2]
[1]Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794, United States; [2]UMass Amherst, Amherst, MA 01003, United States

The ordering dynamics of lamellae forming diblock bottlebrush polymers is orders of magnitude faster than ordering and rheology of conventional linear diblocks even at high molecular mass. This is attributed to the suppression of entanglements in bottlebrush molecules and to the formation of internal slip layers (ISLs) in the microphase separated state. Internal slipping is a recently discovered relaxation mechanism (2019 Macromolecules 52:1557-1566), facilitated by a high concentration of free backbone chain ends in the middle of the lamellar domains. Viscoelasticity and ordering will be shown for polystyrene-block-poly(ethylene oxide) (PS-b-PEO) diblock bottlebrush copolymers with short side chain lengths. The viscoelasticity can be expressed by a finite long-time modulus together with a dual power law relaxation time spectrum, H(t), consisting of relaxation processes at short and intermediate time scales. Scaling on short time scales (powerlaw exponent n1) is attributed to the cooperative mobility of internal ISLs. Relaxation processes at longer time scales (powerlaw exponent n2) are dominated by grain boundaries of microphase separation in globally disordered states. We utilize the ISL rapid relaxation dynamics towards processing of oriented morphologies via. controlled oscillatory shearing.

Monday 4:10 Room 201 SM11

Rheological fingerprinting of nanoscale structure of block copolymer micelle liquid crystals

Connor S. Valentine and Lynn M. Walker
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15217, United States

At high polymer concentrations, solvent-selective block copolymer molecules self-assemble into concentrated micellar solutions that form highly-ordered, nanostructured, soft solids. Controlling the solvent quality allows for high densities of deformable (soft) particles to be achieved. The phase diagrams of these materials are shown to be extremely rich, exhibiting high symmetry cubic phases and low symmetry phases (Frank Kasper) as well as phases with other base units. This is especially true as the molecular weight of the block copolymers decreases and fluctuations in micelle aggregation number increase; connecting to the similarly rich phase behaviors observed in concentrated surfactant solutions. The goal of this work is to use rheology to fingerprint and then map out the phase behavior of low molecular weight diblock copolymers in solution. Providing a mechanical probe of structure will guide nanostructural studies (SAXS) by providing realizable search spaces; having rheological data will also aid in processing of these materials. Results will be presented for a diblock copolymer system in aqueous solution at different temperatures. We will discuss the feasibility of developing rheology fingerprints for these different materials.

Monday 4:35 Room 201 SM12

Structure and rheology of aqueous solutions of triblock copolymers

Giacomo Marotta, Alfonso Di Sarno, Marina D'Apuzzo, Salvatore Costanzo, and Rossana Pasquino
DICMaPI, University of Naples Federico II, Naples 80125, Italy

Pluronics are triblock copolymers consisting of two polyethylene oxide (PEO) segments spaced by a polypropylene oxide (PPO) one. Due to the different hydrophobicity of the blocks, these molecules undergo self-assembly in aqueous medium, akin to surfactants. The ability to form micelles and the high degree of biocompatibility promoted their use in applications such as drug delivery, microencapsulation and tissue engineering. Depending on the relative length of the different blocks and the total molecular weight, Pluronics are liquids (L), solid flakes (F) or pastes (P) at ambient conditions. Pluronics are commonly labelled with a letter indicating the state at room temperature followed by two numbers, the first referring to the molecular weight, and the second to the fraction of PEO block. In this work, we study the structures detected in aqueous solutions of Pluronics L64 and F68 at different concentrations and temperatures by means of rheology, dissipative particle dynamics (DPD) simulations, and Small Angle X-ray Scattering. The morphological transitions induced by varying temperature or concentration allowed for the determination of a complete rheological phase diagram for both systems. Our results are in agreement with previous literature. In addition, non-linear start-up shear measurements were performed on some specific lamellar solutions, containing Pluronic L64. From the time-dependent viscosity and first normal stress difference, it was possible to confirm a morphological transition from lamellar structures to vescicles induced by flow. We found that the process is shear rate-controlled and that the vesicles size can be tuned by the flow strength. The experimental results were compared with equilibrium and non-equilibrium DPD bulk simulations obtained by using the software LAMMPS.

Pasquino R. et al Soft Matter 2019, 15, 1396-1404; Wanka G. et al Macromolecules 1994, 27, 4145-4159; Wu Y.L. et al J. Phys.: Condens. Matter 2006, 18, 4461-4470.

Monday 5:00 Room 201 SM13

Theory of interchain packing and the interplay of caging and physical bonding on segmental relaxation and shear elasticity in associating copolymer liquids

Ashesh Ghosh[1] and Kenneth S. Schweizer[2]

[1]Department of Chemistry, University of Illinois at Urbana-Champaign, Champaign, IL 61820, United States; [2]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

We employ liquid state statistical mechanical theory to elucidate the role of attractive groups regularly co-polymerized in a chain backbone on the intermolecular packing structure and activated dynamics of unentangled polymer liquids that can form thermo-reversible bonds. Coarse-grained polymer physics models of the macromolecular scale dynamics and mechanics of transient networks typically adopt several key parameters determined by local physics such as the alpha relaxation time and sticker association lifetime and bond strength as phenomenological input. Our aim is to predict how the latter are determined from microscopic interchain forces, sticker clustering and packing correlations. This problem is addressed by combining equilibrium polymer integral equation (PRISM) theory and non-linear Langevin equation based dynamical methods that capture steric caging and physical bond formation to construct the dynamic free energies of sticker and non-sticker groups which control segment scale stochastic trajectories. Knowledge of this local physics allows the calculation of the high frequency elastic shear modulus due to interchain stresses, and the dynamic transient localization lengths, barriers and activated relaxation times for stickers and non-stickers. How these properties vary with polymer volume fraction or temperature, fraction of stickers, strength and spatial range of the attractive interaction, and chain length has been studied. Of particular interest is how non-sticker local hopping events (alpha process) are perturbed by sticky group clustering and bond formation, and the degree to which the sticker unbinding process is coupled with non-sticker segmental relaxation. Results for a limiting strong association case will also be presented based on an idealized partially pinned homopolymer model.

Monday 5:25 Room 201 SM14

Tri- and penta-block polymer gelation in the presence of small molecules

Michelle A. Calabrese[1], Rong Yang[2], Bradley D. Olsen[3], and Daniel S. Kohane[2]

[1]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States; [2]Harvard Medical School, Boston Children's Hospital, Boston, MA, United States; [3]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Treatments for ear diseases typically require high-dose oral administration. Until recently, direct treatment through the tympanic membrane (TM) was not possible. We have developed a thermoresponsive block polymer system that gels upon contact with the TM, which has successfully treated middle ear infections. The formulation consists of a drug and three chemical permeation enhancers (CPEs) that facilitate drug transport across the TM, within a hydrogel comprised of either a triblock (Poloxamer-407, P407) or a pentablock (P407-polybutylphosphoester, PBP) polymer. Gelation is tuned primarily by the polymer architecture and the presence of CPEs (sodium dodecyl sulfate, limonene, and bupivacaine). Differences in gelation in the presence of CPEs markedly affect the efficacy of the delivered drug. In P407, CPE addition weakens the elastic modulus during gelation, reducing structural integrity when applied to tissue. Upon modifying the polymer with hydrophobic endblocks, the resulting PBP formulation shows enhanced gelation with CPE addition. Using a combination of contrast variation small angle neutron scattering and rheology, we demonstrate that significant morphological differences result during heating that explain the rheological behavior. With P407, FCC structures form and the CPEs concentrate within the micelle core. The micelle size and lattice spacing increase with CPE concentration, reducing the elastic modulus. With PBP, disordered, bridged micelles are formed due to its endblock hydrophobicity; this bridging increases the modulus. In the PBP gel, the CPEs are more uniformly distributed, improving drug flux across the TM. This fundamental understanding of the gelation mechanisms and the roles played by the CPEs may enable the rational design of thermoresponsive drug delivery systems that can overcome biological barriers. Additionally, this research provides insight into the effect of small-molecule additives on polymer self-assembly, which can establish new methods for controlling macromolecular topology.

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Monday 1:30 Room 305B IN6

Effects of shear and extensional rheology on liquid transfer between two flat surfaces

Jyun-Ting Wu[1], Lorraine F. Francis[1], Marcio S. Carvalho[2], and Satish Kumar[1]

[1]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55113, United States; [2]PUC-Rio, Rio de Janeiro 22451-900, Brazil

Liquid bridges with moving contact lines play a central role in several industrial applications and natural phenomena. In printing processes, liquid bridges undergo significant extension so that liquid can be transferred from one surface to another. In addition, shear deformation arises as the contact lines move along the surfaces. Although the liquids involved often exhibit non-Newtonian rheology, the influence of rheology on liquid transfer is not well understood. To address this issue, flow visualization experiments complemented with numerical simulations are used to determine the role of shear and extensional rheology in liquid transfer between two vertically separating flat surfaces. Shear thinning is found to enhance liquid transfer to the more-wettable surface compared to the Newtonian case at the same capillary number, Ca, where Ca is defined based

on the zero-shear viscosity and plate separation speed. This enhancement increases with stronger shear-thinning effects and allows nearly complete transfer for values of Ca > O(0.1) with a sufficiently large surface-wettability difference. The underlying mechanism involves reduced viscosities near the contact line on the less-wettable surface, which allows that contact line to slip more. For strain-hardening liquids, the evolution of the contact radius on the less-wettable surface exhibits two distinct stages during bridge stretching. In the first stage, the contact radius decreases and contact-line motion is primarily governed by shear rheology. In the second stage, a thin liquid thread is formed and the contact radius changes only weakly. During the second stage, extensional rheology dominates and strain hardening stabilizes the thin thread. This extends the breakup time, but has little effect on contact-line motion and the amount of liquid transferred.

Monday 1:55 Room 305B IN7

The Kaye effect: New insights from experiment, theory and modelling

Jack King and Steven J. Lind
University of Manchester, Manchester, United Kingdom

The Kaye effect is a phenomenon whereby a jet of fluid poured onto a surface appears to leap on impact, rather than stagnate or coil as expected. Since it was first described in 1963, several authors have attempted to explain the mechanism by which the phenomenon occurs, although to date no complete explanation for the behaviour exists. The effect is often used as an example of interesting and unexplained phenomena in popular science and outreach. Current evidence points towards the existence of an air layer between the jet and the heap which enables slip. We show experimentally that the Kaye effect does not occur in a vacuum, indicating that the air layer is crucial for the effect to occur. By conducting a theoretical analysis based on control volumes we show that viscoelasticity plays a key role in the Kaye effect, and this role is two-fold. Firstly, viscoelasticity appears to increase air entrainment, and secondly, it reduces the pressure required to bend the jet, allowing a thicker air layer to be sustained. We present the numerical simulations of viscoelastic jets showing how viscoelasticity qualitatively affects jet buckling, increasing the chances of slip, and therefore the initiation the Kaye effect. These new findings provide insight into a problem that has puzzled rheologists for over half a century.

Monday 2:20 Room 305B IN8

Interplay between shear banding and wall slip: Generalized lever rule

Michela Geri[1], Brice Saint-Michel[2], Thibaut Divoux[3], Sebastien Manneville[4], and Gareth H. McKinley[1]
[1]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; [2]Imperial College, London, United Kingdom; [3]MIT,CNRS, Cambridge, MA 02139, United States; [4]ENS Lyon, Lyon, France

Shear banding has been shown to affect the flow of many complex fluids under simple viscometric conditions. A common feature of steady-state shear banding is the presence of a non-monotonic branch in the underlying flow curve. In thixotropic yield stress fluids banding usually occurs when the applied shear-rate is smaller than a critical value and is characterized by an arrested band adjacent to a steady sheared region; the stress measured during flow is usually constant and equal to the apparent yield stress. In this work, we show that steady-state shear banding in a thixotropic yield stress fluid with inherently different thixotropic time scales (for the plastic viscosity and yield stress) allows us to partially measure the non-monotonic branch of the flow curve in a rheometer. The test fluid consists of a suspension of microscopic paraffin platelets in mineral oil at different concentrations. Rheometric tests under decreasing shear rates are performed in a bespoke Couette cell with roughened walls while simultaneously measuring the local velocity field via ultrasonic velocimetry. Results for different concentrations show that, for a specific range of shear rates just below the critical value, the observed shear band develops together with a slip layer that guarantees the sample is always sheared at the globally-imposed shear rate. Using a generalized lever rule and accounting for the different thixotropic time-scales, we can explain not only the existence of this peculiar shear-banding scenario, but also derive a logarithmic scaling law for the slip velocity that is a direct consequence of the thixotropic bulk behavior. Finally, we show that the velocity field measured at the smallest shear rates accessible can be understood in terms of non-local effects related to the finite size of the particles relative to the dimension of the shear band.

Monday 2:45 Room 305B IN9

Investigation of non-linear coarsening mechanism in co-continuous polymer blends via in-situ confocal rheology

Rajas Sudhir Shah, Steven Bryant, and Milana Trifkovic
Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta T2N1N4, Canada

Co-continuous polymer blends offer synergistic effect on mechanical properties and have also found applications in conductive plastics, membranes, etc. However, their morphology is thermodynamically unstable due to the excess local free energy stored in their highly curved interfaces which leads to coarsening of these microstructures upon annealing. Hence, it is important to understand the coarsening mechanism of these blends in-order to determine the optimum melt-processing conditions for such blends. The interdependence of viscoelastic properties of polymer blends and their micro-structures have been widely studied and it is reported that they depend on blend composition, interfacial tension and viscoelastic properties of components. In general, there are two regimes of coarsening, first linear growth regime and second non-linear regime with a slower rate which ultimately plateau-out at very long times. The linear growth regime is well understood, extensively studied and modelled in literature and a few attempts have been made to explain and model the late coarsening regime. However, the explanation of the microstructural changes that occur during the transition from linear to the non-linear regime is still lacking. Primarily, this gap is because almost all morphological measurements are done discretely and independently to rheometry. In this study, laser scanning confocal microscopy (LSCM) is coupled by rotational rheometry of polymer blend melts to simultaneously probe their coarsening dynamics in-situ and understand the interplay between viscoelasticity and morphology. Using LSCM, coarsening is characterized by imaging the 4D (3 spatial and 1 temporal dimension) evolution of the microstructure while the oscillatory shear response of the blend provides data on viscoelastic dynamics. We have studied the effect of interfacial tension between the components on the onset of transition and nature of annealing in the late coarsening regime and evaluated the findings with the available mathematical models.

Monday 3:45 Room 305B IN10

Fully developed capillary flow of a shear-banding solution of wormlike micelles requires L/d > 100

Paul F. Salipante, Vishnu Dharmaraj, and Steven Hudson
NIST, Gaithersburg, MD 20899, United States

The viscosity of a shear-banding wormlike micelle solution at high shear rates is investigated using capillary rheology and particle streak velocimetry. Measurements of the flow profile and pressure gradient show an extended entrance region, which exceeds a length to diameter ratio of 100, to reach a fully developed flow. We characterized this entrance region for capillaries with different cross-sections and use the results to select a downstream portion of the capillary where capillary rheology measurements can be made on fully developed flow. We observe a shear-thinning power- law behavior for all channel geometries above the plateau stress until reaching the solvent viscosity limit.

Monday 4:10 Room 305B IN11

High Weissenberg number flow alignment transitions in wormlike micelles

Javen Weston[1], Katie M. Weigandt[2], and Steven Hudson[3]
[1]Chemical Engineering, University of Tulsa, Tulsa, OK 74104, United States; [2]NIST Center for Neutron Research, Gaithersburg, MD 20877, United States; [3]NIST, Gaithersburg, MD 20899, United States

Simultaneous rheological measurements and Small Angle Neutron Scattering experiments were used to track segmental alignment in semi-dilute wormlike micellar solutions. As would be expected, noticeable segmental alignment begins to occur at Wi ˜ 1 for all tested solutions However, the alignment behavior deviates greatly from sample to sample at higher Wi. Additionally, all of the samples exhibit a peak in segmental alignment at some critical shear rate, above which a sometimes sharp decrease in alignment is observed. The transition appears to be the result of an elastic instability resulting from the curved streamlines present in the Taylor-Couette geometry, but is also affected by the microstructural properties of the micellar solutions. The phenomenon was investigated using a variety of sample geometries and the alignment transition was seen to follow the Pakdel-Mckinley criterion predicting flow instability for viscoelastic fluids. Here, we present work attempting to tie the microstructural properties of the micellar solutions directly to the observed high-Wi transitions in segmental alignment and apparent viscosity. and how various factors affect that transition in order to provide insight into the structure-property relationship in the high shear rate regime for this commercially-relevant system. We also present results showing similar peaks in segmental alignment observed in a microfluidic slit rheometer where the samples are undergoing Poiseuille flow. In this flow cell a peak in alignment is observed in the near-wall region of the slit where the maximum shear rate is observed. Understanding the viscoelastic properties and flow-induced structure of these micelles is beneficial for their use in personal care, oil recovery, and other applications. The system studied here is a useful model, since the micelle alignment is relatively easy to interpret and the formulation is similar to commercial consumer cleansers.

Monday 4:35 Room 305B IN12

An experimental explanation of the G’’ overshoot in yield stress soft materials

Gavin J. Donley and Simon A. Rogers
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

In an effort to gain a deeper understanding of the rheology behind the yielding transition, we perform experimental decompositions of the rheological response of two model yield stress fluids, a Carbopol microgel and a concentrated colloidal silica suspension, to transient shear strains. These decompositions are achieved at different amplitudes of applied shear by means of oscillatory stress jump tests (in the case of stress) and oscillatory shear/recovery tests (in the case of strain). The flow cessation and recovery steps are performed at multiple points over the course of a period of oscillation, in order to map out the decomposition in a thorough manner. The stress jump tests separate stress acquired through elastic and inelastic processes and show that nearly all the stress in the system is elastic under oscillatory shear. The shear/recovery tests, on the other hand, allow for recoverable and unrecoverable strains to be resolved, and show that when above the yield point, both of these components contribute significantly to the overall material response . We utilize the interplay between these two strain components to develop a more comprehensive rheological picture of the yielding behavior in soft materials. We demonstrate that the overshoot in G" seen in many amplitude sweeps is the result of the transition between retardation dominated dissipation at small amplitudes and flow dominated dissipation at large amplitudes. These results suggest that any numerical decompositions for yield stress materials need to consider the existence of both unrecoverable viscoplastic flow above the yield point and a recoverable strain which persists once yielding has taken place.

Monday 5:00 Room 305B IN13

Dean flow of a Bingham plastic

Ian Frigaard[1] and Miguel Moyers-Gonzalez[2]
[1]University of British Columbia, Vancouver, British Columbia V6T1Z4, Canada; [2]University of Canterbury Christchurch, Christchurch, New Zealand

Dean flow of a shear-thinning fluid shares many of the same stability characteristics of Newtonian fluids, but with the secondary flow vortices contributing to drag reduction. The flow is also of interest as an archetypical flow that has controlled streamline curvature and hence of importance for viscoelastic instabilities. In considering a yield stress fluid in similar geometries the picture is less clear. Unfortunately earlier analytical work [1,2] has inconsistencies, so the flow has been barely studied. Firstly, we expect there to be a critical pressure gradient required for flow onset. Secondly, there is the question of whether or not the secondary flow even exists and in what parameter ranges? Thirdly, does the secondary flow result in breaking of the plug that exists in the leading-order azimuthal velocity? Lastly, there is the question of flow stability. We present new results from our analysis and computation of these flows.

[1] D. Clegg & G. Power, "Flow of a Bingham fluid in a slightly curved tube." Appl. Sci. Res. A (1963) 12:199-212
[2] M. Norouzi, B. Vamerzani, M. Davoodi, N. Biglari & M. Shahmardan, "An exact analytical solution for creeping Dean flow of Bingham plastics through curved rectangular ducts." Rheol Acta (2015) 54:391-402

Monday 5:25 Room 305B IN14

Start-up flows of elastoviscoplastic fluids in porous media

Sarah Hormozi[1], Francesco De Vita[2], Quinn Mitchell[1], Marco Rosti[2], and Luca Brandt[2]
[1]Ohio University, Athens, OH 45701, United States; [2]Mechanics, KTH, Stockhom, Sweden

We study flows of elastoviscoplastic fluids through porous media by numerical simulations. The porous media is made of cylinders arranged in a periodic fashion. We solve the Navier-Stokes equations combined with the elastoviscoplastic model proposed by Saramito for the stress tensor evolution. This study has two main contributions. First, we show that a nonlinear relationship exists between the pressure drop and the flow rate in the porous medium. This nonlinear relationship depends on plastic, elastic, inertial effects and the configuration of the porous field. Second, we study the details of flow as the limiting pressure gradient is approached, particularly showing how the start-up flows of yield stress fluids are affected with the elasticity of the fluid.

Symposium SF
Surfactants, Foams, and Emulsions

Organizers: Reza Foudazi and Nick Alvarez

Monday 1:30 Room 306A SF6

Rheology and structure of microgel-surfactant composites

Sarah Goujard[1], Jean-Marc Suau[2], Clémentine Champagne[2], and Michel Cloitre[3]
[1]C3M, ESPCI Paris, Paris, France; [2]Coatex SAS, Genay, France; [3]Matière Molle et Chimie, ESPCI Paris, PSL Research University, Paris 75005, France

Blends of suspensions of soft colloids and nonabsorbing small additives have received a lot of attention, both experimentally and theoretically (Curr. Opin. Colloid Interface Sci. 19, 561, 2014). In these systems, entropic forces, which are inherent to the physics of colloidal suspensions, are responsible for osmotic compression and attractive interactions, leading to various phenomena like aggregation, glass melting, reentrant gelation, and double glass formation. This allows modulating the jamming and gel transitions and offers a mean to design soft composites with tailored rheological properties.

However many applications use additives which can be absorbed by the soft colloid matrix. Very little is known about the phase behavior and rheology of these materials. Here we address the case of soft composites prepared from stimuli-responsive microgels and surfactants of various types. We use linear and non linear rheology combined with SAXS measurements and cryoTEM observations to investigate the state diagram as a function of the composition of the mixtures. The adsorption of the surfactants onto the polymeric network of the microgels provokes an important swelling without the need of additional triggers. At low polymer concentration, the solutions are viscous suspensions at any surfactant content but, at large enough concentration, the particles jam and form a glass with remarkable solid-like properties. When the surfactant concentration is high enough, the glass melts. We show that this reentrant liquid transition is associated with distortions of the local structure and phase separation caused by depletion forces. Our results open new routes to design yield stress fluids for a variety of applications by tuning the microgel architecture and the nature of the surfactant.

Monday 1:55 Room 306A SF7

Recovery rheology via rheo-SANS: Application to step strains under out-of-equilibrium conditions

Johnny Ching-Wei Lee[1], Lionel Porcar[2], and Simon A. Rogers[1]
[1]Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Institut Laue-Langevin, Grenoble, France

Stress relaxation from a step strain test provides important information about constituent dynamics, but if a material has experienced a complex shear history, the underlying physics is not straightforward to access. We use recovery rheology and rheo-small-angle neutron scattering (rheo-SANS) to probe the nonlinear dynamics of an entangled wormlike micelle solution by applying step strains after complex shear histories enforced by large-amplitude oscillatory shear (LAOS) flow. We show that a universal relaxation modulus can be obtained from step strain tests with complex shear histories, as long as the modulus is defined in term of the recoverable strain. The shear and normal stresses, as well as the alignment of micellar Kuhn segments, are shown to be positively correlated with the recoverable strain. We identify re-entanglement of polymeric chains after cessation of LAOS and show that this process occurs over the same timescales as linear-regime stress relaxation. This work therefore lays the foundation of how to accurately probe out-of-equilibrium rheology in a consistent manner.

Monday 2:20 Room 306A SF8

Mesoscale simulation approach for dynamics and assembly of deformable objects

Toluwanimi Bello, Sangwoo Lee, and Patrick T. Underhill
Rensselaer Polytechnic Institute, Troy, NY 12180, United States

In dilute suspensions, surfactant micelles and emulsion droplets often take spherical shapes. But at high enough concentrations, contact among the micelles or droplets leads to nonspherical shapes. In this limit, the dynamics and assembly of the suspension depend more on the interfaces between objects than the bulk objects themselves. This has similarities with foams and biological tissues in which the interfaces between deformable objects (gas bubbles or cells) play a critical role. We have adapted a mesoscale approach (called vertex models) in order to apply it to the dynamics and assembly of small deformable objects. In this way, we are developing a unifying framework to understand micelles, emulsions, and even small molecule metals and glasses. In this talk, we will describe the application of vertex models to small deformable objects. In particular, we have quantified the phase diagram of assembly in thin films of particles (2D simulations) and bulk assembly of particles (3D simulations). A balance of thermal fluctuations and deformability leads to an order-disorder transition in both cases, which also corresponds to a transition in mechanical properties. Of particular importance to the mechanical properties are the dynamics of defects. A unique feature of 3D materials is that multiple ordered states are possible. We have quantified the meta-stability of these ordered states and found a "diffusionless transformation" between ordered states. These transformations are well-known in metallic systems, but have only recently been found in experiments with soft materials.

Monday 2:45 Room 306A SF9

The role of deformability in determining the structural and mechanical properties of bubbles and emulsions

Arman Boromand[1], Alexandra Signoriello[1], Eric R. Weeks[2], Fangfu Ye[3], Mark D. Shattuck[4], and Corey S. O'Hern[1]
[1]Mechanical Engineering and Material Sciences, Yale University, New Haven, CT 06511, United States; [2]Physics, Emory University, Atlanta, GA, United States; [3]Institute of Physics, University of Chinese Academy of Sciences, Beijing, China; [4]Physics and Levich Institute, The City College of New York,, New York, NY, United States

We present computational studies of jammed particle packings in two dimensions undergoing isotropic compression using the well-characterized soft particle (SP) model and deformable particle (DP) model that we developed for bubbles and emulsions. In the SP model, circular particles are allowed to overlap, generating purely repulsive forces. In the DP model, particles minimize their perimeter, while deforming at fixed area to avoid overlap during compression. We compare the structural and mechanical properties of jammed packings generated using the SP and DP models as a function of the packing fraction ρ, instead of the reduced number density ϕ. We show that near jamming onset the excess contact number $\Delta z=z-z_J$ and shear modulus ${\cal G}$ scale as $\Delta \rho^{0.5}$ in the large system limit for both models, where $\Delta \rho = \rho-\rho_J$ and $z_J \approx 4$ and $\rho_J \approx 0.842$ are the values at jamming onset. Δz and ${\cal G}$ for the SP and DP models begin to differ for $\rho \gtrsim 0.88$. In this regime, $\Delta z \sim {\cal G}$ can be described by a sum of two power-laws in $\Delta \rho$, i.e. $\Delta z \sim {\cal G} \sim C_0\Delta \rho^{0.5} +C_1\Delta \rho^{1.0}$ to lowest order. We show that the ratio C_1/C_0 is much larger for the DP model compared to hat for the SP model. We also characterize the void space in jammed packings as a function of ρ. We find that the DP model can describe the formation of Plateau borders as $\rho \rightarrow 1$. We further show that the results for z and the shape factor ${\cal A}$ versus ρ for the DP model agree with recent experimental studies of foams and emulsions

Monday 3:45 Room 306A SF10

Formation, growth and coalescence of nanoscopic mesas in stratifying foam films

Chenxian Xu, Subinuer Yilixiati, Chrystian Ochoa, Yiran Zhang, and Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States

Ultrathin micellar foam films exhibit stratification due to confinement-induced structuring and layering of micelles. Stratification proceeds by the formation and growth of thinner domains at the expense of surrounding thicker film, and flows and instabilities drive the formation of nanoscopic terraces, ridges and mesas within a film. The detailed mechanisms underlying stratification are still under debate, and are resolved in this contribution by addressing long-standing experimental and theoretical challenges. Thickness variations in stratifying films are visualized and

analyzed using interferometry, digital imaging and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). Using IDIOM protocols we developed recently, we characterize the shape and the growth dynamics of mesas that flank the expanding domains in micellar thin films, and we track their evolution, as well as coalescence dynamics.

Monday 4:10 Room 306A SF11

Bubble-size predictions for polyurethane foam using a population balance equation

Rekha R. Rao[1], Weston Ortiz[2], and Christine Roberts[3]
[1]Fluid and Reactive Processes, Sandia National Laboratories, Albuquerque, NM 87185-0836, United States; [2]Chemical and Biological Engineering, University of New Mexico, Albuquerque, NM 87131-0001, United States; [3]Diagnostic Science & Engineering, Sandia National Laboratories, Albuquerque, NM 87185-0346, United States

Polyurethane foams are widely used in manufacturing in part due to their ease of use and beneficial material properties, such as low thermal conductivity, stress and shock cushioning, and tunable density. Our goal is to develop computational models to predict these foam properties as a function of precursor formulations and processing conditions to aid in the manufacturing of polyurethane products. In this presentation, we focus on PMDI polyurethane foams, which are chemically blown foams used for electronic encapsulation and lightweight structural parts. A recently published kinetic model [1] is extended with a population balance equation using the Quadrature Method of Moments (QMOM) [2] in order to predict bubble size evolution as well as density variations during mold filling. We use a stabilized finite element method to solve the conservation equations; equations of motion, energy balance equation, species conservation with reaction, and transport of moments for QMOM. We combine these equations with the level set method in order to track the free surface between the foam and the surrounding gas. This model is used to predict final foam properties including density, thermal conductivity, and bubble size evolution in a three-dimensional foam bar geometry. Results for final densities are compared to experimental X-ray CT data. Bubble size evolution and final distributions are compared to experimental optical and SEM data.

[1] Rao, Rekha, et al., Computers & Fluids 175 (2018): 20-35. [2] Karimi, Mohsen, et al., Macromolecular Symposia. Vol. 360. No. 1. 2016.

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

Monday 4:35 Room 306A SF12

Rheology of carbon nanotube foams

Sadjad Arzash, Steven M. Williams, Matteo Pasquali, and Fred C. MacKintosh
Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77030, United States

Carbon nanotubes (CNTs) are materials with excellent mechanical and electronic properties that can be used for a variety of applications. Assembling CNTs into different macroscopic structures such as thin films are useful for practical applications. One interesting CNT-based structure is a foam-like bulk material composed of self-assembled nanotubes, which has a very low density, high flexibility and porosity. The behavior of these materials under compressive loads has been studied in recent years. We study the shear rheology of these nanotube-based foams, both dry and wet with different solutions and provide a theoretical model to explain the stress-strain curves. The effects of microscopic anisotropy on the macroscopic properties is discussed as well.

Monday 5:00 Room 306A SF13

The formation and stability of foams for particulate delivery in biomedical applications

Nicolas J. Alvarez and Todd Lewis
Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States

In certain biomedical applications, the delivery of particles to specific locations in the body with minimal fluid volume is an important engineering problem. In such applications, we are investigating foams as delivery vehicles which both homogenize the particle dispersion as well as decrease the fluid volume required for delivery. We are interested in the formation and stability of foams that use surfactants in saline solution as the foaming agent. We restrict our investigation to surfactants that are biocompatible. In some cases, we examine the use of surfactants that undergo phase separation at elevated temperatures to form highly stable nanostructures as a way to stabilize the gel. We present systematic rheological studies of slurries and foams as a function of formulation and foaming methods. We determine foam persistence as a function of time under relevant biological conditions. Finally, we discuss in-vivo delivery efficacy in terms of slurry and foam rheological properties.

Monday 5:25 Room 306A SF14

Elastic and mechanically robust polymeric foams to stop bleeding

Hema Choudhary, Michael Rudy, and Srinivasa R. Raghavan
Chemical and Biomolecular Engineering, University of Maryland, College Park, College Park, MD 20742, United States

Bleeding from injuries in the truncal region is a leading cause of fatalities in the military and in young adults. Direct pressure cannot be applied to stop bleeding in these cases. Our lab has been particularly interested in developing foams to treat such 'non-compressible' hemorrhage. Foams can be effective because the expansion of the foam in the injured cavity can counteract blood loss without the need for compression. As an active 'hemostatic agent' in these foams, we use hydrophobically modified (hm) derivatives of biopolymers like chitosan and alginate (termed hmC and

hmA, respectively). These polymers have the ability to coagulate blood cells and thus stop bleeding. In this talk, we will describe aqueous foams that can be delivered out of a double-barreled syringe by combining precursors in the two barrels that produce bubbles of gas in situ. In addition, one barrel contains hmC and the other hmA, and the amphiphilic nature of these polymers enables them to stabilize gas bubbles without the need for additional surfactants. Most interestingly, these polymer-based foams have enhanced rheological properties compared to typical foams that can be prepared in a lab. This rheological enhancement is quantified in our work, and is due to electrostatic interactions between the cationic hmC and the anionic hmA chains. Preliminary studies in animal wound models also confirm that hmC-hmA foams form effective barriers to blood loss due to their greater mechanical integrity.

Symposium BB
Biomaterials and Biofluid Dynamics

Organizers: Xiang F. Cheng and Amanda Marciel

Monday 1:30 Room 306B BB6

Modeling of the human blood rheology and simulation of its flow in elastic micro-vessels

Pantelis Moschopoulos, Ellie Chrysou, Kostas Giannokostas, Christina Kaltsoukala, Yannis Dimakopoulos, and John Tsamopoulos
Department of Chemical Engineering, University of Patras, Patras, Achaia, Greece

Human blood is a suspension in plasma of formed elements, mainly erythrocytes, that exhibits plasticity, elasticity, shear thinning, and thixotropic behaviors [1]. Thus, it can be classified as a thixo-elasto-visco-plastic (TEVP) material. Complications in its flow are apparently more pronounced when the size of the vessel, wherein blood flows, is comparable to the radius of a Red Blood Cell. In the present work, we test previous hemorheological models [2,3], and employ our recently proposed macroscopic model for TEVP materials [4], which fits LAOS and non-linear hemorheological data perfectly. After the successful rheological characterization of the human blood, we perform flow simulations of a two-phase system in elastic microvessels, where migration of the RBCs toward the core region and formation of an annular layer of plasma occur. Human blood plasma is assumed to behave as a viscoelastic fluid [5], the core region follows the TEVP, and the vessel walls have a multilayer anisotropic hyperelastic structure. A systematic investigation is performed on the effect of blood and plasma viscoelasticity on the hemodynamics in microcirculation as well as the structural dynamics of small and microvessels.

[1] J. S. Horner, M. J. Armstrong, N. J. Wagner, and A. N. Beris, J. Rheol. 62, 577, (2018). [2] M. Armstrong, J. Horner, M. Clark, M. Deegan, T. Hill, C. Keith, L. Mooradian, Rheol. Acta 57(11), 705-728 (2018). [3] Owens R. G., J. Non-Newt. Fluid Mech. 140, 57 (2006). [4] S. Varchanis, G. Makrigiorgos, P. Moschopoulos, Y. Dimakopoulos, J. Tsamopoulos, J. Rheol., 63(4) (2019). [5] S. Varchanis, Y. Dimakopoulos, C. Wagner, J. Tsamopoulos, Soft Matter 14 (21), 4238-4251 (2018).

Monday 1:55 Room 306B BB7

Measurements and modeling of interspecies hemorheology and hemodynamics

Jeffrey S. Horner, Yu-Jiun Lin, Antony N. Beris, and Norman J. Wagner
Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Across species, blood is universally a complex suspension primarily composed of red blood cells (RBCs) suspended in an aqueous plasma with several dissolved proteins. Compared to order of magnitude changes in body mass and unique anatomies, the composition of blood and the constituent sizes remain relatively constant across species. Interestingly, key aspects of the shear rheology of blood vary substantially across species. For example, blood from species such as chickens, cows, and sheep, exhibits minor shear thinning and viscoelasticity at higher shear rates arising from RBC deformation. However, for other species such as humans, pigs, and horses, the RBCs form rouleaux, which gives rise to pronounced pseudoplasticity, viscoelasticity, and thixotropy at low shear rates. Under Poiseuille flow, blood from these species also exhibits inhomogeneities such as the Fahraeus and Fahraeus-Lindqvist effects, corresponding to a decrease in the local hematocrit and viscosity, respectively. We present new measurements of steady and transient rheology for blood from various species using recently developed protocols that ensure accurate in vitro measurements of blood. Complementary to this, we present optical measurements of blood flow through a microfluidic device designed to study inhomogeneities and visualize the state of RBC aggregation. Using the rheological profile, we fit a previously established model for transient human blood rheology and determine the dependence of the model parameters on species. The model is subsequently used in combination with multiphase CFD simulations to reproduce the full inhomogeneous flow profile in the microfluidic device. Through this analysis, we elucidate and quantify the rheological changes in blood across species to understand the physical and evolutionary origins of these variations and identify allometric scalings. Additionally, we offer a computationally inexpensive way to simulate blood flow for a variety of common species, which can be valuable for clinical drug scaleup.

Monday 2:20 Room 306B BB8

Multiscale characterization of nanoparticle diffusion in cellular blood flow under shear

Zixiang Liu[1], Jonathan R. Clausen[2], Rekha R. Rao[3], David N. Ku[1], and Cyrus K. Aidun[1]
[1]The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States; [2]Thermal and Fluid Processes, Sandia National Laboratories, Alburqueque, NM 87185-0836, United States; [3]Fluid and Reactive Processes, Sandia National Laboratories, Albuquerque, NM 87185-0836, United States

Blood is a complex fluid of polydisperse particulate suspension that involve both nanoscale biomolecules and microscale cells. Characterizing the transport and rheology of such a complex fluid system requires spatial resolution at various scales. In this work, we apply a lattice-Boltzmann/Langevin-dynamics/spectrin-link (LB-LD-SL) multiscale method (Liu et al. Int. J. Numer. Methods Fluids 2019) to calculate the three-dimensional shear-induced diffusivity tensor of nanoscale particles (NP) in a sheared blood flow over a wide range of shear rate and hematocrit (Liu et al. J. Fluid Mech. 2019). The diagonal diffusivity terms show nonlinear dependence on shear rate, where the cross-stream terms exhibit sublinear scales $\sim O(\gamma^{0.8})$ and the longitudinal diffusivity shows superlinear scales $\sim O(\gamma^{k})$ $(1 \leq k \leq 1.8)$. The hematocrit dependence is found to be mostly linear $\sim O(\varphi)$ except at high hematocrits, where the longitudinal term scales quadratically $\sim O(\varphi^{2})$ while the vorticity term varies sublinearly $\sim O(\varphi^{0.6})$. The nonlinear scales are found to be associated with the hemorheology-dependent alteration of the microstructure and red blood cell morphology. Based on the scaling observations, a constitutive law of the diffusivity tensor is proposed to bridge hemorheology and NP diffusive properties. The characterized NP diffusivity tensor provides an accurate constitutive relation for large-scale continuum modeling of NP biotransport applications. Extension of this computational method to applications in thrombosis will also be discussed.

Monday 2:45 Room 306B BB9

Microstructure and rheology of blood - before and after cardiovascular surgery

Yeng-Long Chen[1], Yi-Fan Wu[1], Po-Shun Hsu[2], and Chien-Sung Tsai[2]
[1]Institute of Physics, Academia Sinica, Taipei, Taipei City 11529, Taiwan; [2]Tri-Services General Hospital, Taipei, Taipei City, Taiwan

We characterized human blood physical properties before and after cardiovascular surgery by microscopy and concentric cylinder rheometry. We collected samples from healthy subjects and patients before and after the surgery. For up to one week after the surgery, red blood cell (RBC) aggregates become larger and more rounded, indicating increased attraction between RBC, which also correlates with significantly elevated fibrinogen and C-reaction protein concentrations. In contrast, blood viscosity and the shear thinning behavior of different samples does not vary significantly. However, increased blood yield stress is observed after the surgery. We proposed a model to account for this behavior.

This work was approved by the IRB of Academia Sinica and Tri-Services General Hospital.

Monday 3:45 Room 306B BB10

Using freely suspended biofilms to study the interactions among engineered proteins displayed on the bacteria cell surface

Priya K. Chittur, Hanwei Liu, David A. Tirrell, and Julia A. Kornfield
Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Biofilms, communities of bacterial cells associated with their extracellular polymeric matrix, are unique in that their "bulk" characteristics as a cohesive material arise from a transient, nonuniform composition and structure that the microorganisms create and modify over time. We are interested in correlating mechanical properties of biofilms across length scales from the single cell to the bulk material. The Tirrell Group at Caltech engineers E. coli K-12 DH10B, inherently poor biofilm formers, to display membrane-tethered peptides and proteins on their surface to modify intercellular association: noncovalent (coiled coil proteins) or complementary covalent bonding partners (SpyTag-SpyCatcher), can be installed with precisely defined linkers (e.g., elastin-like polypeptides). These precisely tailored building blocks then grow and assemble into bulk materials. The Ravichandran Group at Caltech uses nanoindentation to probe the properties of a single cell or the surface of a biofilm. We have fabricated microfluidic apparatus to study the mechanical properties at the continuum (0.05 to 1 millimeter) scale. We prepare freely suspended biofilms and impose hydrostatic pressure differences (in the pascal to kilopascal range) across the biofilm. The deformation that results as a function of the imposed pressure difference is visualized using optical coherence tomography (OCT). Preliminary results confirm that non-engineered DH10B biofilms cannot remain cohesive at a millimeter length scale, while biofilms of DH10B that only display an elastin tethered are cohesive. Effects of the length of the elastin-like tether and the choice of associative peptide on the mechanical properties of the biofilm will be presented.

Monday 4:10 Room 306B BB11

Effects of non-ionic surfactant on the formation of P. aeruginosa pellicles

Gordon Christopher and Lingjuan Qi
Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States

Pellicles, bacterial biofilms at liquid interfaces, are found in crude oil processing, aquatic ecosystems, and wastewater treatment. Depending on the application, enhancing or preventing their growth can be important. Previously, using interfacial rheology, we have shown that biological attachment mechanism are supplemented by surface tension mediated attachment for pellicle formation. In this work, we continue to explore this phenomenon by using non-ionic CxEy surfactants to modify an air/water interface in a controlled manner.

Surfactants delay pellicle attachment and growth when added to growth media at concentrations close to the CMC. Surprisingly, attachment delays continue to increase as surfactant concentration exceeds the CMC. The delay in growth is affected not only by concentration but also how and at what time surfactant is added to the system, indicating that surfactant can be used to destabilize already forming pellicles. Additionally, pellicle moduli decrease as polyoxyethylene chain size increases; a similar effect was not observed for alkyl chain size. To better understand the mechanisms causing these changes, contact angle of water on solid surface biofilms and surface tension of surfactant with growth media have been measured. Preliminary results confirm the importance of the surface tension as a non-biological means of attachment for pellicles and identify ways to modify pellicle formation in a controlled manner.

Monday 4:35 Room 306B BB12

Role of collagen on the viscoelasticity of P. aeruginosa biofilms

Minhazur Rahman[1], Vernita Gordon[2], and Gordon Christopher[1]

[1]Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]Physics, UT Austin, Austin, TX 78712-1199, United States

Bacterial biofilms are well known for providing enhanced antibiotic resistance and virulence at wound sites, leading to increased infections and medical complications. The enhanced resistance and virulence are attributed to the self-secreted extracellular polymeric substance (EPS), a scaffold of proteins and polysaccharides. EPS viscoelasticity aids in adhesion to host extracellular matrix components (ECM). At wound/surgery sites, collagen is one of the primary components of host ECM which may interact with biofilm EPS.

To characterize collagen's effects on biofilm viscoelasticity, P. aeruginosa biofilms were in-vitro grown in a wound like media, which included collagen at physiological concentrations, in custom microfluidic channels. To measure these biofilms' viscoelasticity, passive microrheology was utilized by incorporating tracer particles into the media, which were then enveloped by growing biofilms.

By examining distribution of slopes from particle mean-squared-displacements vs. time, variation of biofilm viscoelasticity was investigated at 12, 24, 36, and 48 hours. As biofilms age, analysis of slope distribution indicates increased stiffness, seen by decreasing value of the distribution mode, and increased uniformity, seen in reduced distribution half width. Addition of collagen yields stiffer films with greater overall uniformity, indicating that increased collagen at wound sites results in stronger biofilms more likely to cause infections. Changes to EPS compositions, studied through use of genetic mutants, indicate that certain combinations of polysaccharides are of importance to the development of the biofilm viscoelasticity in general. Furthermore, certain polysaccharides were seen to have more interaction with collagen in the wound like media.

Monday 5:00 Room 306B BB13

Non-equilibrium dynamics of vesicles in flow using a Stokes trap

Dinesh Kumar, Channing Richter, and Charles M Schroeder

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

Vesicles are membrane-bound soft containers that play an integral role in key biological processes. In this work, we study the non-equilibrium dynamics of giant unilamellar vesicles in precisely-defined steady and time-dependent extensional flow. In particular, we use a Stokes trap to control the position and time-dependent strain and strain rate schedules applied to single vesicles in flow. In this way, we directly observe non-equilibrium vesicle shapes as a function of reduced volume, viscosity contrast, and Capillary number using fluorescence microscopy. Vesicles are found to deform through a wide-range of interesting shapes in flow, including asymmetric and symmetric dumbbells, in addition to pearling, wrinkling, and buckling instabilities depending on membrane properties. Using this approach, we precisely determine the flow phase diagram for vesicles in Capillary number-reduced volume space. We further study the non-equilibrium stretching dynamics of vesicles, including transient and steady-state stretching dynamics in extensional flow. Our results show that vesicle stretching dynamics are a strong function of reduced volume and viscosity ratio, such that the steady-state deformation of vesicles exhibits power-law behavior as a function of reduced Capillary number. We identify two distinct relaxation processes for vesicles stretched to high deformation, revealing two characteristic time scales: a short time scale corresponding to bending relaxation and a long-time scale dictated by the relaxation of membrane tension. We further discuss a method to estimate the bending modulus and intermonolayer friction of lipid membranes from the steady-state and relaxation data. Overall, our results provide new insights into the flow-driven shape-instabilities for vesicles using new experimental methods based on the Stokes trap.

Monday 5:25 Room 306B BB14

Vesicle shape stability in general linear flows

Charlie Lin and Vivek Narsimhan

Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47097, United States

Vesicles have become a paradigmatic system for studying cell-like dynamics. While the dynamics of vesicles in simple shear or extensional flows have been extensively studied, vesicles in more complex flow types, such as those seen in microfluidic devices or industrial processing conditions, warrant greater investigation. In this study, we used the boundary element method to investigate the stability of moderately deflated vesicles in a general linear flow (i.e., linear combinations of extensional and rotational flows). We modelled the vesicles as a droplet with an incompressible interface with a bending resistance. We simulated a range of flow types from purely shear to extensional at viscosity ratios ranging from 0.01 to 5.0 and reduced volumes from 0.60 to 0.70. A surprising result is that the vesicle's viscosity ratio appears to play a minimal role in describing the droplet shape and stability for many mixed flows, even in cases when significant flows are present in the vesicle interior. By scaling the capillary number by an effective extensional rate, we find the critical capillary number in mixed flows collapse onto similar values. These results are in contrast to what is observed for liquid-filled systems (droplets, capsules), and we discuss the physics behind these observations in this talk. Our simulations suggest that as long as the flow type is not close to pure shear flow, one can accurately quantify the shape and stability of vesicles in a wide range of flow types by using the results from pure extension.

Symposium GG
Out of Equilibrium Systems: Gels and Glasses

Organizers: Suzanne Fielding, Ran Tao and Rosanna Zia

Monday 1:30 Room 306C GG6

The hydrodynamics of the colloidal glass transition

Monica E. A. Zakhari, J. Galen Wang, Gaddiel Ouaknin, and Roseanna N. Zia
Department of Chemical Engineering, Stanford University, Stanford, CA, United States

An understanding of the colloidal glass transition requires at least, a description of the glassy state and a mechanistic explanation of the vitrification process, both of which have formed a challenge for the past few decades. The challenge originates primarily from the temporal convolution of the structural, dynamical, and mechanical effects during aging; their competition simultaneously advances aging and deepens arrest. Our recent work shows that dynamics do not vanish at the putative glass transition. In this work we study the mechanics of this competition by considering both the equilibrium and non-equilibrium solidification processes, i.e. crystallization and vitrification, respectively, utilizing large-scale Stokesian dynamics simulation. Jumps from liquid into the solid region are executed via controlled volume-fraction, where the speed of the quench permits toggling between equilibrium and arrested states. The relative influence of many-particle hydrodynamics and polydispersity on aging and crystallization dynamics is studied, and we elucidate the influence of the quenching process on long-time fate of the material.

Monday 1:55 Room 306C GG7

Microscopic theory of spatially heterogeneous dynamics, elasticity and vitrification in confined colloidal suspensions and polymer melts

Anh Phan[1] and Kenneth S. Schweizer[2]
[1]Department of Physics, University of Illinois, Urbana, IL, United States; [2]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Spatially heterogeneous structural relaxation, diffusion and mechanical properties in glass-forming liquids induced by a surface is a rich but poorly understood problem. Depending on the physical nature of the confining interface, dynamics can be enormously sped up, slowed down, or hardly affected. For example, a vapor surface can effectively melt a nonequilibrium glass, and a rough solid substrate can effectively vitrify a liquid, often over surprisingly long length scales near the interface. We address this problem by building on our microscopic force-level theory of the alpha relaxation in bulk colloidal, molecular and polymeric fluids in which the fundamental activated rearrangement event has a mixed local-nonlocal character involving cage scale hopping strongly coupled to a collective elastic distortion of the surrounding medium. A new description of how dynamical caging constraints at surfaces are modified and spatially transferred into a film has been formulated and integrated with the bulk theory concepts. This allows quantitative calculation of spatial gradients of the shear modulus, relaxation times and other properties for thick and thin films, and their film-averaged consequences. New predictions include an exponential spatial variation of the amplitude of dynamic caging constraints, the near factorization of the temperature and spatial location dependences of the activation barrier, a double exponential form of the structural relaxation time gradient, position-dependent power law decoupling of the relaxation time from its bulk analog, a more (less) mobile layer near a vapor (solid) surface that thickens with cooling or densification, and spatial variation of the glass transition temperature. Representative numerical results will be presented as a function of the nature of the surface (vapor, rough and smooth hard wall), chemical structure, and thermodynamic state, and key results compared with simulations and experiments.

Monday 2:20 Room 306C GG8

Microscopic dynamics of stress relaxation in a nanocolloidal soft glass

Chen Yihao[1], Simon A. Rogers[2], Suresh Narayanan[3], James L. Harden[4], and Robert L. Leheny[1]
[1]Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218, United States; [2]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [3]Argonne National Laboratory, Lemont, IL 60439, United States; [4]Department of Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Following the cessation of flow-inducing shear, soft disordered solids often display a protracted recovery during which the stress slowly decreases to a finite value known as the residual stress. While numerous rheology studies have characterized the macroscopic nature of this stress relaxation, little is known about the underlying microscopic structural dynamics. We report x-ray photon correlation spectroscopy (XPCS) experiments with in situ rheometry performed on a soft glass composed of a dense suspension of charged silica nanoparticles subject to step strains that induce yielding. The XPCS measurements characterize the particle-scale and mesoscale motions within the glass that underlie the subsequent slow decay of the stress. The XPCS correlation functions indicate these dynamics are anisotropic, with slow, convective-like particle motion along the direction of the preceding shear that persists for surprisingly large times after flow cessation and that is accompanied by highly intermittent motion in the perpendicular (vorticity) direction. The close correspondence between these dynamics and the stress relaxation is demonstrated by power-law scaling between the characteristic velocity of the convective motion and the rate of stress decay.

Monday 2:45 Room 306C GG9

Gelation and relaxations of nanofibrils suspended in viscoelastic media

Ryan Poling-Skutvik and Chinedum O. Osuji
Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States

Suspensions of spherical colloids exhibit substantial changes to their dynamics and structure as a function of volume fraction, interactions, or the viscoelasticity of the surrounding medium. The physics becomes even complex when describing suspensions of anisotropic fibrils. The long aspect ratios of fibrils lead to anisotropic structural orientations while their flexibility introduces additional relaxation modes that are not present in spherical particulate systems. In this work, we use cellulose nanofibrils (CNF) as a model system to understand how fibrillar suspensions gel and relax in a variety of different media. Cellulose nanofibrils are anisotropic colloidal objects composed of largely crystalline cellulose. Cellulose is an abundant biopolymer that is biodegradable and sustainably derived. CNF can be functionalized and possess a high tensile modulus. We disperse TEMPO-oxidized CNF into simple Newtonian fluids and viscoelastic fluid. At low volume fractions, the CNF do not strongly interact with each other but at higher volume fractions they form a network that is sufficiently robust to support measurable macroscopic stresses. These networks appear isotropic without local ordering or packing of the CNF. We characterize these composite materials using steady and oscillatory rheology and relate the bulk moduli to relaxations of the nanofibrils. The viscoelasticity of the dispersed phase perturbs the CNF relaxations of individual fibrils but does not prevent the fibrils from forming a physical network. We compare the relaxations of these physical networks to the gels that are formed in the presence of salt, which destabilizes the CNF and leads to local order. By investigating the dynamics of semiflexible nanofibrils in complex environments, our work provides insight into the design and production of biodegradable and renewable composite materials. These materials can be tailored to exhibit multi-scale relaxations by tuning the dynamics of the dispersed and continuous phases quasi-independently.

Monday 3:45 Room 306C GG10

Large-scale structural rearrangement during yielding of heterogeneous colloidal gels revealed by rheo-microscopy

Tuan Nguyen[1], Abhishek Shetty[2], and Matthew E. Helgeson[1]
[1]UC Santa Barbara, Santa Barbara, CA 93106-5080, United States; [2]Rheology Division, Anton Paar, Ashland, VA 14850, United States

Colloidal gels can show complex behavior during the transition to flow, including rate-dependent yield stresses and strains, thixotropy and shear localization. This behavior is usually hypothesized to arise from structural or dynamical heterogeneity within the gel. However, confirming the role of heterogeneity during yielding remains elusive due to a lack of methods to measure structure and rheology simultaneously. We report novel rheo-microscopy measurements to track the evolution of structure in model heterogeneous colloidal gels during the yielding transition. We employ an established thermoresponsive colloidal system to form pristine gels in situ with controlled length scales of heterogeneity due to arrested phase separation. We probe the evolution of gel structure during yielding in both creep and large amplitude oscillatory shear measurements. The former provide unambiguous measures of changes in gel structure during yielding, whereas the latter allow separation of viscous and elastic contributions to the stress using local measures of the stress trajectory. We find that yielding proceeds through a sequence of processes involving large structural rearrangements at the length scale of heterogeneity. The onset of yielding is marked by a significant overshoot in viscous response coincident with the formation of large fluid voids, suggesting that poroelastic deformation drives the initial transition to flow as well as large-scale concentration fluctuations. These concentration fluctuations are initially isotropic, and become aligned along the vorticity direction at large strains, consistent with what is observed in experiment and simulation on attractive colloidal suspensions. Importantly, we find that the length scale of these flow-induced structures is seeded by the initial length scale of heterogeneity, providing a route to control the rheological signatures of yielding. These results reveal the importance of large-scale structure in understanding the nonlinear rheology of colloidal gels.

Monday 4:10 Room 306C GG11

Rejuvenation protocols and pre-shear history in non-ergodic states of attractive colloids

George Petekidis and Esmaeel Moghimi
Material Science and Technology, IESL-FORTH, University of Crete, Heraklion, Crete 70013, Greece

Attractive colloids form out-of-equilibrium states, colloidal gels and attractive glasses, which may exhibit thrixotropic effects. Their mechanical properties are affected by pre-shear history and show a time evolution after nonlinear steady or oscillatory shear tests due to structural changes induced by preshear and subsequent restructuring and relaxation after shear cessation. Both in model and industrial systems such preshear protocols have been shown to enable fine tuning of the structure and mechanical properties as such systems may be driven in different metastable states, often not easily accessible by change of the thermodynamics parameters. A main question is to what extend and under what conditions (of the external applied fields or the system's characteristics) a shear rejuvenation is equivalent with instantaneous temperature quench, that in experiments or in computer simulations induce attractions in an isotropic suspension of repulsive particles. Here we present a variety of existing and new experiments and computer simulations on colloidal gels with different attraction strengths and volume fractions. We discuss the implications of steady and oscillatory rejuvenation protocols and their effect on microstructural measures as well as the linear and non-linear rheological properties. In comparison with computer simulation and experiments where a thermal quench (or rejuvenation) is implemented we show how and when the two protocols (shear and thermal) are equivalent both at the microstructural level and the macroscopic mechanics, and when shear induced structural anisotropies or residual stresses introduce differences.

Monday 4:35 Room 306C GG12

Microscopic dynamics and failure precursors of a gel under mechanical load

Stefano Aime[1], Laurence Ramos[2], and Luca Cipelletti[2]
[1]School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States; [2]Laboratoire Charles Coulomb, Université de Montpellier, Montpellier, France

Material failure is ubiquitous, with implications from geology to everyday life and material science. It often involves sudden, unpredictable events, with little or no macroscopically detectable precursors. A deeper understanding of the microscopic mechanisms eventually leading to failure is clearly required, but experiments remain scarce. Here, we show that the microscopic dynamics of a colloidal gel, a model network-forming system, exhibit dramatic changes that precede its macroscopic failure by thousands of seconds. Using an original setup coupling light scattering and rheology, we simultaneously measure the macroscopic deformation and the microscopic dynamics of the gel, while applying a constant shear stress. We show that the network failure is preceded by qualitative and quantitative changes of the dynamics, from reversible particle displacements to a burst of irreversible plastic rearrangements.

Monday 5:00 Room 306C GG13

Large amplitude oscillatory shear study of a colloidal gel at the critical point

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

The nonlinear viscoelastic behavior of a fractal colloidal gel of Laponite at the critical gel state is investigated using large amplitude oscillatory shear (LAOS) rheology. The critical gel is characterized by presence of the weakest space spanning percolated network. The colloidal gel at the critical point is subjected to oscillatory shear flow with increasing strain amplitude at different frequencies. The first harmonic of elastic and viscous modulus is observed to exhibit a monotonic decrease as the material undergoes linear to nonlinear transition. The stress waveform is analyzed in the linear as well as nonlinear region and the Chebyshev polynomials are obtained as a function of frequency and strain amplitude. The positive value of strain hardening ratio (S) and elastic Chebyshev coefficients (e3/e1) at all explored frequencies suggests intracycle strain hardening behavior in the critical colloidal gel. The stretching of the percolated network structure within a cycle is believed to result in intracycle strain hardening. Furthermore, the negative value of viscous Chebyshev coefficients (v3/v1) and shear thickening ratio (T) indicates intracycle shear thinning behavior of the critical gel arising from the flow of the deformed network structure. The decrease in the minimum strain modulus G'_M with an increase in the strain amplitude suggests overall softening which explains the no-flow to flow transition in the material. A series of step strain experiments are conducted in the linear and nonlinear region and the damping function is obtained using the time-strain separable relaxation modulus. The overall LAOS behavior is modelled by incorporating the nonlinear relaxation modulus associated with the critical state into the K-BKZ constitutive equation and the model prediction is compared with the experimental data.

Monday 5:25 Room 306C GG14

Controlling microstructures in depletions gels: Effects of quenching rate, depth and shear flow history

Gabriele Colombo and Jan Vermant
Department of Materials, ETH Zurich, Zurich 8049, Switzerland

Depletion flocculated colloidal gels are versatile and industrially relevant systems. Pronounced changes in their mechanical properties often result from subtle, highly localized microstructural rearrangements in a locally heterogeneous, disordered structure, which are difficult to resolve using ensemble averaged techniques as e.g. light or X-ray scattering, but require microscopy techniques. In the present work, we evaluate the microstructural basis of the rheological properties, and in particular of the thixotropy and yielding in gelled colloidal suspensions by directly imaging colloidal gels during transient simple shear deformations and steady state flows. The experimental approach relies on the quantitative study of the gel microstructure using ultra-high-speed, structured illumination confocal microscopy. Model systems of depletion flocculated PMMA-g-PHSA are used, and particular attention is given to controlling residual charges and how to screen those in a controlled manner by diffusion of an organic salt. This way, well controlled initial structures can be produced. Flow experiments are performed using a rheometer with a home-made shear cell for counter-rotation of the lower glass plate, allowing single particles to be imaged for long times at the stagnation plane. Fast axial scanning is implemented using an electric focus tunable lens, circumventing issues of immersion oil squeeze flow typical of mechanical focus repositioning. The unprecedented combination of temporal and 3D spatial resolution of our setup allows the study of intermediate volume fraction gels at high shear rates and with larger than usual fields of view, a critical factor to resolve the large length scales of structural heterogeneity developing in these systems. The results show that the anisotropic nature of a shear flow, combined with the subtle hydrodynamic interactions, first leads to an increased heterogeneity and anisotropy, which will be compared in detail with recent full hydrodynamic simulations.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Room 306 PL2

Molecular rheology and synthetic chemistry: A critical partnership for designing flow-responsive matter

Dimitris Vlassopoulos
Institute of Electronic Structure & Laser, FORTH, Heraklion 70013, Greece

An intimate, molecular-level characterization of soft materials is crucially important for understanding their response to external fields. This, in turn, allows tailoring rheology at the molecular scale and designing materials, which frequently relies on bridging polymers and colloids, with desired properties. We discuss this singular interplay of synthetic chemistry and rheology in the context of two material classes. The first is multiarm star polymers, a paradigm for soft colloids with repulsive interactions. We highlight the decoupling of polymeric and colloidal contributions to their viscoelastic response in solutions and in the melt. Mixing such soft colloids is a powerful means of tuning their flow properties, leading to a variety of phases from liquid to glasses and gels. The associated transitions are understood in the context of effective interactions and the osmotic compression of stars. Examples of star - linear polymer mixtures are discussed. Introducing attractions offers a new strategy for obtaining soft patchy particles with complex, albeit tunable rheology. The resulting understanding can be framed into simple dynamic state diagrams and serves as a unifying guide for exploring the hybrid dynamics of soft materials with practical interest, for example grafted nanoparticles. A second material class comprises architecturally complex macromolecules. We address aspects of the dynamics of entangled combs and linear-ring polymer mixtures. The shear and extensional rheology of the former exhibit signatures of hierarchical relaxation due to dynamic dilution. The threading of the rings is responsible for the viscosity enhancement of the linear matrix in the latter case. Shear viscosity and normal stress differences are dominated by the linear chains contribution, which is very different from that of rings. These findings may improve our understanding of entangled polymer dynamics with implications for diverse applications ranging from materials processing to biological function.

Symposium TM
Rheometry: Advanced Techniques and Methods

Organizers: Joseph Samaniuk and Michelle Calabrese

Tuesday 9:50 Room 305A TM15

Transition criteria between scaling regimes in capillary thinning rheometry

Christian Clasen[1], Formenti Susanna[1], Karel Verbeke[1], Naveen Reddy[2], Francesco Briatico-Vangosa[3], Patrick D. Anderson[4], and Mitrias Christos[4]
[1]Department of Chemical Engineering, KU Leuven, Leuven, Belgium; [2]Faculty of Industrial Engineering, Universiteit Hasselt, Hasselt, Belgium; [3]Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milabo, Italy; [4]Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands

Capillary breakup extensional rheometry has proven to be a powerful tool for the investigation of extensional material functions of low viscous and weakly viscoelastic fluids. In particular the identification of scaling laws for the minimum filament diameter decay, when either viscosity, inertia, elasticity or combinations thereof dominate the fluid response, allows to fit the thinning profile in order to extract relaxation times of apparent extensional viscosities. One problem that arises, however, is the identification of the applicable scaling law for an observed filament thinning. This arises because the transition between scaling regimes is often broad, and different dominant material properties can lead to similar scaling laws that differ only in their respective coefficients, so that selection of the correct scaling law even in the absence of a transition can be ambiguous. In this paper we present therefore for the first time a two-dimensional map spanned by the Ohnesorge number Oh and the viscosity ratio p between the fluid viscosity and the viscosity of the outer medium, that allows to identify the filament diameters at the transitions between different thinning regime. We demonstrate that a quantitative description requires the incorporation of an additional dimensionless geometrical parameter that accounts for the critical axial and radial length scales of the filament. The validity of this map is demonstrated over six orders of magnitude for the Ohnesorge number, as well as nine orders of magnitude for the viscosity ratio, by experimental observation of filament thinning dynamics of model silicon oil and water/glycerol mixtures, as well as finite element numerical simulations for experimentally not accessible regimes.

Tuesday 10:15 Room 305A TM16

Stability of liquid filament stretching and implications for rheometry

Ole Hassager

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

In a recent series of landmark publications [1, 2] Hoyle and Fielding have derived criteria for extensional necking instability in extensional filament stretching. For most complex fluids undergoing start-up of constant strain-rate, a necking instability is predicted to occur at relatively low Hencky strains. In apparent contrast to this, the technique of Filament Stretching Rheometry (FSR) is routinely used to characterize the non-linear extensional properties of complex liquids including their steady extensional viscosity. As shown, here there is in fact no conflict between the application of the FSR technique to access extensional viscosity and the Hoyle-Fielding necking criteria. For start-up of constant strain rate extensional flow, Hoyle and Fielding have derived two criteria and associated necking modes: The so-called "Stress curvature mode" and the "Elastic Considere mode". Both of these modes will be considered for a spectrum of fluids ranging from the highly stain hardening Upper Convected Maxwell model to the extremely stain softening non-stretch Rolie-Poly model. The two modes act rather differently with respect to the wavelength of the resulting deformation, with the elastic Considere mode having the shorter wavelength. The main conclusion, however, is that even in the presence of both modes the FSR technique is perfectly able to access steady extensional viscosity. The stability of a liquid filament after an interrupted extensional strain ramp will be examined theoretically in the light of the Hoyle-Fielding criteria and experimentally for specific complex fluids. It will be demonstrated how meaningful stress relaxation measurements may be obtained even for fluids prone to the so-called delayed necking phenomenon. [1] D.M. Hoyle and S.M. Fielding, J. Rheol. (2016) [2] D.M. Hoyle and S.M. Fielding, J. Non-Newtonian Fluid Mech. (2017)

Tuesday 10:40 Room 305A TM17

Drop dynamics of viscoelastic filament

Hrishikesh Pingulkar[1], Jorge Peixinho[2], and Olivier Crumeyrolle[1]

[1]Normandie Univ, UNIHAVRE, CNRS, LOMC, Le Havre 76600, France; [2]Laboratoire PIMM, CNRS, Arts et Metiers, CNAM, HESAM, Paris, France

Understanding the dynamics of capillary driven thinning of viscoelastic liquid bridges and extensional rheology response is of great interest for many commercial applications. The stretching of viscoelastic solutions close to break-up creates filaments and drops-on-a-string structures. The thinning and break-up dynamics of aqueous polymer solutions of high molecular weight poly-ethylene oxide (PEO) and poly-ethylene glycol (PEG) are investigated using high-speed digital video microscopy. Then a Hencky strain-space-time (SST) diagram is developed in order to monitor the spacial and temporal evolution of viscoelastic threads, its filament thinning, and the migration, coalescence and draining of drops. In addition, the calculation of filament width, the number of drops and their positions, the diameters of drops and the filament breakup time are quantified. It is found that with addition of PEO, the diameter of the big central drop decreases. Interestingly, the number of drops increases with increasing PEO concentration. SST diagrams also quantify the large Hencky strains in the filament before pinch-off, as well as, at different positions and drops after the pinch-off. Additionally, the digital microscopy enables the calculation of extensional viscosity from the minimum diameter of the filament and calculation of the relaxation time from minimum, as well as, mid-plane diameter of the filament. The average extensional viscosity of aqueous PEG+PEO solutions is found to be higher than the aqueous PEO solutions. Three distinct regimes of extensional viscosity can be characterised based on stretching of capillary bridge, separation of solution pools with simultaneous appearance of the cylindrical shaped filament and initiation of pinching respectively. The difference between extensional viscosity calculated from minimum and mid-plane diameter, as well as, their relationship with SST will be discussed.

Tuesday 11:05 Room 305A TM18

Micro gel beads produced by inkjet system and its application to biorheology measurement

Mitani Shujiro, Hirano Taichi, and Sakai Keiji

Institute of Industrial Science, University of Tokyo, Tokyo, Japan

The typical size of inkjet droplets is about 10 µm, which is almost the same as that of biological particles, such as human red blood cell. We developed an original inkjet device, which is composed of a glass capillary nozzle to continuously emit liquid droplets and microscope to observe flying droplets with strobe light. The time and spatial resolutions of the system are 100 ns and 0.1 µm, respectively. Using a glass capillary as a nozzle, we can observe the droplet shape from generation to landing on a substrate such as paper. Using the system, we developed measurement method of liquid properties such as the dynamic surface tension and viscosity with high time resolution, and we observed the adsorption process of surfactant molecules on to the surface of liquids. In another experiment, we measured dynamic interfacial tension between two different liquids by observing the shape of integrated particles; two nozzles emit droplets of different liquids and they collide in the air. In addition, with this ink-jet technique, we developed a method to produce suspension containing spherical soft gel beads with a diameter of ~ 30 µm at the formation rate of ~ 20,000/s. In this process, two different droplets, those of aqueous solutions of sodium alginate and calcium chloride collide in air. After the collision, the droplet of calcium chloride spreads over the surface of alginate droplet instantly due to the difference of their surface tension, and two droplets form one sphere and then gelation starts from the surface into the inside. This suspension has similar structure and mechanical properties to those of human blood and is expected to be mimic blood for biorheology measurements.

Tuesday 11:30 Room 305A TM19

Flexibility-dependent contrast in capillary break-up dynamics, coil-stretch transition, and extensional rheology of polymer solutions revealed using Dripping-onto-Substrate (DoS) rheometry

Jelena Dinic[1] and Vivek Sharma[2]

[1]Institute for Molecular Engineering, University of Chicago, Chicago, IL, United States; [2]Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States

We elucidate the influence of chemical structure on macromolecular hydrodynamics, rheological response, and drop formation/liquid transfer by utilizing solutions of two polymers with matched overlap concentration. We contrast the shear and extensional rheology response of aqueous solutions of semi-flexible 2-hydroxyethyl cellulose (HEC) with solutions of flexible, polyethylene oxide (PEO). We show that the HEC solutions display a higher shear viscosity and a stronger concentration-dependent increase in specific viscosity above overlap concentration. In contrast, the PEO solutions exhibit distinctively higher values of extensional relaxation time, extent of strain hardening and transient extensional viscosity as well as overall delay in pinch-off at matched concentration. We critically analyze the radius evolution data obtained using Dripping-onto-Substrate (DoS) rheometry to argue that the solutions of flexible PEO macromolecules exhibit signatures of underlying coil-stretch transition and hysteresis manifested as a discontinuous, non-monotonic variation in extensional rate. In contrast, the solutions of semi-flexible HEC show a monotonic increase in extensional rate with time, implying that the macromolecules undergo progressive stretching and orientation without coil-stretch transition or hysteresis. We identify the influence of flexibility on the critical minimum concentration below which elastocapillary response and extensional relaxation time cannot be measured, and also define a stretched overlap concentration below which extensional relaxation time becomes concentration-independent. We distill out how length, diameter and number of Kuhn segments affects macromolecular dynamics, rheological response and processability, and infer that the ratio of packing length to Kuhn length, a parameter we term as segmental dissymmetry, helps to hone in on the contrast related to flexibility and extensibility, that are determined by chemical structure for macromolecules comparable molecular weight.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Tuesday 9:50 Room 304 SC15

Short and long time relaxation processes determine the macroscopic rheology of soft particle glasses

Fardin Khabaz[1], Michel Cloitre[2], and Roger T. Bonnecaze[1]

[1]McKetta Department of Chemical Engineering, University of Texas, AUSTIN, TX 78712, United States; [2]Matière Molle et Chimie, ESPCI Paris, PSL Research University, Paris 75005, France

Soft particle glasses (SPG), which are suspensions composed of the deformable particles, show a solid-like behavior at rest and flow under applied stress, which exceeds the yield stress of the material. It is shown empirically that the flow curve of SPG (i.e., the relationship between shear stress and shear rate) under steady shear flow follows a Herschel-Bulkley equation (e.g., Seth et al. Nat. Mater. 10, 838 (2011)) with an exponent close to 0.5 at high shear rates. Here we utilize the three-dimensional particle-dynamics simulation to characterize the relationship between the local motion of the particles and shear stress in steady shear flow. Analysis of particles motion at short times show that the sustained elastic force, which is exerted on the particles due to frequent contacts in the particle's cage, determines the macroscopic rheology of SPGs. The anomalous shear-dependent behavior of the diffusion coefficient also can be rationalized using the elastic force autocorrelation function obtained at different shear rates. A simple power balance between the shear flow energy and the dissipated energy shows that the shear stress can be related to the magnitude and the relaxation time of the elastic force autocorrelation function. Finally using experiments, this relaxation time is determined from a stress relaxation test that allows one to establish a linkage between the elastic force autocorrelation function and macroscopic rheological measurements.

Tuesday 10:15 Room 304 SC16

Start-up shear flow of soft particle glasses reveals microscopic dynamics

Fardin Khabaz[1], Michel Cloitre[2], and Roger T. Bonnecaze[1]

[1]McKetta Department of Chemical Engineering, University of Texas, AUSTIN, TX 78712, United States; [2]Matière Molle et Chimie, ESPCI Paris, PSL Research University, Paris 75005, France

Soft particle glasses (SPG), which are jammed beyond the random close-packing fraction of equivalent hard spheres, show rich rheology under shear flow. The startup flow of these suspensions is studied using three-dimensional particle-dynamics simulations and experiments at different particle packing fractions and shear rates. Experimental data show that the shear stress undergoes an overshoot after a linear elastic response, and then it attains a steady-state value as a function of the shear strain. The value of the strain at which the stress overshoot occurs is close to 0.1, and it slightly increases with the shear rate. Furthermore, the rheological experiments demonstrate that the magnitude of the stress overshoot increases with the aging of the suspensions. Simulations are used to characterize the effect of aging and applied shear rate on the stress overshoot and rationalize the experimental observations. Results show that the overshoot occurs in both shear stress and elastic energy of the system as a function strain. There is a substantial microstructural change before the overshoot, in which particles significantly accumulate on the axis of compression of the test particle. Simulations are also used to understand the microscopic origin of the stress overshoot in the aged suspensions. Finally, a simple

equation that combines linear elastic response with a power-law decay is used to characterize transient results of shear stress in both experiments and simulations.

Tuesday 10:40 Room 304 SC17

One-step, in-situ jamming point measurements by immobilization cell rheometry

Yimin Luo[1], Yu-Fan Lee[1], Scott C. Brown[2], Kimberly A. Dennis[1], Eric M. Furst[1], and Norman J. Wagner[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]The Chemours Company, Wilmington, DE 19805, United States

Particle jamming is a challenge in handling highly concentrated slurries in a wide variety of industries, whereupon the suspension discontinuously shear thickens and dilates, often with deleterious consequences. Such systems are shear sensitive wherein a significant increase in viscosity occurs within a few percent of change in volume fraction. Thus, identifying the jamming point is critical for properties pertaining to plant operation and cost reduction. Within the colloidal rheology community, factors contributing to discontinuous shear thickening and jamming are actively under investigation. Many studies point to surface contact friction. Consequently, there is an increasing interest in relating particle properties, such as friction coefficient to the onset of jamming. Conventional rheometry identifies the jamming point by mapping out the flow curves of a few different concentrations and extrapolating to where the viscosity diverges, but risks altering the sample during consolidation and subsequent redispersion. Furthermore, the time required to measure a sufficient number of concentrations, and the accuracy of flow curves, especially when dilatant, ultimately limits the accuracy of the fit and the number of suspensions investigated. We present an alternative approach to the experimental determination of the jamming point. The procedure monitors the shear stress under constant shear as the sample is dewatered using immobilization cell rheometry. While this setup has long been used in paper industry for qualitative characterization of the water content of the pulp, here we demonstrate that it can also robustly determine the jamming point by comparing to the studies using conventional rheometry for a wide variety of systems. It is extended to study the behavior of mixtures of systems, system aging, and pH effect, a sample parameter space too vast to be screened by conventional rheometry. In addition, the method facilitates rapid determination of critical suspension properties at the point of manufacture.

Tuesday 11:05 Room 304 SC18

Cracking and self-healing of shrinkable, granular materials

H. Jeremy Cho and Sujit S. Datta
Princeton University, Princeton, NJ 08544, United States

Shrinkable, granular materials-materials composed of hydrated grains that individually shrink when dried-arise in many diverse settings; prominent examples include clays, soils, biological tissues, foods, and coatings. In many cases, these materials crack during drying, critically hindering applications. By combining experiments with hydrogels, discrete-element simulations, and poroelasticity theory, we reveal how grain shrinkability dramatically alters crack evolution during drying-in some cases, even causing cracks to spontaneously self-heal. Moreover, we elucidate the rich physics underlying cracking, and develop new strategies to controlling crack evolution and patterning.

Tuesday 11:30 Room 304 SC19

Anomalous creep in jammed suspensions

Hiya Goswami and Jyoti R. Seth
Chemical Engineering, Indian Institute of Technology Bombay, Mumbai, Maharashtra 400076, India

Structuring agents are often used to modify the rheological properties of many products from the consumer goods industries. Fats and fatty acids are typical examples of such structuring agents. A stiff, solid-like suspension can be formed, by first heating to dissolve the fat or fatty acid in a solvent and then cooling for crystallization. During cooling, crystals nucleate and grow. As low as 2 wt.% concentration of solids is found to be sufficient for the particles to form a dense, jammed, solid-like network. Here, the elastic nature of these suspensions is explored under an applied stress, which is important for the long-term stability of these suspensions.

In this study, a model suspension of stearic acid in light mineral oil was used. Creep tests were performed, where a constant stress was applied to investigate the dynamics of deformation of these materials and two regimes were identified. For applied stresses above the yield stress, the suspension continued to deform at increasing rates. However, for applied stresses below the yield value, an unusual behaviour was observed. There was observed an initial deformation, commensurate with the expected elastic response, but at longer times the strain was observed to decrease, indicating the deformation to be in a direction opposite to the applied stress. The reversal in strain was seen to be coincident with the relaxation of the normal stresses stored during crystallization of the sample. In addition, for a fixed applied stress, different waiting times post-crystallization result in varying creep behaviour. In this talk, we present a framework to understand the above creep behaviour of these jammed suspensions.

Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Tuesday 9:50 Room 201 SM15

Molecular dynamics (MD) simulations of entangled melts in shear and extension

Yexing Zheng, Mesfin Tsige, and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

MD simulations are carried out to study the nonlinear rheological responses of entangled polymers to startup deformation in both shear and extension. In the cases of shear, creep (controlled-stress) is found to result in entanglement-disentanglement transition (EDT) in the sense that the shear rate is found to transient increase over time, as having been observed in experiment [1]; controlled-rate startup shear is found to produce shear stress overshoot. In the limit of high Hencky rate, startup melt extension is found to result in a breakup of the system, corresponding to regime IV behavior [2]. In order to evaluate the state of entanglement at the different stages during startup and stepwise deformation, a new method (different from the primitive-path analysis and Z1 code) is proposed to monitor the process of chain disentanglement. Employing the method, the nature of the nonlinear responses is clarified in each case. For example, our analysis assigns specific meaning to the essence of the EDT: there is indeed a loss of entanglement during the creep, little entanglement remaining in steady shear.

[1] P. Tapadia and S. Q. Wang, Macromolecules 37, 9083 (2004); S. Ravindranath and S. Q. Wang, J. Rheol. 52, 957 (2008); R. Ge, X. Y. Zhu and S. Q. Wang, Polymer 125, 254 (2017). [2] Zhu, X.; Wang, S.-Q. Mechanisms for different failure modes in startup uniaxial extension: Tensile (rupture-like) failure and necking. Journal of Rheology 2013, 57, (1), 223-248.

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Tuesday 10:15 Room 201 SM16

Shear thinning of unentangled polymer melts due to flow-induced reduction of monomeric friction coefficient

Giovanni Ianniruberto and Giuseppe Marrucci
Department of Chemical, Materials and Production Engineering, Federico II University, Napoli, NA 80125, Italy

Nonlinear shear data of an unentangled polystyrene melt (Santangelo and Roland, J. Rheol., 45, 583-594, 2001) are compared to Brownian dynamics predictions of Fraenkel chains. All parameters needed to perform the comparison are obtained from the known molar mass (M = 13.7 kDa), from the linear viscoelastic response, and by properly accounting for the glassy contribution. Comparison reveals that the magnitude of shear thinning of the unentangled melt cannot be explained unless account is taken of the flow-induced reduction of the monomeric (Kuhn segment) friction coefficient.

Tuesday 10:40 Room 201 SM17

Elucidating the molecular rheology of entangled polymeric fluids via direct comparison of NEMD simulations and model predictions

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

The startup and steady shear flow properties of an entangled, monodisperse polyethylene liquid ($C_{1000}H_{2002}$) were investigated via virtual experimentation using nonequilibrium molecular dynamics. The simulation results for transient and steady-state rheological functions were directly compared with several versions of the tube model including the DEMG, MLD, GLaMM, and Rolie-poly models. These comparisons demonstrated that all the studied tube models performed poorly under startup conditions for shear rates higher than the inverse Rouse time, τ_R^{-1}, of the system due to inaccurate evolution equations for the tube orientation and tube stretch variables. Nevertheless, the factorization of the stress tensor into tube segmental orientation and tube stretch contributions appeared to be reasonable for shear rates up to the inverse disentanglement time, τ_e^{-1}, of the liquid. At higher shear rates, the entanglement dynamics (*i.e.*, flow-induced disentanglement) began to influence the stress relaxation significantly. A simple modification to the stress expression was proposed to incorporate the entanglement dynamics into tube-based models.

The comparison of transient shear viscosity with the dynamic responses of key variables of the tube model, including the tube segmental orientation and tube stretch, revealed that the stress overshoot and undershoot in steady shear flow of entangled liquids are essentially originated and dynamically controlled by the shear component of the tube orientation tensor, rather than the tube stretch, over a wide range of flow strengths.

Tuesday 11:05 Room 201 SM18

Spatially anisotropic relaxation dynamics in deformed polymer melts

Wen-Sheng Xu, Christopher Lam, Jan-Michael Carrillo, Bobby Sumpter, and Yangyang Wang
Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

The spatiotemporal structure of gyration tensor relaxation in deformed entangled and unentangled polymer melts is investigated by small-angle neutron scattering and nonequilibrium molecular dynamics simulations. Several classical models, including the Rouse model, the tube model, and the interpolation model of de Gennes and Léger, predict spatially homogeneous relaxation dynamics of the gyration tensor under a number of conditions. Our experimental and computational investigations of polymer melts after a step uniaxial deformation show, however, that the relaxation dynamics is homogeneous only in the linear response limit, i.e., at small strains, and becomes spatially anisotropic when the molecules are brought far away from the equilibrium. This theoretically unanticipated observation reveals that the environment of a polymer chain is anisotropic in the highly nonequilibrium state, resulting in spatially heterogeneous relaxation pathways. To enhance insight, we further analyze the relaxation behavior of the gyration tensor in terms of the conformational space trajectory. These new analyses, together with the recent results from neutron scattering and computer simulations [Phys Rev X **7**, 031003 (2017); ACS Macro Lett **7**, 190 (2018); Phys Rev Lett **121**, 117801 (2018); Phys Rev Lett **121**, 167801 (2018)], highlight several important issues that are not (properly) addressed by the classical theories of polymer rheology.

Tuesday 11:30 Room 201 SM19

Inhomogeneous yielding and chain disentanglement upon "constrained" planar extension

Ruchao Yuan, Xiangguang Li, and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

Startup fast deformation of entangled melts is signified by yielding as a consequence of polymer disentanglement. For both shear and extension, it was found that the response after yielding may not be spatially homogeneous. In the case of shear, shear banding occurs only when there is sufficient entanglement as measured by the number of entanglements per chains. When it does occur in well entangled solutions it is not due to edge fracture. There are also two cases [1-2] whether shear strain localization occurs in absence of any edge fracture. In contrast, tensile strain localization takes place even in the limit of weak entanglement [3]. In this work, we show for the first time the consequence of spatially inhomogeneous disentanglement involving constrained planar extension, i.e., lubricated one-dimensional squeezing [4].

[1] "Exploring shear yielding and strain localization at the die entry during extrusion of entangled melts", X. Y. Zhu and S. Q. Wang, J. Rheol. 57, 349 (2013). [2] "Strain localization during squeeze of an entangled polymer melt under constant force", X. G. Li and S. Q. Wang, J. Rheol. 62, 491 (2018). [3] "Exploring rheological responses to uniaxial stretching of various entangled polyisoprene melts", Yi Feng, Jianning Liu, and Shi-Qing Wang, K. Ntetsikas and A. Avgeropoulos, J. Rheol., under review (2019). [4] Nonlinear Polymer Rheology: Macroscopic phenomenology and molecular foundation, Shi-Qing Wang, Wily (2018). This work is supported by NSF-DMR (1609977).

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Tuesday 9:50 Room 305B *Keynote* IN15

Using rheometry and MRI to predict transfer of pastes and gels

Andrei Potanin[1] and Nina Shapley[2]
[1]Colgate-Palmolive, Piscataway, NJ 08855-1343, United States; [2]Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08854, United States

Rotational and capillary rheometry and MRI imaging were used to characterize transferability of pastes and polymer gels. Model pastes, emulating typical toothpaste compositions, were studied to establish methods of predicting pumping pressure. Polymer gels discharge from tanks was studied to develop methods of predicting heel, i.e., the amount left in the tank. Flow visualization with MRI allowed to discriminate different mechanisms of flow.

Tuesday 10:15 Room 305B IN16

Creating strain hardening polypropylene via multilayers for improved thermoformability

Alex M. Jordan[1], Kyungtae Kim[2], Bongjoon Lee[2], Ehsan Behzadfar[3], Olivier Lhost[4], Shaffiq Jaffer[4], Frank Bates[2], and Christopher W. Macosko[2]
[1]Plastics Engineering, University of Wisconsin-Stout, Menomonie, WI 54751, United States; [2]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States; [3]Chemical Engineering, Lakehead University, Thunder Bay, Ontario, Canada; [4]Total S.A., Feluy, Belgium

Polypropylene (PP) is notoriously difficult to thermoform. Increasing strain hardening in extension has been found to reduce sag and increase wall thickness uniformity during thermoforming. Recently we have fabricated films consisting of 100s of layers of polypropylene and polyethylene (PE). Although neither polymer shows strain hardening during extension the multilayers have extensional viscosities significantly greater than what is predicted with a simple 2-component volume average model. This behavior is predicted with a 3-component model that accounts for the many PE/PP interfaces using only interfacial tension as a model fitting parameter. The extracted interfacial tension from transient elongational viscosity measurements agrees with the interfacial tension extracted from fitting small amplitude oscillatory shear data with the Palierne model. We demonstrate the importance of the observed strain hardening behavior on thermoformability and also flammability reduction in multilayer PP/PE films.

Tuesday 10:40 Room 305B IN17

Structure-property relationships via recovery rheology in viscoelastic materials

Johnny Ching-Wei Lee[1], Katie M. Weigandt[2], Elizabeth Kelley[2], and Simon A. Rogers[1]
[1]Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]NIST Center for Neutron Research, Gaithersburg, MD 20877, United States

The recoverable strain is shown to correlate to the temporal evolution of microstructure via time-resolved small-angle neutron scattering (SANS) and dynamic shear rheology. Investigating two distinct polymeric materials of wormlike micelles and fibrin network, we demonstrate that, in addition to the nonlinear structure-property relationships, the shear and normal stress evolution is dictated by the recoverable strain. A distinct sequence of physical processes under large-amplitude oscillatory shear (LAOS) is identified that clearly contains information regarding both the steady-state flow curve and the linear-regime frequency sweep, contrary to most interpretations that LAOS responses are either distinct from, or somehow intermediate between the two cases. This work provides a physically-motivated and straightforward path to further explore the structure-property relationships of viscoelastic materials under dynamic flow conditions.

Tuesday 11:05 Room 305B IN18

Non-linear analysis of extrusion instabilities in polymer melt processing

Stylianos Varchanis, Dionisis Pettas, Yannis Dimakopoulos, and John Tsamopoulos
Department of Chemical Engineering, University of Patras, Patras, Achaia, Greece

It is well-known that, as the flow rate increases in extrusion of polymer melts, the stable flow turns unstable, since the smooth extrudate surface becomes wavy and disordered to an increasing degree. A critical Weissenberg number exists above which the first type of instability, called "sharkskin" instability arises, while at even higher Wi other types of instability arise. All these affect many industrial processes, limiting the production rate and product quality in many extrusion operations such as the manufacture of polymeric rods, tubes, sheets and wire coating. Recently, our group performed a linear stability analysis of the extrusion process through a planar die [1] and identified the critical Weissenberg numbers, up to which the flow remains steady. At these values, a Hopf bifurcation takes place, giving rise to time-periodic flow of very short wavelength confined outside the die. Given new advances in numerical methods by our lab [2] that allow for stable FEM simulations of viscoelastic flows at very high Weissenberg numbers, we revisit the extrusion process in order to investigate its non-linear dynamics. The polymer melt is modelled as an exponential PTT fluid, and the planar extrusion process is simulated as a 2-dimensional flow. More specifically, we perform transient simulations at supercritical values of Wi [1], and we capture a periodic solution. We demonstrate that when the limit cycle is reached, the surface of the extrudate features an oscillating wave that decays rapidly after 2-4 die widths. Finally, through a wide parametric study, we attempt to understand the underlying physics of the melt fracture instability. This is achieved by examining the impact of the interplay of elasticity, capillarity, and wall slip on the non-linear dynamics of the extrusion process.

[1] D. Pettas, G. Karapetsas, Y. Dimakopoulos, and J. Tsamopoulos, J. Non-Newt. Fluid Mech., 224, 61-77 (2015). [2] S. Varchanis, A. Syrakos, Y. Dimakopoulos and J. Tsamopoulos, J. Non-Newt. Fluid Mech., 267, 78-97 (2019).

Tuesday 11:30 Room 305B IN19

Microphase separation in entangled polymeric solutions

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

The existence of a coil-stretch transition and a conformation hysteresis within a critical range of extension rates is a well-known phenomenon in dilute polymeric solutions. Recently, NEMD simulations of a well-entangled polyethylene melt revealed that within intermediate extensional rates, entangled melts could undergo a qualitatively similar coil-stretch transition, and exhibit bimodal configurational distributions with peaks corresponding to coiled and stretched configurations. Furthermore, it was shown that through a configurational microphase separation, the coiled molecules develop distinct domains surrounded by relatively stretched molecules.

On the other hand, various experimental studies have shown that the response of entangled polymeric melts to elongational flow fields could be very different from those of entangled solutions. Experiments also suggest that the solvent molecule architecture plays an important role in the dynamic behavior of entangled solutions. Such complexities bring up many questions about the coil-stretch transition in entangled polymeric liquids. Do entangled solutions undergo a coil-stretch transition? Do they experience any configurational or chemical microphase separation? How does the solvent molecular architecture affect this phenomenon?

To address these questions, we performed a series of NEMD simulations for entangled $C_{1000}H_{2002}$ polyethylene solutions in oligomeric $C_{16}H_{32}$ and benzene solvents. The solutions were subject to planar elongational flows within a wide range of extension rates of $0.05 < De < 20$, where De is the extension rate made dimensionless using the Rouse relaxation time, τ_R. The simulations revealed both similarities and differences between entangled melts and solutions that will be discussed.

Symposium SF
Surfactants, Foams, and Emulsions

Organizers: Reza Foudazi and Nick Alvarez

Tuesday 9:50 Room 306A SF15

Micellar structures, stepwise thinning and nanoscopic thickness variations in foam films formed by aqueous sodium naphthenate solutions

Chrystian Ochoa[1], Shang Gao[2], Samanvaya Srivastava[2], and Vivek Sharma[1]
[1]Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States; [2]Chemical Engineering, University of California at Los Angeles, Los Angeles, CA, United States

Sodium Naphthenates found in crude oils can act as surfactants and self-assemble in aqueous solutions to form micelles and liquid crystals. Understanding and controlling the drainage kinetics of thin films is an important problem that underlies the stability, lifetime and rheology of petroleum foams and emulsions. Here, we show that foam films formed by aqueous solutions of sodium naphthenates exhibit step-wise thinning or stratification, due to the influence of non-DLVO forces, including supramolecular oscillatory structural forces. We utilize Interferometry, Digital, Imaging, Optical Microscopy protocols, previously developed by our group, to investigate the drainage and stratification in micellar foam films (< 100 nm) with high spatial (thickness < 10 nm) and temporal resolution (< 1 ms). We determine how the concentration of added sodium naphthenates influences the nanoscopic topography, stratification kinetics and step size of foam films, and contrast the results with behavior observed with stratifying foams made with sodium dodecyl sulfate (SDS) solutions. We span a relatively wide concentration range, such that micelle shape and size vary, as is revealed by complementary small angle x-ray scattering experiments. We supplement scattering and foam film studies with a characterization of rheological behavior of the NaN solutions.

Tuesday 10:15 Room 306A SF16

Wormlike micelles in cold and sub-zero conditions: New insights into the self-assembly of ionic surfactants in polar organic solvents

Niti R. Agrawal[1], Xiu Yue[2], and Srinivasa R. Raghavan[1]
[1]Chemical and Biomolecular Engineering, University of Maryland, College Park, College Park, MD 20742, United States; [2]Xinjiang Technical Institute of Physics& Chemistry, Urumqi, China

Wormlike micelles (WLMs), also known as "living polymers", are long, flexible cylindrical chains formed in water by the self-assembly of surfactants. WLMs have attracted great interest from both academia and industry because their solutions exhibit viscoelastic properties. However, most studies on WLMs concern their assembly in water. To our knowledge, there are no known examples of WLMs in polar organic solvents like glycerol, formamide or ethylene glycol. In this study, we have devised a strategy to induce WLMs of a long-tailed cationic surfactant in these solvents. To form WLMs in these systems, we show that the surfactant has to be combined with a "binding" salt, containing an organic counterion that can bind to the micelles. Interestingly, the addition of simple, inorganic salts, such as NaCl, to the same surfactant does not induce WLMs in these polar solvents (although it does so in water). Thus, the rules for inducing WLMs in polar solvents are quite distinct from those in water. WLMs are known to display interesting rheological properties as a function of temperature, and aqueous WLMs have been studied from room temperature to much higher values. However, few studies have examined WLMs under cold conditions, a chief reason for this being crystallization of the surfactants below their Krafft temperature (~ 20°C). Here, we have carefully selected a surfactant with low Krafft point and induced its self-assembly in solvent mixtures with low freezing points. Thereby, we have been able to extend the range for WLM formation to temperatures as low as -20°C. Rheological techniques as well as small-angle neutron scattering (SANS) have been used to characterize the WLMs under these conditions. The dynamic rheology of the WLMs is very interesting and different from the rheology of WLMs in water. In addition to academic interest, WLMs in polar solvents could also find applications in diverse areas including anti-freezing fluids or synthetic lubricants.

Tuesday 10:40 Room 306A SF17

Effect of wetting on pinch-off dynamics of wormlike micellar fluid

Shijian Wu and Hadi Mohammadigoushki
Chemical and Biomedical Engineering, Florida State University, Tallahassee, FL 32310, United States

We conduct experiments by gradually depositing non-Newtonian wormlike micellar fluids onto a big solid substrate via a vertical needle. We investigate the filament thinning dynamics of the non-Newtonian fluids in combination with wetting on the flat substrate. Our work considers two wormlike micellar solutions based on CPCl/NaSal and OTAB/NaOA over a broad range of surfactant and salt concentrations. Two distinct flow behavior is observed. In regime I, the wetting does not significantly affect the filament thinning dynamics of the micellar solutions as the extensional relaxation times and Trouton ratios remain unchanged. However, in regime II, the fluid wetting on solid substrate impacts the filament thinning dynamics significantly by lowering the extensional relaxation time and the Trouton ratio. Our analysis shows that spreading of the wormlike micelles are reasonably well captured by Tanner's law proposed for spreading of Newtonian fluids on solid substrates. We propose a scaling analysis based on a combination of the wetting forces and viscous dissipation that can successfully distinguish these two flow regimes from each other.

Tuesday 11:05 Room 306A SF18

Scaling of flow-induced alignment and the possibility of flow-induced scission in wormlike micelles

Jiamin Zhang, L. Gary Leal, and Matthew E. Helgeson
Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States

Wormlike micelles (WLMs) are ubiquitous in consumer products and oilfield applications, and have rheology similar to that of entangled polymer solutions. Although there have been considerable experimental and theoretical studies of the rheology of WLMs, there are still relatively few models for their rheology that incorporate the physics of reversible chain scission and recombination that distinguishes WLMs from polymers. In particular, it is still unknown how flow affects the scission and recombination process and the resulting length distribution of the micelles. Although flow-small angle neutron scattering (flow-SANS) is suitable for characterizing the effects of flow on micelle length distribution, previous flow-SANS studies of WLMs were complicated by micelle branching as well as flow instabilities such as shear banding and elastic instability. To circumvent these issues, we report flow-SANS experiments on a series of linear, weakly entangled WLMs, and focus measurements on stable flows before the onset of elastic instability. These measurements are used to characterize flow-induced alignment and changes in micelle length distribution. We find that, for fixed micelle concentration, the degree of micellar alignment is determined only by the Weissenberg number, regardless of the equilibrium length distribution of micelles, which we modulate through changes in temperature. We test whether the observed power law scaling of micellar alignment with Weissenberg number can be predicted from constitutive models commonly used for WLMs. Furthermore, we use simulations of scattering from rod-like objects in shear flow in order to deconvolute the contributions to the scattering due to changes in micelle orientation from effects due to changes in micelle structure in flow. These comparisons are used to provide an outlook for whether the length distribution of wormlike micelles is significantly affected by flow.

Tuesday 11:30 Room 306A SF19

Probing topological transitions of reverse worm-like micelles subject to transient shear flow using dielectric spectroscopy

Jeffrey J. Richards[1], Noah H. Cho[1], and John K. Riley[2]
[1]Chemical & Biological Engineering, Northwestern University, Evanston, IL 60208, United States; [2]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

Worm-like micelles (WLMs) are ubiquitous in industrial materials. WLMs exhibit unique dynamics due to their self-assembled structure that permits the chains to break and reform. These dynamics contribute to a rich and not well-understood microstructural behavior in response to deformation. Recent work has focused on the important role that linear and branched worm topology plays in the approach to non-linearity and on the onset of shear-banding in steady and transient flows. While linear to branched topological transitions in aqueous worm-like micelles are commonly induced through the addition of salt, questions remain about the role that electrostatic interactions play in determining the onset of shear banding and dynamics shear banding. We have recently used dielectric rheology to study the transition from linear to branched WLMs using inverse microemulsion system formed from lecithin/water/decane. A topological transition from linear to branched WLMs occurs as water is added to the microemulsions and is marked by a maximum in the zero-shear viscosity. Due to the nonpolar nature of decane, this system enables the use of dielectric measurements to distinguish between the segmental chain and branch-breaking/formation dynamics during Rheo-dielectric measurements in steady shear. Combined with in situ small angle neutron scattering, we found that shear-induced alignment of branched WLMs is preceded by the breaking of branch points that contributes to the stress-dissipation and is marked by a distinct increase in the low-frequency permittivity. This behavior was distinct from that observed in linear WLMs. We report the extension of this approach to study transient flows, including large-amplitude oscillatory shear, start-up and cessation experiments. The additional contributions of the branch breaking mechanism on the primary relaxation process will be presented in terms of the dielectric, the rheological responses, and the alignment-driven anisotropy under the transient shear flow.

Symposium BB
Biomaterials and Biofluid Dynamics

Organizers: Xiang F. Cheng and Amanda Marciel

Tuesday 9:50 Room 306B BB15

Determining how human mesenchymal stem cells change their degradation strategy in response to microenvironmental stiffness

Maryam Daviran, Jenna Catalano, and Kelly M. Schultz
Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Human mesenchymal stem cells (hMSCs) reengineer and degrade the extracellular matrix (ECM) by secreting matrix metalloproteinases (MMPs) to enable migration, an initial step in wound healing. During healing, hMSCs migrate from their niche through various tissue environments to the injury where they regulate inflammation. Each tissue presents unique chemical and physical cues to the cells, changing cell-material interactions. To understand the role of stiffness in cell-material interactions, we use a model system that mimics aspects of the complex ECM. We encapsulate hMSCs in a hydrogel composed of 4-arm poly(ethylene glycol) end-functionalized with norbornene cross-linked with an MMP degradable peptide. Elastic modulus is varied from 81 to 2400 Pa by changing the peptide cross-linker concentration, mimicking the elasticity of lung, breast and endothelial tissue. We use multiple particle tracking (MPT) microrheology to measure spatio-temporal rheological changes in the pericellular region. In MPT fluorescent probes are embedded in the material and their Brownian motion is measured. A reverse reaction-diffusion profile is measured around encapsulated hMSCs in a soft hydrogel (G'= 270 - 720 Pa), where the greatest degradation is far from the cell center. Increasing the moduli (G'= 640 Pa) results in the inversion of the degradation profile with the greatest degradation directly around the cell, a reaction-diffusion profile. We hypothesize that in higher stiffness materials cells secrete more MMPs to degrade paths for migration. No degradation is measured around hMSCs in hydrogels with G'= 2400 Pa. In this material, the increase in MMPs secreted does not degrade enough cross-links to create a path for migration. Cell speed decreases significantly with increasing hydrogel stiffness. Studying cell-material interactions at different hydrogel elasticities gives insight into cell-material interactions in native tissue environments and can further the design of implantable scaffolds that better mimic these tissues.

Tuesday 10:15 Room 306B BB16

Cell nucleus as a microrheological probe to study the rheology of the cytoskeleton

Moslem Moradi and Ehssan Nazockdast
Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27516, United States

Eukaryotic cells are soft hierarchical assemblies with time- and force-dependent rheology and substantial heterogeneity in their properties. The mechanical behaviour of eukaryotic cells is determined by three main structural components: (1) the cell interior cytoskeleton composed of microtubules and intermediate filaments; (2) the cell nucleus, and (3) the cell membrane composed of plasma membrane and the cortical actin network. Differentiating between the contributions of each of these components to the overall rheology of the whole cell remains challenging. We propose a novel method to decouple the mechanics of membrane and cytoskeleton, by analysing the correlation between the membrane and nucleus displacements. In a sense, we use the nucleus as a microrheological probe to study the rheology of the interior cytoskeleton, without the need to specify the membrane rheology. The motion of the nucleus is driven by membrane deformations, which themselves are driven by external flows (microfluidic platforms) and forces (atomic force microscopy). We provide simple analytical results in linear regime to demonstrate how the experimental measurements of cell membrane and nucleus displacements can be deployed to compute the mechanical properties of the cell. We consider four different models for the interior cytoskeleton, namely porous, elastic, poroelastic and viscoelastic, and calculate the nucleus displacements with time as a function of the material properties of each model.

Tuesday 10:40 Room 306B BB17

Putting the mitotic spindle in its place

Ehssan Nazockdast[1], Hai-Yin Wu[2], Daniel Needleman[2], and Michael Shelley[3]
[1]Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27516, United States; [2]Applied Sciences and Engineering, Harvard University, Cambridge, MA 02138, United States; [3]Computational Biology, Flatiron Institute, New York, NY 10010, United States

A cell is a complex fluidic environment in which many fundamental biological processes take place. One such process is the proper positioning and elongation of the mitotic spindle, which is crucial for chromosome segregation and asymmetric cell division and involves the interaction of microtubule assemblies with motor-proteins and subcellular organelles. In an integrated experimental and computational study, we use a combination of laser ablation, fluid flow measurements, molecular perturbations, large scale fluid mechanics simulations, stochastic simulations, and analytical theory to argue that proper positioning is primarily achieved by the action of motor-proteins bound to the cell boundary. This allows us to develop a unified theory of how oscillations, stable positioning, and migration result from the underlying behaviors of microtubules and motors. Theory should be broadly applicable to a wide variety of circumstances.

Tuesday 11:05 Room 306B BB18

Linear and nonlinear rheology of collagenase-treated breast cancer tumors

Ria D. Corder and Saad A. Khan
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States

Extracellular matrix (ECM) rigidity has been shown to increase the invasive properties of breast cancer cells, promoting transformation and metastasis through mechanotransduction. Tumor ECM degradation can be used to enhance chemotherapeutic penetration and cytotoxic effectiveness. In this study, we examine the effects of injectable collagenase treatments on the linear and nonlinear rheology of xenograft human breast cancer tumors grown in athymic nude mice. A subset of treatments also included co-injection of Liquogel (LQG), a thermoresponsive polymer that transitions upon heating from an injectable solution to a gel, to reduce diffusion of collagenase from the injection site. Linear rheological measurements demonstrated that all tissues, including untreated controls, exhibited gel-like behavior. Co-injection of LQG and collagenase reduced tissue modulus (G') and increased viscoelasticity (tan d) compared to both controls and free collagenase injections. Large amplitude oscillatory shear (LAOS) experiments were also performed on the same tissues and the results were analyzed using MITLaos. Examination of intracycle elastic and viscous Chebyshev coefficients and intercycle elastic and viscous moduli were used to characterize the onset of nonlinearity and provide information about the types of nonlinear behavior present in different treatment groups. Elastic and viscous Lissajous-Bowditch curves plotted in Pipkin space elucidate additional nonlinear characteristics and yield interesting differences between treated and untreated tumors. We conclude by presenting results from parallel mouse studies on *in vivo* ECM degradation and metastasis to show how rheological measurements are related to physiological response.

Tuesday 11:30 Room 306B BB19

Rheological characterization, experimental studies, and computer simulation of polytetrafluoroethylene (PTFE) paste extrusion and expansion for vascular tissue engineering grafts

George Schmidt, Yiyang Xu, Yujyun Lin, Galip Yilmaz, and Lih-Sheng Turng
Department of Mechanical Engineering, University of Wisconsin, Madison, Madison, WI 53706, United States

The rheological behavior of polytetrafluoroethylene (PTFE) powders and lubricant paste was characterized for computer simulation and process optimization of PTFE paste extrusion into tubular vascular grafts. The paste-extruded PTFE tube was subsequently stretched (expanded) to multiple times its original length in an environmental chamber under constant temperature and strain rate. The expanded PTFE (ePTFE) tubes exhibited a porous structure consisting of solid islands and fibrillated PTFE fiber domains that will then be used for cell culture after further surface modifications. The PTFE/lubricant paste viscosity was characterized using a parallel plate rheometer with sandpaper applied to reduce slip at the paste-disk interface. Viscosity data from oscillatory shear was fitted to a Carreau model and used in the simulation. A time-dependent laminar flow simulation using COMSOL Multiphysics was employed to model the flow behavior of the PTFE preform. The paste extruder consisted of a barrel to house the PTFE preform and a convergent cone region and die that had a reduction ratio of 100. Predicted extrusion flow behavior and extrusion pressure were compared with the extrudate, formulated with alternate white and black stripes for flow visualization purposes, and the pressure was measured experimentally. The extruded paste exhibited plug flow behavior in the barrel and the upper regions of the cone. In the convergent regions of the cone and within the die, it showed evidence of a non-uniform velocity profile. Overall, comparisons of the computer simulation and flow visualization provided useful information for the paste extrusion of PTFE vascular grafts. Furthermore, the modeling techniques and material property models can be further refined to accurately capture the wall slip condition and compressibility of the PTFE paste.

Symposium GG
Out of Equilibrium Systems: Gels and Glasses

Organizers: Suzanne Fielding, Ran Tao and Rosanna Zia

Tuesday 9:50 Room 306C GG15

The linear viscoelastic spectrum and non-affine rearrangements in soft particulate gels

Minaspi Bantawa[1], Mehdi Bouzid[2], Bavand Keshavarz[3], Michela Geri[3], Thibaut Divoux[4], Gareth H. McKinley[3], and Emanuela Del Gado[1]
[1]Department of Physics, Georgetown University, Washington, DC 20007, United States; [2]Universite Paris Sud, Orsay, France; [3]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; [4]MIT,CNRS, Cambridge, MA 02139, United States

We have investigated the connection between the structural and mechanical heterogeneities of soft particulate gels and their linear viscoelastic spectrum in a 3-D microscopic numerical model, using large scale simulations with Optimally Windowed Chirp (OWCh) signals. In the model, particles spontaneously self-assemble into disordered, stable porous networks (even at low volume fractions) that feature extended relaxation spectra, microscopic dynamics, and mechanics consistent with several observations in colloidal and protein gels. To recapitulate the basic features of the particle contacts in those systems, the main ingredients of the model are short-range attractive interactions and bending stiffness for the inter-particle bonds. We will analyze how the shape of the frequency-dependent dynamic modulus $G^*(\omega)$ varies with the solid volume fraction and the age of the gels and how it is connected to the distribution of microscopic non-affine rearrangements the network experiences under small-amplitude oscillatory deformation. We will show that the changes in the relaxation spectrum can be captured by the parameters of a fractional constitutive model and discuss how the underlying changes of the microscopic dynamical processes determine the rheological response.

Tuesday 10:15 Room 306C GG16

Accelerated gelation kinetics in binary colloidal gels of two different attraction strengths

Jae Hyung Cho and Irmgard Bischofberger
Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

When two types of colloids of different attraction strengths are mixed, the resulting gel displays linear viscoelastic moduli and a relaxation time that fall in-between those of the gels formed by the two individual types. By using differential dynamic microscopy (DDM), however, we find that, at the microscale, the binary gels evolve in a way that is not intermediate between the kinetics of the individual systems; the characteristic time scale of thermal fluctuation in a mixed gel reaches its steady state more rapidly than in either individual system at the same total particle volume fraction. Employing the thermal sensitivity of our home-made polystyrene-poly(N-isopropylacrylamide) core-shell particles, we systematically study the dynamics of the binary gels at different mixing proportions, both during and after the network formation. We explore how the discrepancy could be resolved by unravelling the governing parameters of the dynamics that we capture in DDM.

Tuesday 10:40 Room 306C GG17

Shear-induced microstructure and mechanical characterization of composite organocolloid-hydrogels

E. Daniel Cárdenas-Vásquez, Lauren Kass, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Thermoresponsive nanoemulsions that contain a bridging polymer are known to self-assemble into colloidal gel structures above the critical gel temperature. We incorporate thermoresponsive nanoemulsions into composite single (SN) and double network (DN) hydrogels by using ultraviolet (UV) light to photopolymerize the liquid precursor at controlled temperatures and flow conditions through a spinneret. The oil-in-water nanoemulsions consist of fluorescently dyed poly(dimethyl siloxane) (PDMS) droplets (droplet size 2a = 30 nm, volume fraction f = 0.2) suspended in a continuous phase of poly(ethylene glycol) diacrylate as the crosslinker and first network, sodium dodecyl sulfate as the surfactant and sodium alginate as the second hydrogel network. Steady shear experiments of the precursor show a shear thinning behavior at temperatures higher than the gel point, and temperature ramp rheology (rate = 1ºC/min) performed on the precursors shows that the gelation temperatures are T_{gel} = 29 and 33 ºC for SN and DN hydrogels, respectively. We tune the precursor flow rate (0.2-0.8 mL/min) as well as the precursor temperatures (22 ºC = T = 45 ºC) to obtain photopolymerized SN hydrogel fibers with various microstructures. The characteristic length scales of the colloidal microstructure are quantified using confocal microscopy and cryogenic scanning electron microscopy. The results show that local gradients in shear rates could be used to deliberately introduce microstructural variations in the manufacturing of composite soft materials, with applications such as hydrogel membranes, microfluidic platforms, and functional fibers. Additionally, we perform tensile mechanical measurements, which show that the incorporation of a second hydrogel network in the system increases the rupture stress, fracture energy and Young's modulus in DN hydrogels when compared to SN hydrogels.

Tuesday 11:05 Room 306C GG18

On the viscosity of adhesive hard sphere dispersions: Critical scaling and the role of rigid contacts

James Swan[1] and Gang Wang[2]
[1]Chemical Engineering, MIT, Cambridge, MA 02139, United States; [2]MIT, Cambridge, MA 02139, United States

The viscosity of colloidal dispersions is a highly sensitive function of the microstructure of the dispersion and the nature of the interactions among the particles. While the viscosity of solutions of colloidal hard spheres is well understood, the viscosity in a broader array of colloidal solutions remains poorly studied. Here, we use immersed boundary simulations to investigate the viscosity of a prototypical colloidal solution, adhesive hard spheres, which under the right conditions can percolate to form sample spanning networks. We examine how rigidity of the particle-particle contacts in these dispersions can enhance the dispersion viscosity. By rigidly constraining a fraction of the adhered particles, we establish a reaction coordinate, the extent of rigidity, along which we can track the development of a gelled state characterized by a diverging viscosity. The fraction of rigid bonds is analogous to the extent of reaction for cross-linking in chemical gels, which suggests a close connection between chemical gelation with polymers and physical gelation with adhesive hard spheres. A critical gel point is identified when particles connected by rigid bonds begin to percolate the sample. In the vicinity of critical gel point, we observe a diverging viscosity and critical scaling behavior in agreement with previous studies on adhesive hard spheres. We use these results to formulate empirical equations for the viscosity across a broad range of volume fractions as a function of the extent of rigidity. Most importantly, through these simulations, we show that rigid constraints among the bonded particles are essential to producing the large viscosities measured experimentally in dispersions of adhesive hard spheres. Hydrodynamic interactions alone are insufficient for reproducing experimental observations.

Tuesday 11:30 Room 306C GG19

Anisotropic self-assembly and percolation of nanoparticles in nanoparticle-incorporated supramolecular hydrogels

Jake Song[1], Mehedi H. Rizvi[2], Jan Ilavsky[3], David Mankus[4], Joseph B. Tracy[2], Niels Holten-Andersen[1], and Gareth H. McKinley[5]
[1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; [2]Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, United States; [3]Advanced Photon Source, Argonne National Laboratory, Lemont, IL, United States; [4]Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, MA, United States; [5]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Nanoparticle incorporation has recently emerged as a novel strategy to control the mechanical rigidity of supramolecular hydrogels; however, the microstructural origin of the resulting mechanical reinforcement in such nanoparticle-incorporated supramolecular hydrogels (NISH) remains relatively unexplored. Here, we investigate this relationship by systematically incorporating metallic nanoparticles into a metal-ion-coordinated polymer hydrogel matrix. Using a combination of ultra-small-angle x-ray scattering, scanning electron microscopy, and oscillatory shear rheology, we show that the nanoparticles also participate in metal-coordination with the polymer matrix, and undergo preferential self-assembly within the hydrogel. We show that this self-assembly is anisotropic and hierarchical across multiple length-scales, which in turn leads to mechanical percolation at ultralow concentrations, as evidenced by the dramatic reinforcement of the viscoelastic properties of the supramolecular hydrogel. Surprisingly, we find that the presence of metal-ion/ligand coordination in the hydrogel matrix is essential to the low percolation threshold of the nanoparticle assembly: by occupying a substantial number of associating groups in the hydrogel, the metal ions stabilize the nanoparticle network from otherwise collapsing via precipitation. These results provide unique insights into the intriguing self-assembly behavior of nanoparticles that are incorporated into supramolecular hydrogels, and a rational way to engineer their mechanical properties through such means.

Tuesday Afternoon

Symposium TM
Rheometry: Advanced Techniques and Methods

Organizers: Joseph Samaniuk and Michelle Calabrese

Tuesday 1:30 Room 305A TM20

A filament stretching rheometer for in-situ X-ray experiment: Combining rheology and in-situ crystalline morphology characterization

Jessica Pepe, Ruth Cardinaels, Gerrit Peters, and Patrick D. Anderson
Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands

During processing, polymers are subjected to various flow fields, consisting of both shear and extensional contributions. Whereas shear-induced crystallization has received substantial attention since decades, the effects of extensional flow on the nucleation, crystal structure formation and polymorphism are less known. This is mainly caused by the fact that suitable devices for the application of controlled uniaxial extensional flow combined with X-ray characterization are not available for the moment. We have designed and constructed a filament stretching rheometer that combines the possibility to perform in-situ X-ray experiments with a precisely controlled local uniaxial extensional flow. A homogeneous, uniaxial deformation of the sample with constant deformation rate is ensured thanks to a fast control scheme that drives the movement of the upper and bottom plate based on laser micrometer measurements of the smallest diameter[1]. The rheometer has a temperature-controlled oven with the ability to reach 250°C and to use an inert gas to avoid degradation of the sample. The oven has four ad-hoc windows: two glass windows for laser access and two kapton windows for X-ray access. The key feature of our in-house developed rheometer is the fixed location of the midfilament position, possible because of the simultaneous movement of the two end plates. This can be perfectly aligned with the laser micrometer and the incoming X-ray beam in a synchrotron radiation facility, allowing us to investigate structure and morphologies developed during extensional flow. The rheological response measured with our rheometer for a low density polyethylene (LDPE) is in agreement with the linear viscoelastic envelope and with the results obtained from commercial extensional rheometers. To demonstrate the capability of the instrument we have performed in-situ time resolved X-ray experiments on flow-induced crystallization of LDPE.

[1] J.M. Romám Marín et al., Journal of Non-Newtonian Fluid Mechanics 194 (2013) 14-22

Tuesday 1:55 Room 305A TM21

Measurements of yield stress materials using 3D printed fractal vanes

Crystal E. Owens, Anastasios J. Hart, and Gareth H. McKinley
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

We design and print a family of novel vane tools that combines desirable features of the standard 4-arm vane and cylindrical bob into a hybrid fractal structure. These vanes, produced by stereolithographic (SLA) 3D printing, has a more axisymmetric stress distribution than the 4-arm vane, less material damage/displacement upon sample loading than the bob, and help eliminate wall slip. Meanwhile, SLA permits creation of intricate structures with resolution <200μm on tooling >5 cm in size, with print-to-print repeatability <30μm, from materials having wide chemical compatibility and good mechanical stability. We discuss principles for design optimization for a given sample in terms of displaced material volume and stress homogeneity, showing fractal designs by tuning the number of vane arms. We add a 3D printable self-centering cup with ribbed inner surface (and solvent trap) to complete the vane-in-cup geometry.

Furthermore we develop and validate a torque-to-stress conversion equation for fractal vanes with 4-24 arms. Applying this equation to several printed vanes, we show that we can measure the viscosity of Newtonian silicone oils (10-1000mPa.s) within 8% of reference values from cone-and-plate tests. We also measure the stress-strain rate flow curve of a simple yield stress fluid (Carbopol) within 5% (or within 0.2% for a 24-arm fractal vane), showing that these fractal designs are useful, not just made in vain. Finally, we use the optimal fractal vane for measuring transient stress growth measurements on a series of complex thixo-elasto-viscoplastic materials including a jammed emulsion (mayonnaise), an alkaline battery slurry (pH=12), and a multicomponent fibrous dispersion (tomato ketchup).

Tuesday 2:20 Room 305A TM22

Making rheology fun again – case studies in practical rheometry

David J. Moonay
Quality, Brookfield Ametek, Middleboro, MA 02346, United States

This paper discusses new tools for rheologically analyzing various materials. Understanding flow behavior is important in numerous industries because it helps optimize processing. It is also critical to providing products that satisfy end-user demands. The behavior may range from simple to complex, corresponding to material structure ranging from homogeneous to highly heterogeneous. Data are provided for various products, in case studies involving different rheometry tools and methods.

Tuesday 2:45 Room 305A TM23

Elastic and viscoelastic characterization of gellan gum microcapsules and the effects of aging

Yun-Han Huang[1], Fleur E. Salmon[2], Abhijeet Kamble[1], Xu Xu[1], Mariano Michelon[3], Bruna C. Leopercio[3], Marcio S. Carvalho[3], and John M. Frostad[1]

[1]University of British Columbia, Vancouver, BC V6T1Z3, Canada; [2]Chemical Engineering, École Nationale Supérieure des Ingénieurs en Arts Chimiques, Toulouse, France; [3]PUC-Rio, Rio de Janeiro 22451-900, Brazil

Tunable microcapsules have a wide range of applications such as functional food, drug delivery vehicles, and models for cells. Because these applications involve the microcapsules undergoing forces and deformations, it is necessary to understand their mechanical properties to optimize the design and maintain their integrity. In this research, we present the elastic and viscoelastic characterization of gellan gum microcapsules using a cantilevered-capillary force apparatus (CCFA). The microcapsules are composed of a sunflower oil core and a gellan gum shell. The CCFA is capable of providing axial deformation to individual colloidal particles, and direct and dynamic measurements of force. We further characterized the viscoelastic properties of the microcapsules by applying a sinusoidal axial strain. Finally, we quantify the loss of capsule integrity by changes in the mechanical properties over time.

Tuesday 3:45 Room 305A TM24

How to produce unbiased experimental results for time-dependent materials: Pre-shear with strain recovery

Jiho Choi and Simon A. Rogers

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

Most traditional pre-shear protocols can be classified into one of two classes based on the manner by which mechanical energy is added: one-directional shear and oscillatory shear. Residual stress after pre-shearing can occur as a result of both steady and oscillatory shearing. This residual stress, which can be small, can be a manifestation of unrecovered elastic strain. This residual stress and unrecovered elastic strain are caused by unwanted structural anisotropies. If structural anisotropy exists in the system, the interpretation of any subsequent experimental results must be modified to reflect the complex material state. Here, the criteria for an optimal pre-shear protocol for time-dependent materials are suggested. An optimal pre-shear should: (1) lead to a state of zero residual stress and zero recoverable strain, (2) lead to a material state that has rheological responses that are independent of the choice of shearing direction, and (3) not induce an irreversible (chemical or physical) change in the material. It is experimentally shown that addition of strain recovery step to traditional one-directional pre-shear guarantees not only repeatability, but also unbiased experimental results by comparing positive and negative directions of fixed shear rate with thixotropic fumed silica suspension. This result has implications for determining model parameters for thixotropic and aging materials when it is assumed the experiments are carried out on unbiased isotropic structures. Further, we apply pre-shear with strain recovery to traditional experiments such as frequency sweeps and the generation of flow curves. Traditionally, data points in those tests have been measured consecutively, but we apply our new pre-shear before measuring every single point of trajectory in separate manner. This method enables us to separate the effects of different shear histories.

Tuesday 4:10 Room 305A TM25

Weakly-nonlinear viscoelastic rheometry

Randy H. Ewoldt[1], Luca Martinetti[1], Olivia Carey-De La Torre[1], Piyush K. Singh[1], Kenneth S. Schweizer[2], Irene Natalia[3], and Erin Koos[3]

[1]Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [3]Soft Matter, Rheology and Technology Section, KU Leuven, Leuven, Belgium

Weakly-nonlinear excitations are a fundamental characterization technique used in optics, acoustics, heat transfer, and other fields, but rheometry methods have comparatively lagged in this area. Here we describe our work to develop a paradigm of weakly-nonlinear viscoelastic rheometry that has allowed for experimental and theoretical advances with significant implications for microstructure inference and insight. For example, recently our group collaborated [1] to use MAOS measurements with a novel asymptotically-nonlinear viscoelastic model and the Polymer Reference Interaction Site Model (PRISM) to settle a 70-year debate and infer the nonlinear mechanisms of a reversible polymer network. Application to different soft matter microstructures demonstrates that the weakly-nonlinear regime is a type of "sweet spot," nonlinear enough to provide additional information, but still amenable to theoretical predictions. This is demonstrated with our work on transient polymer networks, polymer melts, soft glassy colloidal suspensions, and capillary suspensions which show anomalous power law scaling. Our recent developments in MAOS make it easier for experimentalists to generate new observations, which in turn provides theorists more opportunities to derive statistical mechanical theories to relate structure to rheology based on the weakly-nonlinear viscoelastic behavior of materials.

[1] Martinetti, L., O. Carey-De La Torre, K. S. Schweizer, and R. H. Ewoldt, "Inferring the nonlinear mechanisms of a reversible network," Macromolecules, 51 (21), 8772-8789 (2018). https://doi.org/10.1021/acs.macromol.8b01295

Tuesday 4:35 Room 305A TM26

Rheological behaviour of wax networks in crude oil

Pooja Saxena, Ankita Jain, Vinay A. Juvekar, and Jyoti R. Seth
Chemical Engineering, Indian Institute Of Technology, Mumbai, India

Crude oil is a mixture of largely organic molecules such as paraffins, asphaltenes and resins. It has a complex phase diagram. For example, asphaltenes may be either dissolved or dispersed as aggregates. Waxes too, may be either dissolved or suspended as crystals. Further, asphaltenes aggregates act as nuclei for crystallisation of waxes. So in a crude oil containing asphaltene aggregates, waxes crystallize at a higher temperature than one in which asphaltenes are well dispersed. This is important because, as more waxes crystallize, the viscosity of crude increases. In some cases, a large enough concentration of waxy solids may form a network, congealing the oil and blocking the pipeline. To prevent pipeline blockage, either the pipeline is kept heated, or more often, polymers known as pour point depressants (PPDs) are dosed in small quantities. These PPDs prevent formation of network and assure continuous flow. But, due to the inherent complexity of the materials involved, the mechanism by which PPDs function is not clear and selection of PPD or its dosage is largely made by trial and error.

In this study, the effect of a few commercial PPDs on the process of wax nucleation and growth has been tested on model oils containing waxes and asphaltenes. The effect of PPDs on wax nucleation, growth and network formation has been observed using a temperature-controlled stage mounted on a microscope. Corresponding rheological measurements have been performed while cooling at a prescribed rate. Based on these experiments, different mechanisms have been identified: (i) delay of nucleation, (ii) promotion of nucleation, (iii) slower growth of crystals, and (iv) change in shape of wax crystals. Finally, with the objective of predicting the effect of PPD on strength of network, observations from visualisation are correlated with rheological measurements of gelation temperature, shear modulus and yield stress.

Tuesday 5:00 Room 305A TM29

Stress relaxation and the exponential data-fitting problem

Sachin Shanbhag
Sachin Shanbhag, Florida State University, Tallahassee, FL 32306, United States

The exponential data fitting problem pervades several branches of science and engineering, including extraction of relaxation spectra from stress relaxation experiments. Despite their abundance, most published methods have not been made available as easy-to-use software. An open-source computer program (pyReSpect) is described; it relies on Tikhonov regularization to determine the continuous spectra, and a new robust algorithm to determine a parsimonious discrete spectra. The algorithms are validated using data generated from synthetic spectra, and tested on stress relaxation signals drawn from polymers of different architectures (stars, binary linear blends, rings) and sources (theory, simulation, experiment). Overall, pyReSpect is an excellent choice to obtain the discrete spectrum from stress relaxation experiments, when the number and placement of modes is not known in advance.

Tuesday 5:25 Room 305A TM28

Calculation of molecular weight distribution using fixed point iteration method from linear viscoelastic model of monodisperse polymers

Junghaeng Lee and Kwang Soo Cho
Department of Polymer Science and Engineering, Kyungpook National University, Daegu, Republic of Korea

We are interested in an inverse problem, the calculation of molecular weight distribution(MWD) from linear viscoelasticity of polydisperse polymers. The calculation needs the followings: [1] A model for linear viscoelasticity of monodisperse polymer melt which involves the effects of molecular weight. [2] A mixing rule which gives the viscoelastic function of polydisperse polymer in terms of those of monodisperse polymers with different molecular weights and the disctribution of molecular weight. [3] An effective algorithm to calculate the MWD by soving the mixing rule. We adopted a precise phenomenological model instead of molecular model for easy conversion between relaxation and dynamic moduli. Solving the equation of the mixing rule is not easy because the MWD should not be negative and the calculation method should be stable for the errors imbedded in the data. Hence, we adopted the fixed-point iteration which has been invented by Cho and Park.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Tuesday 1:30 Room 304 SC20

Rheology of dense granular flows: The effect of particle and boundary properties

Farnaz Fazelpour, Zhu Tang, and Karen E. Daniels
Physics, North Carolina State University, Raleigh, NC 27607, United States

In the field of granular rheology, one of the most promising advances of the past decades has been the development of various nonlocal rheologies. One of these models is the nonlocal rheology model proposed by Kamrin and Koval. This model extends a local Bagnold-type granular flow law to include a Laplacian term governing the diffusion of fluidity via cooperative effects. It has been observed to successfully capture the dynamics of quasi-2D flows without the need to provide the details of every particle's dynamics, using just a single set of model parameters determined from

empirical experiments. In order for it to be successful as a modeling tool for realistic flows, the next step is to make predictions for particles with any particle shape/size, and correctly model the response to various boundary conditions. We perform experiments to study particles of three different shapes (circles, ellipses, pentagons) and of three different stiffnesses to explore their influence on the nonlocal rheology of granular flow. We find that the nonlocal and frictional parameters vary based on both particle shape and material, but the local parameter is consistent for many particle shapes. Finally, we identify how the roughness of the boundary changes both the flow and the interparticle forces using photoelastic force measurement.

Tuesday 1:55 Room 304 SC21

Modes of particle association in clay slurries

Mohammad Shoaib[1], Erin R. Bobicki[1], and Cruz Nestor[2]
[1]Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, ON M4Y1R5, Canada; [2]Thiele Kaolin Company, Toronto, Canada

As high-grade base metal resources become depleted, the processing of low-grade and complex ores has become necessary. Low-grade ores often contain problematic gangue minerals, such as clays. Clay mineral particles are anisometric and anisotropic with pH dependent surface charges. This results in several types of particle aggregates types in suspension which can increase the viscosity of slurries, reduce the efficiency of grinding and flotation circuits, and create challenges in dewatering and tailings management. To select the most sustainable and efficient mitigation option for mineral processing, knowledge of how clay mineral particles interact in slurries is required. In this research, we investigate the modes of clay particle association using small amplitude oscillatory shear (SAOS) rheology for two different clays, a swelling (bentonite) and a non-swelling clay (kaolinite). Effect of factors such as pH, pH modifiers, particle concentration have been studied. The results have been complemented with the recent AFM based edge and basal surface zeta potential measurements to understand the modes of association. The SAOS results are compared with the high shear rheology results. For the non-swelling clay, the high shear viscosity evolves exponentially as a function of storage modulus within linear viscoelastic region, however, similar relationship is not obtained for the swelling clay attributed to its swelling which impacts its shear viscosity more than the storage modulus.

Tuesday 2:20 Room 304 SC22

Connecting structure to bulk rheology in dense disordered solids

Larry Galloway[1], Xiaoguang Ma[2], Nathan C. Keim[3], Arjun G. Yodh[2], Douglas J. Jerolmack[4], and Paulo E. Arratia[1]
[1]Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States; [2]Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, United States; [3]Department of Physics, California Polytechnic State University, San Luis Obispo, CA 93407, United States; [4]Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, PA 19104, United States

How soft materials yield is a question of fundamental interest to material engineers and rheologists alike. Often, we model complex fluids from observations of the bulk response alone. However, it may be possible to predict material response by understanding the constituent particle interactions and their arrangements. This possibility is investigated here via experiments with a custom built Interfacial Stress Rheometer and densely packed monolayers of repulsive particles. The bulk rheology (G', G") is measured while simultaneously tracking the positions of up to 50,000 particles spanning the needle and the wall. Previous work has shown that yield of jammed monolayers is linked to non-affine motions of individual particle trajectories. Here, I will discuss recent findings that suggest bulk rheology of a colloidal monolayer can be related to particle motions and microstructural arrangements, which is quantified by excess entropy.

Tuesday 2:45 Room 304 SC23

Connections between bulk rheology and microstructure of dense granular flows at the flow-arrest transition

Ishan Srivastava[1], Leonardo E. Silbert[2], Gary S. Grest[1], and Jeremy B. Lechman[1]
[1]Sandia National Laboratories, Albuquerque, NM 87185, United States; [2]School of Math, Science, and Engineering, Central New Mexico Community College, Albuquerque, NM 87106, United States

Granular materials exhibit a dynamical transition between arrested and steady flowing states at a critical stress ratio. Although their simple-shear steady-state rheology is now well characterized, the transition itself is accompanied by interesting dynamical phenomena such as transient dilatancy, shear jamming and a non-trivial evolution of the granular fabric, most of which are not well understood. The transition is highly stochastic which makes its continuum modeling quite challenging. Additional complications are introduced by a dependence on loading paths, with important differences between transient rheology of shear-induced and compression/extension-induced flows. We demonstrate complex rheological scenarios that emerge at the flow-arrest transition of granular materials using discrete element simulations. The stochastic nature such transitions is highlighted. Using a standard rheological basis applicable to viscometric and extensional flows, connections between the evolution of granular fabric and bulk rheology are illuminated in various flow scenarios, thus providing significant microstructural inputs towards the development of rheological laws beyond steady state and simple shear granular flows.

Tuesday 3:45 Room 304 SC24

Self-organization and flow of rod-like colloidal particles with tunable interactions

Mohan Das and George Petekidis
Material Science and Technology, IESL-FORTH, University of Crete, Heraklion, Crete 70013, Greece

Introducing short-ranged attractions between rod-like colloidal particles leads to formation of various phases with rich structural and dynamical properties. At low volume fractions, colloidal rods with short range attraction undergo dynamical arrest leading to a liquid to solid like phase transition (gelation) of the suspension. Furthermore, at very high volume fractions they form gels with nematic ordering. Here we probe the kinetics of melting and gelation and the associated microstructural changes in a suspension of rod like colloids with tunable attraction. Silica rods (L = 4.5 µm, L/D = 10) grafted with poly - (dimethylaminoethyl methacrylate) brushes suspended in a pH = 8 buffer solution acts as the model system with tunable aspect ratio and attraction strength. The grafted polymer layer undergoes phase separation above the lower critical solution temperature (LCST) inducing interparticle attraction. Using dynamic time sweep measurements in the linear viscoelastic regime, we probe the kinetics associated with thermally induced dynamical arrest. Dynamic frequency sweep measurements capture linear viscoelasticity and internal relaxations approaching the arrested state arising from reversible phase transitions occurring above and below the LCST of the grafted polymer. Furthermore, we studied the yielding behaviour of different phases by a combination of dynamic strain sweep and step rate experiments. Confocal microscopy was also used to capture the microstructural changes that provided complimentary information corroborating the mechanical response.

Tuesday 4:10 Room 304 SC25

Characterization of rheological properties for both polydisperse and monodisperse colloidal rod systems

Shiqin He[1], Seth Lindberg[2], and Kelly M. Schultz[1]
[1]Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; [2]Corporate Engineering, The Procter & Gamble Company, West Chester, OH 45069, United States

Rheological modifiers are used to tune the rheology of products with the addition of a small amount of material. Hydrogenated castor oil (HCO), a fibrous polydisperse colloid is used as a rheological modifier in fabric and home care products. However, this polydisperse system can be inefficient because only some of the colloids meet the size requirement that imparts the desired rheology. In a monodisperse system, the aspect ratio has a narrow range enabling almost all colloids to contribute to rheological modification. In this work, we characterize monodisperse and polydisperse colloidal rod systems, polyamide (PA) and HCO, to quantify the change in rheological properties between these systems. We are also interested in whether PA can be a more efficient rheological modifier than HCO. Multiple particle tracking microrheology (MPT) is used to characterize the gelation of PA and HCO. In MPT, fluorescent probe particles are embedded into the sample and their Brownian motion is measured and related to rheological properties. Non-adsorbing polyethylene oxide (PEO) induces depletion interactions in the system to drive gelation. We measure these systems changing the concentration of the colloid, PEO and the stabilizing surfactant, linear alkyl benzene sulfonate (LAS). We first characterize gelation at a low colloid concentration (0.2wt%). By increasing PEO concentration, PA gels but HCO does not. Next PEO concentration is fixed and colloid concentration is increased. In these experiments, PA gels at a lower colloid concentration than HCO. In order to quantify this disparate gelation behavior, LAS concentration is tuned. In PA, high LAS concentrations stabilize the suspension and inhibit gelation. However, in the HCO system increasing LAS destabilizes the suspension and causes gelation. This work provides a road map to the design of products by providing the compositional dependent rheological modification over a large parameter space, thereby eliminating trial-and-error steps to achieve desired material properties.

Tuesday 4:35 Room 304 SC26

Settling of two spheres in a suspension of Brownian rods

Gaurav Kumar and Giovanniantonio Natale
Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, AB T2L2C7, Canada

Sedimentation of solids in complex fluids is of great interest in several industrial operations, e.g. oil and gas exploration where these fluids are used as drilling fluids. In these systems particles with characteristic lengths that differ of several order of magnitudes, interact. These interactions control the rheology of the whole system and consequently they affect the settling dynamics. As model system, we numerically investigate the settling of two rigid spheres in a dilute suspension of Brownian rods. The purpose of this study is to study the coupling between the settling of the spheres and the orientation of the nanoparticles affect the overall settling dynamics. The Brownian motion of the nanorods introduces a finite relaxation time in the suspending medium which is modelled as a continuum. Moreover, the suspending fluid can be considered thixotropic since the orientation state of the nanorods will always want to go back to its isotropic state. When the spheres are falling along their centerline, the spheres experience two contributions: (1) Newtonian drag force and (2) Non-Newtonian force due to the presence of Brownian nanorods. The interactions between the two settling spheres is evaluated as function of Pe, distance between the centers of the spheres and the spheres' diameters. An effective repulsion between the two spheres was observed when both spheres are of the same size. By changing the spheres' sizes, repulsive and attractive forces can also be obtained. These forces were calculated numerically as a function of center-to-center distance between them at different Péclet numbers (Pe) (0.001-10) when both were of same size. Also, a study was conducted when either of the particles was larger in size compared to another, keeping distance between them constant and forces were calculated as function of size of the particle again at different Pe.

Tuesday 5:00 Room 304 SC27

Quantitative understanding of sheared colloidal rods and the effect of particle size and flexibility

M. Pavlik Lettinga[1], Christian Lang[1], Christian Clasen[2], Jan k. Dhont[3], and Jan Hendricks[2]
[1]Physics and Astronomy, KU Leuven, Leuven, Flanders, Belgium; [2]Department of Chemical Engineering, KU Leuven, Leuven, Belgium; [3]ICS3, Forschungszentrum Jülich, Jülich, Germany

High-aspect-ratio colloidal rods are becoming increasingly important in a wide range of technological applications and products. In biology they constitute the frame of the cytoskeleton, in the form of F-actin and micro-tubular networks, while amyloids are responsible for e.g. Alzheimer disease. The mechanical response of complex fluids containing rod-like colloids is hugely affected by the particle dimensions and flexibility, though a direct relation has not been identified so far. The key to a bottom up understanding is to identify the role of rod morphology on the microscopic structural response to flow, underlying the macroscopic mechanical response. Here, we use a library of monodisperse bio-engineered viruses with variable length and stiffness, for which we determine the exact relation between structural and mechanical response by a combination of rheology and Small Angle Neutron Scattering, resolving the orientational ordering of rod-like viruses in the flow-gradient and the flow-vorticity plane [1]. This approach allowed us to quantitatively determine the length dependence of the zero-shear viscosity and shear thinning behavior, using a revised version of the theory developed by Doi, Edwards, and Kuzuu to rationalize the flow behavior. Furthermore, we identified the effect of flexibility, which diminishes viscosity at low shear rates and enhances it at high shear rates. The elongational viscosity of stiff rods obeys theoretical predictions, while it diminishes with flexibility [2]. Thus, this work establishes a fundament for understanding the non-linear flow behavior of more complex rod-like systems. This is demonstrated for mixtures of rods with different length, representing ideal bi-disperse systems, for which we can predict the zero shear viscosity and shear thinning for varying the stoichiometry of the mixture.

Tuesday 5:25 Room 304 SC28

Quantifying order in nonspherical colloidal systems with small-angle scattering

Patrick T. Corona[1], Kevin S. Silmore[2], Christian Lang[3], Lionel Porcar[4], M. Pavlik Lettinga[3], James Swan[2], L. Gary Leal[1], and Matthew E. Helgeson[1]
[1]Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States; [2]Chemical Engineering, MIT, Cambridge, MA 02139, United States; [3]Physics and Astronomy, KU Leuven, Leuven, Flanders, Belgium; [4]Institut Laue-Langevin, Grenoble, France

The orientation of nonspherical particles in flow leads to a nonlinear rheological response that, in turn, affects the flows that develop. Measuring orientation of such systems can be challenging, especially when the particles are on nanometer length scales. Small-angle scattering (SAS) is a powerful technique that enables the measurement of fluid nanostructure on length scales from nanometers to microns and under rheometric flows. However, scattering measurements are made in 'reciprocal-space' with no means to simply relate scattering spectra to 'real space' structure. Therefore, structural models must be employed to extract information about the changes to fluid structure. As the first step toward understanding the relationship between measured scattering spectra and microstructural ordering; we examine the case of dilute, nonspherical, axisymmetric cylindrical particles in Stokes flow for which the orientation probability distribution functions (OPDFs) may be predicted. Analytical solutions for the scattering from oriented particles are derived and combined with numerical solutions for the OPDF to yield the scattering spectra in a variety of flows. We compare the predicted scattering spectra to rheo-SANS experiments on dilute fd-virus dispersions, where the model predictions with zero adjustable parameters show excellent agreement with experiments. Finally, we present a general method for fitting OPDFs using experimental SAS measurements and a model of the fluid microstructure without prescribing a form of the underlying OPDF. This method is demonstrated through the extraction of OPDFs from rheo-SANS experiments on semi-dilute fd-virus dispersions, where models for the full OPDF do not yet exist.

Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Tuesday 1:30 Room 201 SM20

Investigation of the rheological behavior of polymer melts in equibiaxial elongational flows

David C. Venerus[1], Rebecca Mick[2], and Teresita Kashyap[2]
[1]Chemical & Materials Engineering, New Jersey Institute of Technology, Newark, NJ 07102, United States; [2]Illinois Institute of Technology, Chicago, IL 60616, United States

Equibiaxial elongational deformations, where a fluid element is stretched equally in two directions while it contracts in the third direction, occur in numerous polymer processing technologies that include film blowing, compression molding and foaming. However, because of the difficulty of generating rheologically controlled equibiaxial deformations in the laboratory, the rheological behavior of polymeric liquids in equibiaxial elongational flow is largely unexplored. Over the past 20 years, we have developed a novel rheological technique called Continuous Lubricated Squeezing Flow (CLSF) for generating equibiaxial deformations in complex fluids. The CLSF technique involves the squeezing of polymer samples between thin, low-viscosity liquid (lubricant) films; to our knowledge, it is the only experimental technique capable of generating large and homogeneous equibiaxial deformations in complex fluids. The CLSF technique overcomes the problem of lubricant film thinning that severely limits the more common Lubricated Squeezing Flow (LSF) technique. Here, we investigate the behavior of polymer melts with the goal of understanding the relationship between molecular architecture (molecular weight distribution and chain branching) on rheological behavior in equibiaxial deformations. This includes constant strain rate, step strain and creep deformation histories. Experimental results are also compared to predictions from molecularly based models for entangled polymer liquids.

Tuesday 1:55 Room 201 SM21

Using nonlinear extensional rheology to elucidate differences in long chain branching in commercial high density polyethylene

Nicolas J. Alvarez[1] and Samantha L. Morelly[2]
[1]Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States; [2]Drexel University, Philadelphia, PA, United States

The ability to engineer the rheological response of polymeric materials is of great interest to both academia and industry. Efforts in this area include blending polymeric architectures and molecular weights to achieve a prescribed linear and nonlinear shear response of the material. Unfortunately, the bulk of these efforts are trial and error approaches that afford little in the way of predictable processing conditions. Recent work from our group demonstrated the lack of correlation between linear shear response and nonlinear response of long branched chains, such as low-density polyethylene, in extensional flow. Since most processing flows are dominated by extensional flows, more work is needed to better understand the effects of formulation and long chain branching on nonlinear extensional viscosity. In this work, we examine four industrial high-density polyethylene (HDPE) samples in linear shear and nonlinear extension. Small amplitude oscillatory shear shows very little differences in the HDPE samples. Using the van-Gurp Plamen plot, we identify samples with long chain branching and make correlations to nonlinear extensional viscosity. When possible, the results are put into the context of molecular weight and polydispersity as reported by the supplier. We demonstrate the sensitivity of creep compliance and rate dependent strain hardening on long chain branching, average molecular weight, and PDI. Overall, extensional rheology is shown to be very sensitive to polymer formulation and with sufficient well-characterized samples could lead to predictive tools to engineer nonlinear rheological behavior.

Tuesday 2:20 Room 201 SM22

Intermolecular hooking in unentangled semidilute polymer solutions under extensional flow

Charles D. Young and Charles E. Sing
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Polymer solution dynamics and rheology are relevant to a wide range of processing methods including printing, coating, and electrospinning. Developing an understanding of the polymer conformational dynamics and the emergent material properties is challenging because of the interplay of hydrodynamic interactions (HI), excluded volume (EV), and topological constraints. This is particularly true when extensional flow is introduced, which strongly deforms the solution from its equilibrium structure. Using a new technique for rapid Brownian dynamics (BD) simulation, we investigate the transient conformational distributions of semidilute polymer solutions under startup and steady state planar extensional flow at concentrations approaching the entanglement concentration. We find that for moderate strain rates (Wi = 0.5-3.0), intermolecular hooks caused by topological constraints form significantly below the entanglement concentration. We characterize the probability of hooks forming at varying molecular weight, concentration, and strain rate. Finally, we quantify the effect of hooking on molecular properties, such as subpopulations in the ensemble average transient stretch and the coexistence of coiled and stretched conformations, as well as the solution stress.

Tuesday 2:45 Room 201 SM23

Nonlinear rheological behavior of unentangled poly(alkylstyrene) melts

Yumi Matsumiya and Hiroshi Watanabe
Institute for Chemical Research, Kyoyo University, Uji, Kyoto 611-0011, Japan

Nonlinear rheological behavior under uniaxial elongation was examined for unentangled melts of poly(alkylstyrene)s having nearly the same number of Kuhn segments per chain, $n_K \sim 35$. For the materials, η_E exhibited strain-rate-hardening and then strain-rate-softening on an increase of the Rouse-time based Weissenberg number Wi = 0.3. For the unentangled melts, the hardening was unequivocally related to the finite extensible nonlinear elasticity (FENE) of the chain, and the softening, to suppression of the FENE effect due to reduction of the segment friction ζ occurring for the highly stretched and oriented chain. Quantitatively, the hardening at intermediate Wi was stronger and the softening at higher Wi was weaker for the materials having longer alkyl side groups, which suggested that the magnitude of ζ-reduction depends on the chemical structure of the chains. For estimation of this magnitude, the FENE-PM model was modified for the ζ-reduction with an assumption that $\zeta(t)$ is fully determined by the chain stretch/orientation and thus by σ_E. This modified model was able to mimic the steady state σ_E data excellently, and to confirm the dependence of the ζ-reduction on the chemical structure of the chain. Nevertheless, the same modified model failed to mimic the transient stress growth and relaxation data on start-up and cessation of fast flow. Specifically, changes of ζ with time during the relaxation for large Wi were delayed compared to the model calculation. This result suggests that ζ is determined not only by the chain stretch/orientation at respective times but also by the transient changes of the stretch/orientation, with those changes vanishing in the steady state. The origin of this change of ζ with the transient changes of the stretch/orientation is discussed in relation to the local motion of the chain necessary for adjusting its friction to the changes of the stretch/orientation environment.

Tuesday 3:45 Room 201 SM24

Direct visualization of single comb polymer dynamics in semi-dilute solutions: Complex interplay of topology and concentration at the molecular scale

Shivani Falgun Patel and Charles M Schroeder
Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Topologically complex polymers such as branched polymers form the cornerstone of modern technology and advanced materials. Despite their increasing importance, our current understanding of the non-equilibrium dynamic behavior of these topologically complex polymers is limited and is largely based on and limited to bulk rheological and experimental scattering data, theories and simulations. Owing to their complex molecular architectures, comb-shaped polymers exhibit rich dynamic behavior that is not fully understood at the molecular level. To address this, we study the dynamics of single branched polymers in non-dilute solutions using single-molecule fluorescence microscopy (SMFM). In particular, we use a hybrid enzymatic-synthetic approach to synthesize DNA-based branched polymers (comb polymers) that contain a long backbone with multiple side branches grafted at various positions. The backbone and branches are dual-labeled to allow their long-time simultaneous but separate imaging. Following synthesis, we directly study the relaxation and transient stretching dynamics of single comb polymers in unentangled semi-dilute solutions of linear unlabeled polymers in extensional flow. These dynamics are then compared to the dynamics of comb polymers in ultra-dilute solutions, and linear polymers in non-dilute solutions. Interestingly, the dynamic behavior of comb polymers is markedly different in non-dilute polymer solutions, which reveals changes in molecular-scale dynamics due to chain branching and chain-chain intermolecular interactions. We further study the effects of background concentration and polymer topology on comb polymer dynamics in order to elucidate the non-equilibrium behavior of topologically complex polymers in hitherto unexplored concentration regimes. Overall, our work shows that single polymer dynamics can be used to provide a direct link between polymer microstructure and bulk rheological properties.

Tuesday 4:10 Room 201 SM25

Dynamics of bottlebrush polymers in dilute solution

Sarit Dutta, Tianyuan Pan, Matthew A. Wade, Dylan J. Walsh, Bijal B. Patel, Damien S. Guironnet, Ying Diao, Simon A. Rogers, and Charles E. Sing
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Bottlebrush polymers are a canonical example of hyperbranched polymers, characterized by a central backbone with numerous polymeric side chains grafted onto it. The presence of side chains endows the molecule with a thickness, forcing the backbone to adopt an extended conformation, resulting in a significant departure from the conformational behavior of the bare backbone. Such polymers have been studied widely in recent years for numerous applications, e.g. in photonic materials and soft elastomers. Here we present a study of bottlebrush polymer conformations in dilute solution using a combination of Brownian Dynamics and Monte Carlo simulations performed on a suitably parameterized coarse-grained bead-spring model. We present results that highlight the effects of backbone length, side chain length, and grafting density on the equilibrium static and near-equilibrium dynamic properties of bottlebrushes. We compare our simulation results with viscometric and light scattering measurements performed on well-characterized bottlebrush samples with poly(norbornene) backbone and poly(lactic acid) side chains. The simulations results are in good agreement with experimental measurements. Nevertheless, large scale simulations pose considerable computational challenge due to the large number of particles required to model a single molecule. To address this problem, we have developed a implicit side chain model of bottlebrushes based on a wormlike cylinder. Performing simulations based on a appropriately parameterized discretized version of the wormlike cylinder, we show that this model can adequately capture the large-scale conformational properties of these quantities over a wide range of side chain lengths and grafting densities.

Tuesday 4:35 Room 201 SM26

Relating solvent dynamics to the extensional viscosity of entangled polymer solutions

Thomas C. O'Connor[1], Austin Hopkins[2], and Mark O. Robbins[2]
[1]Harry S. Truman Fellow, Sandia National Laboratories, Albuquerque, NM, United States; [2]Physics and Astronomy, Johns Hopkins University, Baltimore, MD, United States

Polymer melts and solutions with the same entanglement Z have similar linear viscoelasticity but can exhibit qualitatively different behavior during nonlinear extensional flow. A popular explanation is that chains in oriented melts experience less friction then chains immersed in unoriented solvent. However, new experiments (Shahid et al., Macromol., 2019) contradict this view, showing the high-rate viscosity of PS solutions is independent of the orientation of solvent. Here, we use molecular dynamics simulations to determine the effects of solvent on the nonlinear extension of entangled bead-spring solutions. Solutions with the same polymer concentration and Z, but varying solvent oligomer lengths are deformed to steady state in uniaxial extension flows for Rouse Weissenberg numbers from 0.1-25. All simulated solutions approach the same high-rate viscosity, independent of solvent orientation. Unlike experiments, simulations allow us to independently adjust polymer concentration, Ne, and Z. We leverage this to design melts with the same Ne and Z as solutions while maintaining the same monomer interactions. These melts show the same rate-dependence in viscosity as the solutions without any solvent. Our results imply that neither the presence nor the orientation of oligomer solvents is essential to produce the nonlinear trends in viscosity often seen in entangled solutions. Instead, we explain them as cross-over from a Newtonian limit to a high-rate limit for aligned chains.

Tuesday 5:00 Room 201 SM27

Rapid simulation of semidilute polymer solutions

Charles E. Sing and Charles D. Young
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Solutions play a critical role in the processing of polymeric materials, in particular in coating, printing, and fiber spinning processes that rely on the ease of manipulating long-chain molecules using forces and flows. In most applications, the solution concentration is sufficiently high that polymer chains overlap and interact, and are thus in the so-called semidilute concentration regime. This concentration regime is computationally costly to simulate, especially when driven out-of-equilibrium by flows, due to the need to calculate hydrodynamic interactions between a large number of particles. We have developed a method to incorporate hydrodynamics into large simulations of linear polymers in planar elongational flow, which we validate against other established methods for polymer simulation. We then use this new method to efficiently simulate polymer dynamics in steady-state and start-up elongation to determine both averaged and bulk properties (polymer extension, extensional viscosity) as well as molecular conformation distributions. We also see evidence of polymer-polymer hooking during start-up elongation, which we expect to be examples of topological interactions that play a major role in rheological properties as polymer length and concentration increase. Ultimately, we are now able to use simulation to connect flow strength and type to molecular conformational features, enabling future studies in how material properties can be affected by processing flows.

Tuesday 5:25 Room 201 SM28

Non-homogeneous flows in entangled polymer solutions driven by flow-concentration coupling

Michael C. Burroughs, Matthew E. Helgeson, and L. Gary Leal
Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93101, United States

Models for entangled polymer solutions often assume that both the flow and fluid composition remain uniform during shearing. However, it is well-known that a coupling of viscoelastic and osmotic stresses drives flow-enhanced concentration fluctuations, which violates the uniformity of the fluid composition. A natural question is thus whether and how such concentration fluctuations can modify the underlying flow of the material. To address this, we study solutions of polystyrene and polybutadiene in a marginal solvent as a model system in which the osmotic compressibility, and therefore the degree of flow-concentration coupling, is varied with temperature. Simultaneous rheology, velocimetry, and microscopy measurements reveal a wealth of non-homogeneous flow behavior which occurs in systems exhibiting flow-induced heterogeneities in concentration. In some systems, flow-concentration coupling produces flow-enhanced local concentration fluctuations that drive a dramatic transient shear banding, in which the local shear rates within bands strongly oppose the geometrically imposed stress gradient. In other systems, steady state shear banding is observed that qualitatively resembles that found in other reports of shear banding in highly entangled polymer solutions. These experimental results are compared to the predictions of a recently developed two-fluid model that accounts for flow-concentration coupling with the Rolie-Poly constitutive equation. The results suggest significant departures from homogeneous flow can occur in highly entangled polymer solutions due to both local and nonlocal heterogeneities in concentration.

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Tuesday 1:30 Room 305B IN20

Numerical simulations of non-Newtonian fluids in melt processes

Nima Sharifi-Mood[1], Mo Masoudian[2], Petr Kodl[2], and Jean-Marie Marchal[3]
[1]Siemens PLM Software, Bellevue, WA, United States; [2]Siemens PLM Software, Nuremberg, Germany; [3]Siemens PLM Software, Louvain-la-Neuve, Belgium

Numerical simulations of non-Newtonian fluids are challenging due to the non-linear form of their constitutive equations and the highly coupled nature of equations associated with the stress and velocity fields. Viscous flow solver in Simcenter STAR-CCM+ is a highly parallel and scalable finite element based computational tool to simulate the flow behaviors of various non-Newtonian constitutive models. In particular case of viscoelastic fluids, equal order interpolation functions for all variables (pressure, velocity and viscoelastic stress component) and a combination of stabilization techniques (SUPG/PSPG/DEVSS-TG) were adopted to obtain a numerically stable and accurate solution for both classical and more recently developed viscoelastic constitutive equations. The parameters associated with these viscoelastic constitutive equations can be determined based on experimental rheometry data by means of the material calibration solver. This includes various non-linear shear and extensional flows along with Small Amplitude Oscillatory Shear (SAOS) tests in the linear regime. Next, an Arbitrary Lagrangian-Eulerian (ALE) method was developed to track the free surface flows in a number of polymer processing applications such as extrusion, co-extruison and film casting. All steps in setting up these simulations were performed completely with Simcenter STAR-CCM+.

Tuesday 1:55 Room 305B IN21

Viscosity control by percolation

Takashi Ochi[1], Junichi Aoki[2], and Hideaki Takahasi[3]
[1]Composite Materials Research Laboratories, Toray Industries, Inc., Masaki-Cho, Iyogun, Ehime 791-3193, Japan; [2]Prepreg Technical Dept., Toray Industries, Inc., Masaki-Cho, Ehime 791-3193, Japan; [3]Research and Development Planning Dept., Toray Research Center, Inc., Otsu, Shiga 520-8567, Japan

< Background > Viscosity control by using certain additives is a widely utilized technique to improve manufacturing process-ability and product quality. There are many methods for controlling the viscosity such as using certain additives. First approach is the addition of fine particles or fillers to improve the thixotropic property, however this method is difficult to obtain a homogeneous solution. The second, polymer additives (high MW, branched etc.) is a more convenient method, however this can cause an increase in viscosity through low temperature to high temperature regions. < Motivation & Objective > An additive with easy handling, viscosity control under certain temperature region and minimal influence of viscosity under low temperature was investigated, shown as Additive-A. The mechanism for this increasing in viscosity was investigated in this study. < Results & Discussion > Investigation showed that Additive-A does not cause reaction that lead to an increase in viscosity which was verified with DSC measurements. In detail, viscosity developments under heat with and without a curing agent was conducted. Both Additive-A mixtures (with and without curing agent) did not start to cure until 170 C. On the other hand, this system has threshold of the amount of Additive-A at 6 wt%. This threshold results in a mechanism known as "Percolation". The glass transition temperature (Tg) of Additive-A is high (155 C) compared to viscosity increase temperature (around 120 C). The rheological characteristics of Additive-A itself was investigated in more detail and it was revealed that Additive-A has a certain transition around 120 C which was not detected by DSC. Finally, we concluded that a certain amount of the additive can form a continuous structure acting as a kind of viscoelastic member to the whole system above 120 C, while this additive can also act as a rigid body under low temperature and does not affect the viscosity.

Tuesday 2:20 Room 305B IN22

Ultrasonication-assisted dispersion of cellulose nanocrystals: A comprehensive study

Mélanie Girard, Jason R. Tavares, and Marie Claude Heuzey
Polytechnique Montréal, Montreal, Québec H3T 1J4, Canada

Cellulose nanocrystals (CNCs) are bio-based nanoparticles with high mechanical strength, making them a promising candidate for polymer reinforcement. However, their high surface area induces strong interparticle forces, making the dispersion difficult. Probe ultrasonication is being widely used for this purpose, providing enough energy to break these interparticle bonds between particles in suspension. Ultrasonication is a complex process, and the role of each parameter is not fully understood. It seems important to fill this gap to implement a reproducible method for optimized dispersion results. Thus, experiments and modeling are compared in this work to shed light on fluid flow inhomogeneity and the presence of mixing/non-mixing zones. This inhomogeneity can affect the efficiency of dispersion and is influenced by the medium, the container geometry and the probe position. The modeling aspect of the ultrasonication process is carried out using a finite element software, allowing to easily change these parameters to study their influence on the local velocity field and on particle dispersion. Preliminary results evidence that for the same power, the mixing velocity is lower for a less dense and less viscous liquid, meaning that power should be proportionally increased to reach the same dispersion level. Container geometry impacts the mixing too, and larger non-mixing zones are obtained for larger beakers. Again, in this case, a higher power may be needed to achieve equivalent dispersion. In addition, if the probe is not close enough to the surface, there is a larger zone where there is no mixing. Thus, for each tested condition, it is possible to evaluate the homogeneity of the dispersion by comparing the non-mixing area size with the whole beaker size. The dispersion efficiency is then related to this information and the values of the velocity obtained with this process. In this specific presentation, we will discuss results on CNC dispersion in various Newtonian and non-Newtonian fluids.

Tuesday 2:45 Room 305B IN23

Shear-dependent structures of microfibrillated cellulose suspensions

Emily G. Facchine[1], Saad A. Khan[1], and Orlando J. Rojas[2]
[1]Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States; [2]Department of Bioproducts and Biosystems, Aalto University, Aalto, Finland

Understanding the rheology of cellulosic nanomaterials is critical to properly tailor their properties and processing conditions, as they increase in popularity as an environmentally friendly replacement for conventional materials. Aqueous suspensions of microfibrillated cellulose form weak physical gels at low concentrations due to entanglement and hydrogen bonding. These gels have complex structural properties that are directly dependent on their recent shear history. Herein we discuss the effects of "slow quench" and "fast quench" shear conditions on the suspension properties, where slow quench describes a treatment in which the suspension is subjected to shear rates in first increasing and then decreasing order, and fast quench describes two subsequent increasing shear rate sweeps. We look in detail at the different effects these treatments have on yield stress, viscosity, and structure elasticity. We assess the recovery of the network structure as a function of the breakdown conditions. These observations give detailed insight to the morphology of the floc-based structure and help quantify critical conditions that characterize the floc dynamics. The discrepancy of low-shear viscosity following fast quench and slow quench flow conditions, the critical window of minimum structure recovery following oscillatory shear conditions, and a two-step yield mechanism can all be related to a progression of floc structures from a percolated network through a log-rolling regime to a system of uniform, spherical flocs. Quantitative agreement is shown between these observed phenomena, with a critical stress value of 1.5 Pa which corresponds to the primary yield stress from elastic stress measurements as well as the onset of incomplete structure recovery and the dynamic yield stress from the slow quench flow curves. These behaviors and their parallel to documented systems make a case for a floc-based system morphology rather than a fibril-based interpretation, even though the suspension is an aqueous suspension of fibrils.

Tuesday 3:45 Room 305B IN24

Measuring the material properties of drying paint films through microrheology

Selwin Varghese[1], Reza Rock[2], Steven V. Barancyk[3], James F. Gilchrist[4], and Christopher Wirth[1]

[1]Chemical and Biomedical Engineering, Cleveland State University, Cleveland, OH, United States; [2]PPG Industries, Allison Park, PA, United States; [3]Coatings Innovation Center, PPG Industries, Inc., Allison Park, PA 15101, United States; [4]Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Multiple particle tracking (MPT) microrheology was used to quantify the transient material properties of drying thin films of model paint with variations in composition and concentration of rheological modifier. Model paint systems experienced strong convection during drying. Such convective fluid flow is potentially detrimental to the MPT measurement because deterministic motion is superimposed on the random fluctuations of probe particles form which rheological properties are calculated. Effects from convection were removed by both a de-drifting algorithm where mean displacements were subtracted from a particle's trajectory and also a relative mean-squared displacement (rMSD) algorithm that tracked fluctuations in separation distance rather than distance. Although there was a strong response in the MSD to drying even prior to correction of convection, experimental results revealed the de-drifting convection correction was more effective in appropriately characterizing material behavior as the model paint dried. However, we did find the inherent material properties of the fluid played a role in the effectiveness of the de-drifting algorithm on our experimental systems. Experimental results were paired with Brownian dynamics simulations to test the effectiveness of convection corrections for probes experiencing non-uniform and uniform convection.

Tuesday 4:10 Room 305B IN25

Tube rolling and tumbling of graphene oxide domains in shear flows

Minji Park and Heon Sang Lee

Chemical Engineering, Dong-A University, Busan, Republic of Korea

The time evolution of a director orientation is crucial for understanding the rheology and 3D structure of platelet dispersions. In graphene oxide aqueous dispersions, domains are formed in which the atomic membranes tend to orient to the same direction. The shape and physical properties of GO domains mainly depend on GO concentration, pH, ion concentration, and lateral size, and defects in the basal plane. We showed that the large GO domains were formed at low pH in a rest state and the GO domains were rolled up to form GO micro-tubes at low shear rate [1]. The tube-rolling was associated with vorticity alignment. The shear rate dependency of the size of microtubes was similar to that of the coarsening of textures in a liquid crystalline polymer. At a high pH, isolated GO domains were observed. The shape of the isolated GO domains is a flat ellipsoid. In this work, we employed the Leslie-Erickson theory in order to fit the stress evolution of GO dispersions during shear flow. Tumbling, twist-tumbling, kayaking, and wagging were examined for the possibility of motions in GO dispersions. We will discuss the effect of the shape of GO domains on the rotational motions of them at low shear rates.

[1] Ok, C. M., S. G. Kim, S. Y. Jeong, and H. S. Lee, "Tube-rolling and formation of mechanically robust micro-tube in graphene oxide aqueous dispersions during shear flow," Soft Matter, DOI: 10.1039/C9SM00564A (2019).

Tuesday 4:35 Room 305B IN26

Air entrainment through viscous fingering in drying colloid-polymer solutions

James F. Gilchrist[1] and Thitiporn Kaewpetch[2]

[1]Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; [2]Polymer Science and Engineering, Lehigh University, Bethlehem, PA 18015, United States

We study experiments of drying colloid-polymer films similar to those used in many chemical and pharmaceutical applications. While flow and drying stresses set the colloidal microstructure of these films, after this microstructure is set we observe various modes of air entrainment into the matrix following various capillary, viscous, and elastic modes of instabilities. In this system, Haines jumps, capillary fingering, and crack formation at the bottom surface of this film follow their general understood physical phenomena. However, the predominant mode of air entrainment at moderate polymer concentrations shows micron-scale viscous fingering reminiscent of the Saffman-Taylor instability, yet at length scales much smaller than expected. In controlled drying in periodic systems using the ordered porosity in colloidal crystals, the viscous fingers are highly ordered and scale with the particle size and porosity. The onset and structure of this instability is characterized and a semi-elastic model driving the instability may be responsible for the short wavelength of the instability.

Tuesday 5:00 Room 305B IN27

Electrokinetic instabilities in viscoelastic fluids with conductivity gradients

Le Song[1], Purva Jagdale[1], Liandong Yu[2], and Xiangchun Xuan[1]

[1]Clemson University, CLEMSON, SC, United States; [2]Hefei University of Technology, Hefei, China

Electrokinetic instabilities (EKI) have been increasingly studied in the past two decades because of their potential impacts on fluid and particle manipulations in microfluidic devices. However, current studies have been mostly limited to Newtonian fluids. In this work, we study the EKI in the co-flow of viscoelastic polyethylene oxide (PEO) solutions with distinct electric conductivities through a T-shaped microchannel. It is found that the addition of PEO polymer suppresses the electroosmotic flow and changes the fluid viscosity and conductivity of the background buffer solution. These changes together pose a significant effect on both the threshold electric field and the flow pattern of EKI. We also develop a three-dimensional numerical model to predict and understand the EKI. The predictions show a favorable agreement with the experiment results at low PEO concentrations. The increasing deviation at high PEO concentrations may be attributed to the enhanced fluid elasticity that is not considered in the current preliminary model.

Tuesday 5:25 Room 305B IN28

Experimental investigation of rheological effects on electroosmotic fluid flow in a contraction-expansion microchannel

Amirreza Malekanfard and Xiangchun Xuan
Clemson University, CLEMSON, SC, United States

Insulator-based dielectrophoresis (iDEP) exploits in-channel insulating structures to create electric field gradients for particle manipulation. Its performance is partially dependent on the control of electroosmotic flow of the suspending fluid. Current studies on iDEP devices have been focused primarily upon Newtonian fluids, even though many biological and chemical solutions are actually non-Newtonian fluids. We present in this work an experimental study of the fluid rheological effects on electroosmotic flow pattern in a typical iDEP microdevice, i.e., a contraction-expansion microchannel. We use four types of non-Newtonian fluids that have varying shear thinning and viscoelastic properties for an improved understanding of both their sole and combined effects.

Symposium SF
Surfactants, Foams, and Emulsions

Organizers: Reza Foudazi and Nick Alvarez

Tuesday 1:30 Room 306A *Keynote* SF20

Rheology as a tool to assess long term stability and robustness in formulation development

Jeremy N. Fowler
Formulation development, Syngenta, Greensboro, NC 27409, United States

Rheology is one of many tools used to design and evaluate industrial agrochemical formulations. Long term stability remains a particular challenge as formulators would like to predict years of stability from initial short term testing. Agrochemical formulations are generally high concentration multi-phase mixtures so theoretical descriptions of simpler systems typically do not apply to these non-ideal systems leaving experimental approaches as the more effective choice to explore their behavior. Combinations of active ingredients also often display time dependent behavior and change significantly over a period of several months or years making extrapolation risky or inaccurate. There are three main types of emulsions within agrochemical formulations: emulsifiable concentrates (EC), oil in water emulsions (EW), and the droplet phase found in suspoemulsions (SE). Designing and stabilizing EC and EW formulation differs in the time scale related to emulsion stability and shear history related to handling the formulation. The former will be made into an emulsion by a grower and used within a short period of time while the latter will travel through the supply chain as a fully formed emulsion, subjecting the microstructure to prolonged shear and highly variable temperature conditions. The emulsified phase of a suspoemulsion is difficult to design correctly because of potential to participate in complex failure mechanisms involving solid active particles, surfactants, and industrial rheology modifiers. Rheology is used widely in agrochemical development projects to better understand shear induced failure mechanisms and evaluate robustness of the final product.

Tuesday 1:55 Room 306A SF21

Direct investigation of solid-stabilized droplet deformation under shear flow

Max Kaganyuk and Ali Mohraz
Chemical and Biomolecular Engineering, University of California, Irvine, CA 92697, United States

Solid-stabilized (Pickering-Ramsden) emulsions are ubiquitously found in many applications including drug delivery, petroleum refining, and various consumer products. The use of colloidal particles, in lieu of surfactants, in their formulation leads to interfacial behaviors that can impact the rheology, stability, and processability of solid-stabilized emulsions. For example, colloids can exhibit nearly irreversible adsorption to a fluid interface. Particles can also possess strong capillary interactions along the interface, which are absent in surfactant-stabilized systems. Finally, the large excluded volume of particles, as stabilizing species, can strongly impact the volume fraction dependence of Pickering emulsion rheology. Therefore, further investigation into the rheology of solid-stabilized emulsions, and how it is impacted by the size of the interfacially active particles, is warranted. In this study, we directly examine the deformation of particle-coated droplets undergoing shear flow. Our experimental system consists of water droplets, stabilized with poly(12-hydroxystearic acid) grafted poly(methyl methacrylate) particles, dispersed within a continuous phase of poly(dimethylsiloxane). Single solid-stabilized droplets are isolated in a cone-and-plate geometry, utilizing a rheometer with a built-in counter-rotation stage. Each droplet is held at the plane of zero velocity, to facilitate its continuous imaging with confocal microscopy through the bottom glass plate. Stabilizing the droplets with different size particles, we are primarily interested in the effect particle size has on the droplet rigidity, or its interfacial rheology, and how the particle distribution on the interface of a deformed droplet may mediate its breakup under shear. From our observations on the simple case of an isolated droplet, we look to gain a more fundamental understanding of particle-laden interfaces and their impact on the behavior of more complex solid-stabilized emulsions.

Tuesday 2:20 Room 306A SF22

Nanodiamonds stabilized Pickering emulsions

Barbara V. Farias, Derek Brown, and Saad A. Khan
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States

Pickering emulsions, stabilized by particles adsorbed on the oil-water interface, are being considered for a wide range of applications including personal care products, pharmaceuticals, oil recovery and biomedical such as therapeutics, diagnostics, and imaging. They are often preferred over surfactants stabilized emulsions because of their enhanced stability, as the presence of the particles at the interface act as a physical barrier, preventing droplets coalescence. Literature studies of solid-stabilized emulsions are based on silica, clay, or polystyrene particles. In this work, we examine the use of nanodiamonds (ND), a relatively novel carbonaceous filler with high adsorption activity, small size (~30 nm), and large surface area to create Pickering emulsions. Using a model system consisting of isopropyl palmitate and water emulsions stabilized by hydroxyl functionalized nanodiamonds, we investigate the stability and rheology of these emulsions as a function ND concentrations and different oil to water ratios. We find all samples to exhibit gel-like features with the elastic modulus increasing with ND concentration. Measurement of yield stress using the elastic stress method reveals a similar trend. Optical microscopy reveals increasing ND concentration results in smaller droplet sizes for the emulsions, probably due to the greater availability of particles that can be adsorbed on the oil-water interface. This behavior is consistent with our rheological results of higher G' and yield stress with increased ND, as the presence of smaller droplets facilitate the formation of a more packed network as they are able to better fill the "voids" in the continuous fluid. Similar behavior is observed when the oil to water ratio is changed, with a decrease in droplets size, and formation of a stronger gel with higher yield stresses. The breakdown and recovery of the microstructure upon exposure to different shear is also examined.

Tuesday 2:45 Room 306A SF23

Structure-function relationship between surfactant and spray drift of emulsions

Brittany M. Rauzan, Abrin Schmucker, and Michael Bishop
Corteva Agriscience, Agriculture Division of DowDuPont, Indianapolis, IN, United States

Corteva Agriscience^{TM} is developing innovative solutions to meet customer and consumer needs for sustainable agriculture solutions, such as reducing off-target movement of crop protection products. Built-in drift reduction technologies can deliver robust reduction in off-target movement over a range of formulation types and application conditions. Spray solution physical properties and droplet size distributions are variably impacted by tank mix adjuvants, providing a framework for minimizing drift potential. We will highlight a fundamental study of emulsions to understand the structure-function relationship between surfactant, spray solution physical properties, and droplet size distributions. This robust characterization exemplifies how chemistry influences physical properties and therefore drift, which is leading to advanced crop protection solutions with reduced environmental impact.

Tuesday 3:45 Room 306A SF24

The effect of the surfactants, predissolved drop fluid and chemistry of the suspending fluid on the wetting of a surface by an emulsion drop

Suraj Borkar and Arun Ramachandran
Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S3E5, Canada

Spinodal theory of wetting of an 'immiscible' emulsion drop on a solid surface requires that a liquid bridge be formed, which connects the drop and the solid surface, and that this bridge moves laterally outwards to complete the spreading process. Here, we show that due to trace solubility of the drop phase in the suspending medium, dissolved drop phase can diffuse to the solid surface, and then nucleate and grow in the form of islands. Coalescence between the parent drop and one of the islands completes the wetting process. In this work, experiments were conducted with buoyancy-driven motion of glycerol drops in viscous suspending mediums, towards a plasma-treated SU8 (pSU8) substrate. Film drainage dynamics and wetting behavior were captured using Reflection Interference Contrast Microscopy (RICM). When drops of glycerol settled in a small molecule liquid, such as castor oil, towards pSU8, glycerol islands were found to nucleate and grow, albeit, barely resolvable using RICM. Moreover, coalescence and wetting were instantaneous upon contact between the parent glycerol drop and one of the islands, unlike our observations with the glycerol-silicone oil system. The addition of a non-ionic surfactant, Span 80, to castor oil at concentrations above the critical micellar concentration (CMC), caused dramatic nucleation of glycerol islands with a foam-like cellular structure. So, while the surfactant molecules compete with glycerol for adsorption on the solid surface, the interfacial tension is also reduced, thereby reducing the barrier for nucleation. Furthermore, a more industrially-relevant system was explored wherein castor oil was presaturated with dissolved glycerol, with Span 80 surfactants. For time scales up to an 1 hr, presaturation did not have any effect on the wetting mechanism, as mass transfer and island growth rates due to dissolved glycerol are weak.

Tuesday 4:10 Room 306A SF25

Manipulating the colloidal interaction in macro- and nano-emulsions

Hamed Salimi-Kenari and Reza Foudazi
Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States

The colloidal assembly is a major route to fabricate materials with tailored functionality. Compared to other conventional colloidal dispersions, nanoemulsions have unique rheological behavior due to nanoscale droplets and significant interdroplet interactions. In this work, we investigate the complex colloidal behavior of nanoemulsions by controlling the depletion attraction, electrostatic repulsion, and oscillatory structural forces within the semi-dilute and concentrated regimes. Therefore, the aggregation behavior, coalescence, and the structure-flow relationship of nanoemulsions are examined through flow curve and oscillatory shear measurements. We change the interdroplet interactions as a function of surfactant type and concentration for droplet sizes ranging from micrometer to nanometer. Therefore, the nature of the aggregation process and the cluster size distribution and its moments are investigated. In the studied range of surfactant concentrations, rheology of emulsions with narrow size distribution shows the flocculation and transition from colloidal gels to a glassy state. In contrast to the rheology of repulsive emulsions, by inducing the depletion interaction at a high concentration of surfactants, the attractive emulsions exhibit tenuous aggregation and gel behavior below the random close packing volume fraction.

Tuesday 4:35 Room 306A SF26

Controlling nanoemulsion self-assembly via thermoresponsive attractive and repulsive interactions

Li-Chiun Cheng, Seyed Meysam Hashemnejad, and Patrick S. Doyle
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States

Nanoemulsions are widely used in applications such as in food products, pharmaceutical materials and cosmetics. Moreover, nanoemulsions have been a model colloidal system due to their ease of synthesis and the flexibility in formulations that allows one to engineer the inter-droplet potentials and thus to rationally tune the material microstructures and rheological properties. In this project, we study a nanoemulsion system in which the inter-droplet interactions are modulated by temperature. At elevated temperatures, the non-monotonic increase of both attractive and repulsive interactions gives rise to a non-intuitive mode of droplet self-assembly, leading to interesting microstructures and rheological properties of the system. The underlying mechanism is obtained by carefully characterizing the nanoemulsion droplets and studying the interactions at the molecular level. Such mechanistic understanding also provides guidance to modulate the inter-droplet potential using another stimulus such as pH and ionic strengths. The control of the competition of attractive and repulsive interactions using external stimuli opens up the possibility to design complex nanoemulsion-based soft materials with highly controllable structures and rheological properties.

Tuesday 5:00 Room 306A SF27

Composition-dependent transition from viscoelasticity to viscoplasticity in a ternary liquid/liquid/particle mixture

Sachin S. Velankar[1], Junyi Yang[1], and Smedha Mohanlal[2]
[1]University of Pittsburgh, Chemical Engineering Dept, Pittsburgh, PA 15261, United States; [2]Sastra University, Thanjavur, India, Pittsburgh, PA 15261, United States

We consider ternary mixtures in which two species are simultaneously dispersed into a majority continuous phase liquid. One of the dispersed species is spherical particles, and the other is a liquid which is immiscible with the majority liquid. The two dispersed phases together constitute 30 vol% of the mixture, and the minority liquid wets the particles completely. We show that the rheology of such ternary mixtures changes qualitatively from viscoelastic to viscoplastic as the relative loading of the two dispersed species is varied. Mixtures that are dilute in particles (e.g. 1% particles and 29% minority liquid) are found to have a droplet-matrix morphology, with particles located inside the drops. As typical for droplet-matrix morphologies, such mixtures are viscoelastic due to the interfacial tension between the immiscible liquids. In contrast, mixtures with a high particle loading (e.g. 29% particles, 1% minority liquid), have a microstructure of a network of particles bound by menisci. Such mixtures are viscoplastic, i.e. flow appears only when a certain yield stress is exceeded. These changes in rheology with composition are examined using the specific example of strain recoil after cessation of shear. The microstructure during recoil is monitored by in situ optical microscopy. We show that the ultimate recoil decreases monotonically as the particle loading increases, whereas the mean retardation time for the recoil is non-monotonic. Recoil is slowest when the particle loading is comparable to that of the minority liquid. At this composition, the two dispersed phases form a combined phase with a very high particle loading, and the corresponding drops recover spherical shapes very slowly and often incompletely.

Tuesday 5:25 Room 306A SF28

Wall slip of direct and inverse emulsions: Origin of wall slip yield stress and slip layer thickness

Philippe Coussot[1], Xiao Zhang[1], and Elise Lorenceau[2]
[1]Université Paris Est, Laboratoire Navier, Champs sur Marne 77420, France; [2]LIPhy, Univ. Grenoble-Alpes, Grenoble, France

Foams, emulsions, concentrated suspensions and colloids, may glide along smooth solid surfaces, in the sense that the bulk material apparently moves as a rigid block for a stress lower than the yield stress. This effect may be used to facilitate the transport of products such as in food digestion, cosmetic sensory perception, coal water slurry in pipes, fresh concrete pumping over long-distance, removal of food debris and microbial films. Our aim is to precise the characteristics of wall slip below the yield stress, for various materials (direct and inverse emulsions) and surface characteristics. The wall slip characteristics are determined from long creep tests at different levels and from internal measurements of the velocity profile in capillary or Couette flow as determined by MRI. First we show that the "slip yield stress" is due either to edge effects in relation with evaporation then pinning around the line of contact, or to a kind of adhesion of the suspended elements along all the wall surface [1]. We then can explore the origin of the (adhesion) slip yield stress which, for a given material and surface type, appears to be mainly dependent on the roughness of the surface. We also show that for all our systems, below the yield stress, the relationship between the slip velocity and the shear stress (minus the wall slip yield stress) is linear [2]. Surprisingly, the corresponding value for the apparent slip layer (a few tens of nanometers) appears to be almost independent of the concentration (and thus, of the osmotic pressure), the droplet size and the surface state and roughness. Nevertheless, under elongational flow conditions (i.e. traction test), wall slip can still occur, with now a much larger apparent wall slip layer (around 10 microns) [3].

[1] X. Zhang et al, J. Rheol., 62, 1495-1513 (2018) [2] X. Zhang et al, Phys. Rev. Lett., 119, 208004 (2017) [3] X. Zhang et al, Phys. Rev. Lett., 120, 048001 (2018)

Symposium BB
Biomaterials and Biofluid Dynamics

Organizers: Xiang F. Cheng and Amanda Marciel

Tuesday 1:30 Room 306B BB20

Length scale dependent human mesenchymal stem cell remodeling of polymer-peptide hydrogels quantified using bi-disperse multiple particle tracking microrheology

John A. McGlynn and Kelly M. Schultz
Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Human mesenchymal stem cells (hMSCs) are integral to the wound healing process. They are recruited from the bone marrow and migrate to injured sites where they coordinate tissue regeneration. hMSCs remodel their surrounding extracellular matrix (ECM) during migration through the secretion of matrix metalloproteinases (MMPs). We encapsulate hMSCs in a well-defined hydrogel which is degraded at the peptide cross-linker by cell-secreted MMPs. This cross-linker reacts with 4-arm star poly(ethylene glycol) molecules end functionalized with norbornene to form a gel. We use multiple particle tracking microrheology (MPT) to measure the remodeling of a cell's microenvironment. MPT measures the Brownian motion of fluorescent particles embedded in the material. Previous work used MPT to characterize remodeling around migrating cells, however only one particle size was used. Cellular remodeling occurs on multiple length scales. On molecular scales, MMPs break individual cross-links while on the micrometer scale, cells protrude extensions and apply traction on the network to be motile. In bi-disperse MPT, two particle sizes are used to probe changes on different length scales. We characterize cellular remodeling in our hydrogel using 0.5 and 2 μm particles. When our material is degraded by enzymes in the absence of cells, the structural evolution of the material is independent of length scale. During cell-mediated degradation, the material is more degraded on the 2 μm scale than the 0.5 μm scale. We inhibit cytoskeletal tension and find that length scale dependent differences in degradation are no longer measured. Therefore, cytoskeletal tension is the source of the length scale dependent degradation. hMSCs remodel larger structures by pulling on surrounding material in order to migrate. These findings could provide insight into how hMSCs interact with more complex materials, such as bundles of myofibrils nested in muscle fiber, by quantifying how structures are remodeled at different length scales.

Tuesday 1:55 Room 306B BB21

Rheological characterization of coordinated physical gelation and chemical crosslinking in gelatin methacrylamide hydrogels

Ashlyn T. Young[1] and Michael Daniele[2]
[1]Biomedical Engineering, North Carolina State University, Raleigh, NC 27607, United States; [2]Electrical and Computed Engineering, North Carolina State University, Raleigh, NC 27695, United States

Three-dimensional scaffolds are a key element of tissue engineering, providing a physiologically similar environment where cells better maintain in vivo characteristics. Popular scaffolds, such as matrigel and collagen, are biocompatible and biodegradable, but are limited by processing temperatures, mechanical strength, and available chemistries. Instead, many groups are starting to use gelatin methacrylamide (GelMA). GelMA is photocurable, allowing rapid crosslinking to create unique shapes and structures, while also possessing native RGD groups for cellular adhesion and proliferation. The mechanical properties of GelMA are highly tunable by modifying available crosslinks during synthesis, though source material and thermal gelation effects have been poorly characterized. Herein, we investigate the rheological properties of GelMA synthesized from different animal sources, as well as the effects of temperature on scaffold mechanical properties, using a parallel plate rheometer. We found that gelatin from a porcine source has more available crosslinks compared to bovine and cold water fish gelatin, resulting in GelMA with a higher storage modulus at frequency ranges 0.1 to 10 Hz. Storage moduli can be further increased in porcine GelMA by taking advantage of thermal gelation. Physical thermoreversible bonds form when GelMA is cooled below gel point, which are 'locked in' by successive UV chemical crosslinking. This method creates gels with storage moduli an order of magnitude higher than chemical crosslinking or gelation alone. Furthermore, the highly elastic rheological properties of these gels are maintained with increasing temperatures (ranging from 4ºC to 50ºC). This allows precise photo-patterning of microstructures by crosslinking cell-laden GelMA after gelation at different temperatures, inducing different cellular behavior depending on the mechanical strength of the GelMA. This work will contribute to defining the available materials space for the engineering of 3D tissue constructs.

Tuesday 2:20 Room 306B BB22

Highly tunable short peptide hydrogels for biomedical applications

Lavenia J. Thursch[1], David DiGuiseppi[2], Nicolas J. Alvarez[1], and Reinhard Schweitzer-Stenner[2]
[1]Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States; [2]Department of Chemistry, Drexel, Philadelphia, PA 19104, United States

We have discovered a unique series of tripeptides that form strong hydrogels. Previous studies found that the tripeptide Glycine-Alanine-Glycine in a water and ethanol solution forms a strong hydrogel with a melting temperature around 36°C. The gel is composed of micron sized fibrils that

are highly entangled and volume spanning. These hydrogels have potential in biomedical applications as they are inexpensive to synthesize and biocompatible. This gel is of particular interest because it defies our current understanding of peptide aggregation mechanisms. This study seeks to understand the consecutive formation of aggregates, fibrils and gel network. We used rheology to investigate the structure formation and stability of the gel. We explored the tunability of the material for future development: the impact of ethanol volume, peptide concentration and temperature on the formation kinetics and strength of the gel have been studied. We show that the gel strength, formation kinetics and even melting point can be tailored by adjusting the ethanol and peptide concentration. We aim with this work to improve aggregation models and develop this novel material for biomedical applications.

Tuesday 2:45 Room 306B BB23

Chitosan-graphene oxide hydrogels and thin films - applications in drug delivery

Sai Geetha Marapureddy and Prachi Thareja
Chemical Engineering, Indian Institute of Technology Gandhinagar, Gandhinagar, Gujarat 382355, India

Hydrogels are 3D crosslinked network structures comprising of hydrophilic polymers holding water in the interstitial spaces of the network. Natural polymers are non-toxic, abundant, and cheap compared to the synthetic but the major drawback of a biopolymeric hydrogel is the lack of mechanical strength. Different organic and inorganic nanoparticles are added to reinforce the polymeric network to acquire the benefits of them. In this study, we investigated the effect of Graphene Oxide (GO) to improve the mechanical properties of biopolymer Chitosan (CH) - Glutaraldehyde (GA) hydrogels and thin films. GO, has a high surface area and density of carboxylic, hydroxyl and epoxy functional groups on its edges and basal planes increases the hydrophilicity and reactivity. GO is added to the CH matrix in various amounts and also chemically crosslinked by using GA. Our experimental results suggest that the oxy-functionalities of GO play a key role in modulating the mechanical strength of CH gels. The oxy-functional groups attach electrostatically with the -NH2 groups of CH results in the multifold increment in the storage modulus (G') of GO-based gels which are confirmed with FTIR characterization. G' value of 0.5 wt% GO comprised gel 7.2 times greater than the pristine. Oscillatory stress sweep studies indicated that the network of CH-GA yielded earlier after incorporating the GO due to an increase in the crosslinking density. Collapse and recovery studies conducted alternatively at 0.5 and 500% showed a 65% recovery in the G' of CH-GA gels whereas 35% recovery in CH-GA-GO gels. The morphology studies by FESEM shows the microporous structure of hydrogel. These nanocomposite hydrogels are cast as films and characterized with DMA, which shows 20 times more Young's modulus than the pristine chitosan which is in line with the observed rheological signatures. Drug delivery studies carried on these films showed an increased drug loading with the addition of GO and a restricted delivery due to the presence of GA.

Tuesday 3:45 Room 306B *Keynote* BB24

Revealing processability of structured fluids comprising biopolymers by microfluidics

Matthew Lynch[1], Yu-Jiun Lin[2], Norman J. Wagner[2], Eric M. Furst[2], and Christine Mourafetis[2]
[1]Corporate Functions, Procter & Gamble, Cincinnati, OH 45224, United States; [2]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Structured fluids are used in a variety of applications including freshening sprays, detergents, cosmetics, and medicine. In particular, yield stress fluids allow the suspension of materials such as encapsulated particles, emulsions, or hydrocolloids, but flow under applied stress to allow delivery by methods such as spraying, injecting, or topical application. Critically, after the dispensing of the materials, the thixotropic properties of the fluids allow subsequent recovery of the structure. Design such systems requires understanding of the history of the applied strain, extensional properties, and flow-induced alteration in these fluids. These properties are investigated in microfluidic devices that contain expansion and contraction elements for three different types for fluids: xanthan-konjac gum as a yield stress and shear-thinning fluid, polyethylene oxide (PEO) as a Boger fluid, and a Newtonian fluid. The flow behavior of these fluids is understood combined with bulk rheology measurements.

Tuesday 4:10 Room 306B BB25

Slime for defense – biophysical design principles in a marine environment

Katerina Rementzi[1], Lukas J. Boeni[2], Peter Fischer[2], and Dimitris Vlassopoulos[1]
[1]Institute of Electronic Structure & Laser, FORTH, Heraklion 70013, Greece; [2]IFNH, ETH Zurich, Zurich 8092, Switzerland

Hagfish are genetically one of the oldest living creatures on earth. Neither charming in appearance or their task they nevertheless brought their defense mechanism up to perfection during the last 150 million years. When attacked by predators, hagfish excrete a concentrated mucin - protein fiber solution, which forms within milliseconds a large body of slime. Although the slime consists out of vast amounts of water, the diluted mucin and fibers span a cohesive network eventually clogging mouth or gills of the predators and enabling the hagfish to escape. Here, we present both the rheological properties of the slime in defense and escape situations as well as the biophysical principles of slime formation in the saline marine environment [1, 2]. We show that the different rheological responses of the slime under shear and elongational flow lead to strain hardening under attack but shear thinning during escape, promoting the survival chances of the hagfish. Considering the slime as a complex polyelectrolyte, a fine-tuned interaction with the different ions present in seawater must be given to employ the full defense capability of the slime, i.e. the rapid unraveling and network formation of both mucins and skeins under charge screening conditions [3, 4]. By elucidating the molecular and biophysical design principles and their consequences on the rheological properties of the slime, we are able to provide guidelines for tailoring mechanical properties of other mucin-like polyelectrolyte systems.

[1] Böni LJ, Fischer P, Böcker L, Kuster S, Rühs PA: Sci. Rep. 6 (2016) 30371
[2] Böni LJ, Sanchez-Ferrer A, Widmer M, Biviano MD, Mezzenga R, Windhab EJ, Dagastine RR, Fischer P: ACS Appl. Mater. Interfaces 10 (2018) 40460-40473

[3] Böni LJ, Zurflüh R, Widmer M, Fischer P, Windhab EJ, Rühs PA, Kuster S: Biology Open 6 (2017) 1115-1122
[4] Rementzi K, Böni LJ, Fischer P, Vlassopoulos D: Soft Matter, submitted

Tuesday 4:35 Room 306B BB26

Tunable rheology and ultra-low interfacial tension of polyelectrolyte complex coacervates

Samim Ali, Debra J. Audus, and Vivek M. Prabhu
Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20877, United States

Complex coacervates formed between oppositely charged macromolecules such as synthetic polyelectrolytes, biopolymers, proteins, and DNA in aqueous media has gained great attention recently owing to their potential use as injectable drug delivery media, spreadable wet adhesives, and bioscaffold. Achieving such goals require a fundamental understanding of the phase behavior, rheology and interfacial tension of coacervate under different physicochemical conditions. This presentation will describe the relaxation behavior of coacervates by measuring viscoelastic spectra and zero-shear viscosities at varying temperatures, salt concentrations and molecular weights using a set of model polyelectrolytes. The relaxation dynamics probed over a wide timescale is analyzed using time-temperature-salt superposition (TTSS) principle and the sticky-Rouse model [1]. The rheological measurement is further combined with the retraction timescale of a deformed dilute drop generated in situ to estimate the ultralow interfacial tension of coacervate [2,3]. The effect of salt concentration, temperature and molecular mass on the interfacial tension will be further discussed and compared to available mean-field theory predictions.

REFERENCES: [1] S. Ali and V.M. Prabhu, Relaxation behavior by time-salt and time-temperature superpositions of polyelectrolyte complexes from coacervate to precipitate, Gels, 2018, 4 (1), 11. [2] S. Ali, M. Bleuel and V.M. Prabhu, Lower critical solution temperature in polyelectrolyte coacervates, ACS Macro Lett., 2019, 8, 289-293. [3] S. Ali and V.M. Prabhu, Characterization of the ultralow interfacial tension in liquid-liquid phase separated polyelectrolyte complex coacervates by the deformed drop retraction method, 2019, Under review with Macromolecules.

Tuesday 5:00 Room 306B BB27

Slow stress relaxation of transient-crosslinked biopolymer networks

Sihan Chen[1], Tomer Markovich[1], and Fred C. MacKintosh[2]
[1]Rice University, Houston, TX 77030, United States; [2]Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77030, United States

It is well established that the unbinding of crosslinkers enables transient-crosslinked biopolymer networks to flow at long times. A recent experiment, however, shows that exerting prestress on such a network leads to near solid-like viscoelastic response. In this talk I will propose a microscopic theory for the rheology of transient networks under prestress. We show that the solid-like dynamics naturally appears as a result of the coupling between the strain-stiffening of semiflexible polymers and the transient nature of the crosslinkers. Our theory predicts the scaling behavior of shear modulus over the whole frequency regime and quantitatively fits the experimental data. This theory may also explain similar slow stress relaxation previously found in living cells.

Tuesday 5:25 Room 306B BB28

Nonlinear Poisson effect in critical mechanical networks

Jordan L. Shivers, Sadjad Arzash, and Fred C. MacKintosh
Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77030, United States

Fibrous networks of stiff athermal biopolymers such as collagen, a major structural component of the extracellular matrix, have been shown to exhibit anomalously large apparent Poisson ratios, i.e. significant transverse contraction under small applied longitudinal extension. Here we show that this effect can be understood in the context of a macroscopic mechanical phase transition from a bending-dominated regime to a stretching-dominated regime at a critical applied extension controlled by the network connectivity. We measure this effect using a variety of 2D and 3D model network structures and propose a phase diagram governing the transition as a function of connectivity and strain.

Symposium GG
Out of Equilibrium Systems: Gels and Glasses

Organizers: Suzanne Fielding, Ran Tao and Rosanna Zia

Tuesday 1:30 Room 306C GG20

Universality of critical exponents in the neighborhood of sol-gel transition

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

The evolution of viscoelastic properties near the sol-gel transition is studied experimentally by performing oscillatory rheological measurements on two different kinds of systems: a colloidal dispersion and a thermoreversible polymer solution. While undergoing sol-gel transition, both the systems pass through a critical point where it forms the weakest space spanning percolated network. The approach towards the critical gel point is characterized in terms of divergence of zero shear viscosity (η_0) and subsequent appearance of the low frequency modulus (G_e). In the vicinity

of the critical gel state, the viscoelastic properties η_0 and G_e, exhibit a distinctive scaling behavior ($\eta_0 \sim \varepsilon^{-s}$ and $G_e \sim \varepsilon^{z}$) where ε is the relative distance from the critical point. Interestingly, the longest relaxation time diverges symmetrically on both the sides of the critical point as $\tau_{max} \sim \varepsilon^{\alpha}$. The critical exponents of the zero-shear viscosity and modulus are related to the exponents of the longest relaxation time by the hyper scaling law. Furthermore, the critical relaxation exponent evaluated from the scaling laws precisely agrees with the relaxation exponent obtained from the Winter criteria. The establishment of the scaling laws validates the presence of hierarchical structure in the colloidal gels at the critical point. The associated critical exponents show remarkable internal consistency and universality for different kinds of systems undergoing the sol-gel transition.

Tuesday 1:55 Room 306C GG21

Mechanical spectroscopy of alumino-silicate hydrogels during gelation

Bavand Keshavarz[1], Arnaud Poulesquen[2], Donatien Gomes-Rodriguez[2], Jean-Baptiste Champenois[2], Michela Geri[1], Crystal E. Owens[1], Thibaut Divoux[1], and Gareth H. McKinley[1]
[1]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; [2]CEA, France, Bagnols-sur-Cèze, France

Alumino-silicate hydrogels are widely used in different industrial applications. These gels are simply made from a class of alumino-silicate materials known as zeolite precursors. Mixing two solutions of sodium aluminate and an alkali-silicate together initiates a series of condensation and bond-breaking reactions leading to a relatively rapid process of gel formation. The rheological behavior of the mature gels that form after gelation show interesting power law signatures in the linear viscoelastic regime over a wide range of timescales and frequencies. However, due to the rapidly mutating nature of these gels in the vicinity of the gelation point, little is known about the temporal evolution of the mechanical properties during the gelation/curing process. We use the Optimally Windowed Chirp (OWCh) technique [1] to obtain the time- and frequency-resolved response from the material every three seconds. This novel method enables us to reduce the mutation number of the system substantially and obtain fast and precise measurements. Parallel to mechanical spectroscopy we also study the structural evolution of these gels using time-resolved SAXS/WAXS measurements. Using these methods we can explore the mechanical/structural evolution of the gel over a wide range of time and length scales. These results enable us to understand connections between the structure and power-law rheology observed in the mature gel and more importantly provide an accurate spatio-temporal record of the timescales and elasticity of the evolving network.

Reference: [1] Geri, M.; Keshavarz, B.; Divoux, T.; Clasen, C.; Curtis, D. J.; McKinley, G. H. Phys. Rev. X 2018, 8 (4), 41042.

Tuesday 2:20 Room 306C GG22

Stress relaxation of model PDMS vitrimers with neutral and ionic crosslinks

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

Polydimethyl siloxane (PDMS) networks were synthesized containing dynamic bonds which undergo associative exchange reactions. These "vitrimers" were made with different crosslinking densities ranging from 7 to 149 repeat units and are all rubbery (> 0.1 MPa storage modulus) at short times but can flow at longer times due to the dynamic bonds. The PDMS rubbers can be reprocessed multiple times, and because of the nature of the bonds the crosslink density does not change during the exchange process. For neutral PDMS vitrimers, the stress relaxation times show an Arrhenius temperature dependence which is a hallmark of this class of material. The activation energy for relaxation is determined and found to be nearly invariant with the molecular weight between crosslinks and similar to small molecule analogues. Upon conversion of a fraction of dynamic bonds to anionic sites (with a sodium countercation), stress relaxation times became supra-Arrhenius and decreased more rapidly with decreasing 1/T than anticipated. This is attributed to a competition between bond exchange kinetics, which accelerate upon heating, and modulus, which increases upon heating of a network and slows the exchange process. This unconventional rheological response will be discussed in the context of processing and related applications.

Tuesday 2:45 Room 306C GG23

Microfluidic filament thinning of aqueous fibrillar methylcellulose solutions

Athena E. Metaxas[1] and Cari S. Dutcher[2]
[1]Chemical Engineering and Materials Science, University of Minnesota-Twin Cities, Minneapolis, MN 55455, United States; [2]Mechanical Engineering, University of Minnesota-Twin Cities, Minneapolis, MN, MN 55455, United States

Methylcellulose (MC), a methoxy- substituted cellulose ether, is used in a variety of food, pharmaceutical, construction, and consumer applications due to its solubility in water at low temperatures. In addition to its low-temperature solubility, MC reversibly transitions to a turbid hydrogel upon heating or upon the addition of NaCl to the solution. The gelation phenomenon in aqueous MC solutions is due to the formation of a fibrillar network. While the small amplitude oscillatory and large amplitude oscillatory shear rheological behavior has been well characterized for many MC solutions, the extensional flow behavior is often more challenging to characterize. Capillary breakup extensional rheometry (CaBER) can be used to characterize larger molecular weight MC solutions. However, MC solutions with lower molecular weights, and therefore lower viscosities, CaBER cannot successfully resolve extensional properties such as the extensional relaxation time and extensional viscosity. Filament stretching using a cross-slot microfluidic channel is a promising method to resolve extensional properties of MC solutions at varying NaCl concentrations. The elastocapillary regime, which determines the extensional relaxation time and viscosity, emerges with the presence of NaCl. This behavior is attributed to the presence of fibrils in the MC solutions containing NaCl annealed at room temperature. The study of the extensional behavior of this already commercially relevant polymer enables new ways to process MC, such as fiber spinning and extrusion.

Tuesday 3:45 Room 306C GG24

Shear-induced gelation of charged liquid crystalline rodlike aggregates

Ryan J. Fox[1], Maruti Hegde[1], Amar S. Kumbhar[2], Samulski T. Edward[1], Louis A. Madsen[3], Stephen J. Picken[4], and Theo J. Dingemans[1]

[1]Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27514, United States; [2]Chapel Hill Analytical and Nanofabrication Laboratory, University of North Carolina at Chapel Hill, Chapel Hill, NC 27514, United States; [3]Dept. of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, VA 24061, United States; [4]Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands

We report the first example of discontinuous shear-thickening in liquid crystalline solutions of a rigid polyelectrolyte that forms rodlike aggregates. Under steady-shear, the shear stress in low viscosity nematic solutions diverges at large strains due to irreversible shear-induced gelation. From the critical shear rate, we determine a concentration scaling law for the rodlike aggregate length that is consistent with prior theory incorporating electrostatics. We investigated the gels with linear shear rheology and applied time-temperature and time-concentration superposition principles to generate a mastercurve spanning over 20 decades in frequency and 5 decades in moduli, confirming the long-lived network structure and sticky interactions of the shear-induced gels. The gels have low moduli in comparison with scaling theory predictions and an anomalous concentration scaling, which we rationalize by calculation of large distances between physical crosslinks. Structural characterization via small-angle X-ray scattering and scanning electron microscopy indicate that the shear-induced gels are composed of a highly heterogeneous structure connected via a network of locally aligned nanofibrils. Our observations indicate that a non-equilibrium, shear-induced phase transition drives divergent growth of nematic rodlike aggregates resulting in gelation.

Tuesday 4:10 Room 306C GG25

Small and large amplitude oscillatory shear behavior of physical and chemical PVA hydrogels

David Kogan and Moshe Gottlieb

Chemical Engineering, Ben Gurion University, Beer Sheva, Israel

Crosslinked poly (vinyl alcohol) forms mechanically stable hydrogels capable of imbibing a large amount of water or biological fluids. The biocompatibility, processing ease and mechanical properties of poly (vinyl alcohol) based hydrogel have encouraged significant research towards developing the materials for various biomedical applications. Poly(vinyl alcohol) hydrogels can be formed either by chemical crosslinking with glutaraldehyde or by freeze-thaw cycles during which cryogels are formed as a result of the freezing of PVA solution, storage in frozen state and subsequent thawing. In these cryogels, the linkages of three-dimensional network of polymer chains are formed through non-covalent interactions. Reaction induced evolution of viscoelasticity during gelation of semi-dilute poly (vinyl alcohol) (PVA) in aqueous dispersions was studied through rheological measurements in the linear and non-linear domains. These measurements are contrasted with the properties of the physical gels formed by the freeze/thaw cycles. The work primarily focuses on the effect of number of freeze/thaw cycle, concentration of the PVA cryogels and on the pH and crosslinker concentration in the case of chemically crosslinked hydrogels.

Tuesday 4:35 Room 306C GG26

Probe rheology simulations of polymer networks: Role of network structure heterogeneity

Rafikul Islam[1], Nestor Valadez-Perez[2], Tsutomu Indei[3], Jay D. Schieber[2], and Rajesh Khare[1]

[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79401, United States; [2]Chemical and Biological Engineering, Illinois Institute of Technology, Illinois, IL, United States; [3]Hokkaido University, Japan, Japan

We previously showed that viscoelastic properties of unentangled and entangled polymer melt systems can be quantified using probe rheology simulations. Application of the technique to polymer networks presents unique challenges arising from the relative size of the probe and the network mesh and the heterogeneity of the network structure. In this context, we have carried out probe rheology simulations of tetra-functional cross-linked polymer networks in both active and passive modes. The effect of relative size of probe and network mesh is elucidated for passive probe rheology simulations. For this purpose, probe particle motion was determined and then inertial generalized Stokes-Einstein relation (IGSER) was used to extract viscoelastic properties of the polymer networks. Furthermore, the effect of network structure heterogeneity on the measured viscoelastic properties is studied by performing active rheology simulations in different locations in the network structure. Our results are compared with the predictions from literature theories.

Tuesday 5:00 Room 306C GG27

Controlling viscoelasticity of phase change salogels via crosslinker geometry

Parvin Karimineghlani and Svetlana Sukhishvili

Texas A&M University, College Station, TX 77843, United States

Strength and reversibility of bonding between physical crosslinkers and polymer chains can strongly determine the ultimate gel mechanics. In this study, we report on controlling the strength of phase-change salogels via crosslinker geometry, functionality, and the density of functional groups in the polymer chain. Phase-change salogels consisted of polyvinyl alcohol (PVA) dissolved in an inorganic phase change material (PCM) - lithium nitrate trihydrate (LNH), crosslinked within temperature-responsive networks by hydrogen-bonding amine-terminated molecules. These systems demonstrated reversible temperature-controlled gelation in the temperature range from 15 to 37 oC. The effect of crosslinker geometry (linear vs. branched) and concentration on the gelation temperature was explored. Diethylenetriamine and a second-generation amino-terminated

dendrimer, G2, respectively, were used as linear and branched amines. Our results indicate that fewer total number of -NH2 groups is required to induce gelation in the case of the linear crosslinker due to higher localization of more homogeneous distribution of amino groups than in the case of branched crosslinker. With matched molar concentration of linear and branched crosslinkers, a slightly higher activation energy for crosslinker-polymer bond dissociation was found for the linear crosslinker as compared with the branched one in dynamic light scattering (DLS) and rheological studies. Finally, our findings revealed that density of -OH groups in polymer chain, regulated by the degree of PVA hydrolysis, is another important factor which controls the gelation temperature and gel mechanical properties.

Tuesday 5:25 Room 306C GG28

Fourier transform fatigue analysis in LAOS and LAOE

Valerian Hirschberg[1], Manfred Wilhelm[2], and Denis Rodrigue[1]
[1]Department of Chemical Engineering, Universite Laval, Quebec City, Quebec G1V 0A8, Canada; [2]Institut for Technical Chemistry and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe 76128, Germany

The stress response of mechanical fatigue testing on solid polymers (PS,PMMA, SAN, HDPE and Nylon 6) in oscillatory torsion or tension was analyzed via Fourier transform (FT) to determine fingerprints of continuous fatigue. The tests were done at room temperature with notched rectangular samples and visualized by a video camera. Large strain amplitudes were applied in shear (LAOS) and tension (LAOE), so the stress response was nonlinear, higher harmonics detectable and its time evolution could be analyzed via decomposition into linear (storage and loss moduli) and nonlinear parameters (higher harmonics). This analysis allows to better understand mechanical fatigue and failure by detecting specific events such as crack initiation and propagation and to predict the fatigue lifetime (cycle number to failure). Independent of the loading direction (torsion or tension), the linear parameters were found to decrease monotonically with time, while the $I_{3/1}$ intensity (amplitude of the third harmonic to the fundamental one) increased steadily until failure. After a transient regime, the parameters change linearly with the cycle number before failure onset. Two concepts for fatigue criteria and the fatigue prediction were established. First, the fatigue lifetime was found to follow a power-law function of the rates of change (slopes) of the linear parameters and $I_{3/1}$. Secondly, the integral of the nonlinearity Q_f ($Q = I_{3/1}/?_0^2$) was found to follow a power-law correlation with the fatigue lifetime. Additionally, the nonlinear parameter $I_{2/1}$ (amplitude of the second harmonic to the fundamental one) was found to be highly sensitive to the occurrence of (macroscopic) cracks. The time evolution of the linear parameters as well as of $I_{3/1}$ and $I_{2/1}$ are proposed as new criteria to predict failure and detect the onset of macroscopic cracks as these parameters can better determine safety limits under different types of solicitation.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Room 306 PL3

Rheology of gel networks: Softness, rigidity and failure

Emanuela Del Gado
Department of Physics, Georgetown University, Washington, DC 20007, United States

Soft matter (colloids, polymers, proteins...) often self-assembles into gels where rigidity emerges in diverse structures with a variety of mechanical features. Through the interplay between their microstructure with an imposed deformation, gels can be stretched, flow, squeezed or fractured, but controlling and being able to design such processes (think for example of soft inks for 3D printing technologies) requires a fundamental understanding that is still lacking. Interesting new insight into the emergence of rigidity and the role of the network topology can be gained through theoretical/computational approaches. I will give an overview of the novel insight gained into the aging, the uniquely wide-ranged viscoelastic spectra and the presence of a topologically controlled softness in gel networks. Such findings can help understand the nontrivial mechanical response of soft gels in different contexts, develop constitutive models and theories further, and design smart materials.

Symposium AM
Additive Manufacturing and Composites

Organizers: Jon Seppala and Samanvaya Srivastava

Wednesday 9:50 Room 305A AM1

An integrated experimental and computational approach to the design of thermoplastic polyurethane/graphene oxide nanocomposites with specific properties

Joao Maia[1], Chaitanya Danda[1], Tyler Schneider[1], Brandy Grove[1], Shaghayegh Khani[1], Ricardo E. Andrade[2], Guilhermino J. Fechine[2], and Leice G. Amurin[2]
[1]Macromolecular Science and Engineering, Case Western Reserve Univ., Cleveland, OH 44106-7202, United States;
[2]MackGraphe, Mackenzie Presbyterian University, São Paulo, SP 01302-907, Brazil

Graphene Oxide (GO) is known to impart enhanced mechanical behavior on polymer composites, but serious challenges remain that have prevented these materials from reaching their full potential, such as their inability to be processed at large scales, e.g., through compounding via twin-screw extrusion, while simultaneously achieving significant improvements in the mechanical properties, the latter being due to the difficulties in preventing exfoliated GO nanosheets from re-agglomerating upon processing and in inducing adequate levels of adhesion to the matrix polymer. Thermoplastic polyurethanes (TPUs) are multi-block copolymers consisting of hard and soft segments. The former (HS) are typically thermodynamically incompatible with the latter and phase separation occurs, with HSs forming domains that consist in either glassy or semi-crystalline regions that act as physical cross-links and provide stiffness and reinforcement, which makes them prime candidates for polymer/GO nanocomposites. In this work, we propose a new hybrid computational and experimental methodology to design TPU/GO nanocomposites with specific and much improved properties, achieving, in particular, major simultaneous increases in ductility and abrasion resistance, while not impacting rigidity relatively to the pristine TPU. In particular, we use Dissipative Particle Dynamics (DPD) to define the ideal combination of TPU type and GO degree of functionalization to achieve the desired structure and then generate said structure experimentally via twin-screw extrusion aided by recently developed Extensional Mixing Elements (EMEs) that are capable of inducing GO exfoliation during processing.

Wednesday 10:15 Room 305A AM2

Uniaxial extension of polymer nanocomposites with well-dispersed nanoparticles: The role of the adsorbed polymers

Ruikun Sun and Shiwang Cheng
Chemical Engineering and Material Science, Michigan State University, East Lansing, MI 48823, United States

In polymer nanocomposites (PNCs), polymers adsorbed onto the surface of nanoparticles form an adsorbed polymer layer. It is widely accepted that the adsorbed polymers significantly influence the rheological properties of the PNCs. However, the explicit role of the adsorbed polymers to the linear and nonlinear viscoelastic properties of PNCs remains to be explored. In this work, we performed uniaxial extension on a set of PNCs with well-dispersed nanoparticles to study the contribution of the adsorbed polymers to the macroscopic stress of the PNCs. At low nanoparticle loadings when the average interparticle surface-to-surface distance, d_{IPS}*, is larger than* $4R_g$*, the adsorbed polymers don't overlap, where* R_g *is the radius of gyration of the polymer. The influence of the nanoparticles to the tensile stress only shows up at* $W_{iR} > 1$*, suggesting the salient features of the interaction between the adsorbed polymers and the polymer matrix under deformation. At an intermediate loading when* $1 < d_{IPS}/2R_g < 2$*,* *the adsorbed polymers start to overlap. A higher tensile stress of the PNCs than the neat polymer can be observed even when the applied deformation rate is as low as* $W_i = 0.01$*, indicating the adsorbed polymer-adsorbed polymer contribution to the macroscopic stress. At high loading when* $d_{IPS}/2R_g < 1$*, the adsorbed polymers start to bridge adjacent nanoparticles and kinetic gelation emerges. The adsorbed polymer-adsorbed polymer contribution and the stress contribution from the bridging chains can be clearly distinguished by the nonlinear rheology. These results clearly unravel the roles of the adsorbed polymers to the linear and nonlinear viscoelastic properties of the PNCs, which is composed of the contributions from the adsorbed polymer-free polymer, adsorbed polymer-adsorbed polymer, and the polymer bridges.*

Wednesday 10:40 Room 305A AM3

Imaging the flow field of polymer nanocomposites by nanoparticle tracking velocimetry

Matthew Melton and Shiwang Cheng
Chemical Engineering and Material Science, Michigan State University, East Lansing, MI, United States

Adding nanoparticles to polymer matrix will significantly influence the flow behavior of the polymer nanocomposites (PNCs), leading to a strong nano-reinforcement effect. So far, there are no clear understandings on how the nanoparticles influence the flow field of the polymer matrix between two adjacent nanoparticles that are 10s - 100s nm away from each other. Consequently, the understandings of the nano-reinforcement of PNCs at the continuum level have not been achieved. In this work, we aim to provide a direct measurement of the flow field of PNCs of well-dispersed nanoparticles by nanoparticle tracking velocimetry through in-situ SEM. We show that the affine deformation assumption adopted in current constitutive equations of PNCs is only valid at the small strain limit. In addition, the influence of the nanoparticles to the strain field dies out at a distance much larger than the radius of gyration of the polymer matrix, Rg, suggesting an intriguing role of the adsorbed polymers. These results have laid out a foundation for the future development of the constitutive equations of PNCs.

Wednesday 11:05 Room 305A AM4

Viscoelastic properties of polymer nanocomposites with soft and hard nanoparticles: A comparison

Shiwang Cheng[1], Jie Yang[2], Zhen Yang[3], and Wei Yang[2]
[1]Chemical Engineering and Material Science, Michigan State University, East Lansing, MI, United States; [2]College of Polymer Science and Engineering, Sichuan University, Chengdu, China; [3]Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, United States

Polymer nanocomposites (PNCs) are important functional and structural materials in many applications of energy, environment, construction, and medication partially due to their high mechanical strength. However, PNCs with high modulus typically exhibit large zero-shear viscosity that turns out to be energy intensive in processing. In this work, we have designed and synthesized soft nanoparticles and compare the viscoelastic properties of polymer/soft-nanoparticle nanocomposites with conventional PNCs based on inorganic nanoparticles (hard nanoparticles). The linear viscoelastic measurements show PNCs with soft nanoparticles can exhibit comparable mechanical reinforcement with conventional PNCs based on inorganic nanoparticles. However, the zero-shear viscosity of the PNCs with soft nanoparticles is around 100-1000 times lower than the traditional PNCs. These observations indicate the stiffness of nanoparticles should be considered for future advanced PNCs design.

Wednesday 11:30 Room 305A AM5

In-situ photocuring and film characteristics of PDMS/zirconia polymer nanocomposites: Role of reactive vs. passive fillers

Ria D. Corder, Joseph C. Tilly, Richard J. Spontak, and Saad A. Khan
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States

The interactions between two functionalized zirconia nanoparticle fillers (one reactive, one passive) and a short-chain UV-curable PDMS in solvent are observed using dynamic photorheology. The effects of reactive vs. passive surface functionality, as well as UV intensity and nanoparticle loading on crosslinking behavior are examined. Both filled systems formed crosslinked networks at up to 85 wt% zirconia of total solids. The gel point displays a power law dependence on UV intensity for both systems at zirconia loadings of 0-85 wt%. The two systems exhibit similar rheological behavior up to the gel point at all filler loadings, indicating that surface functionality does not affect the mechanism of gelation. Nanocomposite films containing >75 wt% reactive zirconia have higher crossover moduli and ultimate gel moduli than films containing passive zirconia, suggesting that the reactive zirconia are being incorporated into the network structure via covalent bonding with PDMS. The ultimate gel moduli decrease with increasing filler content at constant total solids loading due to a dilution effect which lowers the effective crosslink density. We hypothesize that PDMS plays a larger role in the network formation at shorter times and the reactive zirconia is incorporated more slowly into the network. At high loadings of passive filler (>75 wt%), the resulting films appear opaque and have a significantly higher turbidity value as measured by UV-Vis than the reactive fillers, which maintain low turbidity values and high optical clarity with loadings up to 85 wt%. UV-Vis measurements of leached filler demonstrate that the reactive zirconia is incorporated into the network much more strongly than the passive filler, putting the turbidity measurements in agreement with the rheology. SEM micrographs of films containing both reactive and passive filler loadings of 25 and 75 wt% suggest that large-scale nanoparticle aggregation plays a role in the observed turbidity increase in films containing high levels of passive zirconia.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Wednesday 9:50 Room 304 SC29

Brittle solids collapse in simple liquid suspensions

Philippe Coussot and Diogo E. Andrade
Université Paris Est, Laboratoire Navier, Champs sur Marne 77420, France

Thanks to the existence of a continuous network of weak interparticle bonds in a liquid, various materials (flans, agar gels, waxy crude oils, snow, clayey soils, fresh concrete) are generally considered as soft breakable solids, without a clear idea of their behavior beyond this breakage. Here, with a model material of these systems, i.e. a waxy suspension, we show that, under the action of either a large stress over a short time or oscillating low stress (fatigue test), the initially solid network of these materials is broken and dispersed in the liquid, which makes them turn abruptly ("collapse"), and irreversibly, to a low viscous fluid. We explain the physical origin of this collapse and of the yielding properties of these materials through a complete structural (microscopy) and rheological characterization (elastic modulus, yield stress, flow curve) of these systems at different concentrations. It is shown that the yield stress value is associated to the bond breakage during the very small initial deformation after imposing a stress. We also show that when the wax concentration is varied from a low to a large value, the material behavior in the solid regime evolves from a brittle to plastic behavior, whereas its behavior in the liquid regime does not change significantly, and beyond some concentration shear-banding appears. This provides new perspectives for understanding the physical origin of the brittleness or plasticity of solid or pasty materials, provides materials and framework to simulate and explain natural catastrophic events such as landslides and avalanches, and renew the description of waxy crude oil rheology.

Wednesday 10:15 Room 304 SC30

Altering thickening shear rate of fumed silica slurries using spherical silica

Ehsan Akbari Fakhrabadi and Matthew Liberatore
Chemical Engineering, University of Toledo, Toledo, OH 43606-3390, United States

Understanding the behavior of particulate suspensions that shear thicken is essential to their potential in many commercial applications. Dilatancy makes shear thickening fluids unique candidates for liquid body armor and sporting protective clothing because of their adaptive stiffness and damping capabilities. However, shear thickening is not always beneficial. In printing and spray coating, shear thickening causes non-uniform distribution of ink and paint, or in chemical mechanical polishing, particle aggregation causes scratches. Order-Disorder transition, hydroclusters formation, shear-induced agglomeration, and presence of surface friction have been identified as key phenomena for the shear thickening behavior in particulate dispersions. In the present study, commercially available fumed silica suspensions exhibiting irreversible shear thickening at shear rates above 10,000 s^{-1} were used as the base material. Using a specialized experimental protocol with a parallel plate geometry at 30 to 50 micron gap to reach shear rates ranging from 100-200,000 s^{-1}, the impact of spherical silica particles on shear thickening of fumed silica suspensions was investigated. Spherical particles between 10 and 100 nm can increase the critical shear rate when thickening occurs. In addition, rheo-Small-Angle-Light-Scattering (SALS) at high shear monitors the formation of micrometer scale structures, which were observed in pure fumed silica suspensions.

Wednesday 10:40 Room 304 SC31

Rheology of graphene oxide suspensions on aqueous solution of Carbopol&#174

Lorena R. Moraes[1], Mônica F. Naccache[1], and Ricardo E. Andrade[2]
[1]Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22451900, Brazil;
[2]MackGraphe, Mackenzie Presbyterian University, São Paulo, SP 01302-907, Brazil

This work presents an investigation on the rheological behavior of graphene oxide (GO) suspensions on aqueous solution of Carbopol®. The use of nanoparticles in the development of smart fluids leads to excellent opportunities for different industries, and the use of graphene and its derivatives have gained notoriety in the last years. The use of GO in nanofluids have been investigated, however most of research used Newtonian fluids as the dispersed phase. Therefore, there is still lacking information in the literature regarding the rheological behavior of GO suspensions in non-Newtonian fluids. The aqueous solution of Carbopol is a transparent, non-toxic, viscoplastic fluid with rheological behavior well described by the Herschel-Bulkey model, but with elasticity below yield stress. In this work, the effects of the dispersion method, concentrations of GO and Carbopol, types of neutralizer and GO on the rheology of GO suspensions in Carbopol were analyzed. Steady and oscillatory shear flow tests were performed. The results show that the rheology of the suspension is not affected by the dispersion method. It was also observed that increasing GO concentration leads to lower viscosity and yield stress values, and lower levels of elasticity. This behavior is similar for lower and higher levels of Carbopol concentrations. Regarding the type of the neutralizer, the suspensions made with sodium hydroxide presented similar behavior of the suspensions made with triethanolamine. The results obtained using different types of GO, made by different synthesis methods, were also similar. pH measurements indicate that the suspensions become more acidic with increasing GO concentration, although there is no clear relationship between the pH and the yield stress values for the different dispersion methods and Carbopol concentrations. The results obtained will help to obtain better methodologies for the preparation of the GO suspensions in order to develop fluids with the desired rheology.

Wednesday 11:05 Room 304 SC33

Rheologically tunable graphene oxide suspensions – Influence of electrolytes and ultra-sonication time

Prachi Thareja[1] and Abhijeet Ojha[2]

[1]Chemical Engineering, Indian Institute of Technology Gandhinagar, Gandhinagar, Gujarat 382355, India; [2]Biological Engineering, Indian Institute of Technology Gandhinagar, Gandhinagar, Gujarat 382355, India

In recent years, GO has emerged as a promising material for energy systems devices, high surface area adsorbent, and a filler for enhanced thermal, mechanical and optical properties. We report aqueous suspensions of GO at a volume fraction (?GO) of 0.018 which form (a) free flowing liquid-like (b) fragile - gels (c) robust gels by the inclusion of electrolytes or/and varying the time of ultra-sonication. Rheology characterization of the suspensions is performed with flow curve, small amplitude oscillatory time and frequency sweep, and large amplitude oscillatory strain sweep measurements. The storage modulus (G') of all GO-electrolyte gels increases with an increasing concentration of electrolytes and follow the order GO-FeCl3 > GO-MgCl2 > GO-KCl > GO-NaCl > GO-LiCl > GO-NH4Cl. We believe that K+ and Na+ due to their larger ionic radii and smaller hydrated radii can neutralize negative charges on GO more efficiently by forming inner sphere complexes as compared to Li+ and NH4+, which leads to the formation of gels with higher G'. We also show that Mg2+ and Fe3+ ions can form both metal-oxygen bonds and outer sphere complexes, which explains the further increase in G' of the gels. Furthermore, the GO nanosheets with variable lateral dimensions are synthesized with ultra-sonication times of 30, 60, and 120 minutes. The ultra-sonication does not cause a significant variation of C/O of GO, however, leads to a decrease in the lateral dimensions of the GO nanosheets. Our results indicate that the increase in ultra-sonication causes the aggregation of GO nanosheets, causing an increase in G' GO-30 < GO-60 < GO-120. We observe gels in GO-30, GO-60, and GO-120 with [NaCl] and [MgCl2] = 10-1M. Independent of [NaCl] or [MgCl2], the G' for GO-MgCl2 suspensions are relatively higher than GO-NaCl suspensions. Also, at all [NaCl] or [MgCl2], G' decreases with the increase in time of ultra-sonication. The rheology results are interpreted with the aggregation mechanism of GO nanosheets.

Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Wednesday 9:50 Room 201 SM29

Strain hardening during melt stretching of PDLLA and PLLA: Effect of deformation-induced crystallization

Masoud Razavi, Xinyang Zhao, Ruchao Yuan, and Shi-Qing Wang

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

Entangled polymer melts can show different modes of failure during startup uniaxial extension. Depending on the applied rate, four different regimes i) flow, ii) tensile de-cohesion, iii) shear-yielding-induced necking, and iv) melt rupture.1 On the other hand, there is a possibility of crystallization during melt deformation of semicrystalline polymers at temperatures close to their crystallization temperature. In this study we compare the response of two grades of poly(lactic acid), PDLLA and PLLA as well as their blends to the large uniaxial extension, where the later grade has the ability to form crystals when it gets deform sufficiently, from amorphous state at the temperate window between glass transition (Tg) and cold crystallization temperature (Tcc). It is found that strain hardening builds up strongly upon induced crystallization.

1. Wang, S.-Q., Nonlinear Polymer Rheology: Macroscopic phenomenology and Molecular foundation. Wiley: Hoboken, NJ, 2018. This work is supported by NSF-DMR (1609977).

Wednesday 10:15 Room 201 SM30

In situ synchrotron x-ray scattering during extensional flow induced crystallization of PLLA enabled by tube expansion deformation

Karthik Ramachandran[1], Tiziana Di Luccio[2], Riccardo Miscioscia[3], Giovanni De Filippo[4], Giuseppe Pandolfi[3], and Julia A. Kornfield[2]

[1]Alkermes, Waltham, MA 02451, United States; [2]Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States; [3]Sustainable Materials, ENEA, Portici, Italy; [4]Photovoltaics and Smart Networks, ENEA, Portici, Italy

Motivated by the emergence of bioresorbable vascular scaffolds (BVS) as a promising alternative to metal stents for treatment of coronary heart disease [1], we constructed an instrument to study deformation-induced crystallization by imposing a uniaxial elongation on a subcooled polymer melt and recording synchrotron x-ray scattering patterns during and after a brief interval of deformation. The apparatus allows us to mimic a key step in BVS manufacture, stretch blow molding, that expands an initially nearly amorphous poly(L-lactic acid) (PLLA) extruded tube from an outer diameter (OD) of 1.5mm to 3.6mm (final wall thickness 150um). To date, a primitive estimate of the strain has been used (calculated from the transient OD assuming incompressibility). The results have been sufficient to reveal important features of the relationship among temperature, the strain rate (for a fixed total strain) and the rate and morphology of crystallization observed in real time, in situ [2]. The BVS that received clinical approval (2016) is, however, relatively thick (~150 µm, approximately twice as thick as metal stents ~80 µm). Thinner scaffolds would facilitate implantation and enable treatment of smaller arteries. The key to a thinner scaffold is careful control of the PLLA microstructure during processing to confer greater strength in a thinner profile. Ultimately we hope to connect thermal and flow history with structure and strength and to guide the design of thinner yet stronger BVSs.

[1] M.B. Kossuth, L.E.L. Perkins, R.J. Rapoza Interv. Cardiol. Clin. 2016, 5, 349. [2] K. Ramachandran, R. Miscioscia, G. De Filippo, G. Pandolfi, T. Di Luccio, and J.A. Kornfield Polymers. 2018, 10, 288.

Wednesday 10:40 Room 201 SM31

Shear flow-induced crystallization of poly(ether ether ketone)

Jiho Seo[1], Anne Gohn[2], Alicyn Rhoades[2], Richard Schaake[3], and Ralph Colby[1]
[1]Materials Science and Engineering, Penn State University, University Park, PA 16802, United States; [2]School of Engineering, Penn State Behrend, Erie, PA 16563, United States; [3]Engineering and Research Centre, SKF, Nieuwegein, The Netherlands

When a semicrystalline polymer melt is subjected to intense shear flow before crystallization, the crystallization rate is accelerated and the crystalline superstructure is transformed from spherulites into anisotropic structures, referred to as flow-induced crystallization (FIC). In this study, FIC is investigated with a commercial poly(ether ether ketone) under well-defined shearing conditions using a rotational rheometer and X-ray scattering. At a constant shear rate, the nucleation rate increases with the shearing time. As the shearing time is extended, shish-kebab patterns are monitored at lower shear rates. With a constant shearing time, the nucleation rate increases with the shear rate. The combination effects of shear rate and shearing time on the acceleration are investigated in terms of shear strain and specific work. For a constant strain, high shear rates with short shearing times enhance the nucleation rate greater than low shear rates with long shearing times. The specific work reduces all nucleation times, monitored under various shearing conditions, to a common curve. A flow-induced nucleation model is suggested based on the entropy reduction model of Flory.

Wednesday 11:05 Room 201 SM32

Slip-link modeling of a crystallizing entangled polymer melt

Marat Andreev and Gregory C. Rutledge
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States

Modeling of polymer processing is a subject of continuing industrial and theoretical interest. Many industrial polymer melts are entangled and undergo crystallization during processing. Experimental data for the rheology of crystallizing entangled polymers are available in a number of published studies on this topic. In the literature, suspension-based models have been used with considerable success to describe the evolution of the mechanical modulus at a given frequency during crystallization. Meanwhile, over the past few years, slip-link models have been demonstrated to be very capable for describing the rheology of entangled melts under a variety of non-linear deformation conditions, including shear, extension, and start-up. These models are attractive for their physically measurable parameters, and for their ability to represent distributions of composition, molecular weight and branching architecture. In this work, we present a modification of the slip-link model to capture the rheology of an entangled melt undergoing crystallization. Partially crystallized melts are represented by blends of linear or short-chain-branched chains with crosslinked, bridge-like chains that resemble the tie molecules between developing crystallites. The model simultaneously captures the evolution of viscosity and elasticity over the whole range of frequencies in the linear regime. Experimental data for several polymer chemistries, including industrial-grade materials, are well represented by this model. The model is able to describe effects of molecular architecture and molecular weight distribution. However, the main advantage of this approach is the capability to predict the effects of on-going crystallization during non-linear deformation.

Wednesday 11:30 Room 201 SM33

Effect of tungsten disulfide nanotubes (WSNTs) on flow-induced crystallization of polylactide (PLA) for new generation bioresorbable vascular scaffolds

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

Bioresorbable Vascular Scaffolds (BVS) are transient implants designed to substitute metal stents in providing mechanical support and drug delivery to the coronary artery to treat Coronary Heart disease (CHD). The only FDA-approved BVS is made from poly L-lactide to support an artery during the first critical 6 months from the implant but is completely resorbed in 2-3 years, overcoming complications associated with the permanence of metal stents. However, lack of radio-opacity and increased thickness respect to metal stents make BVSs challenging to implant and unable to treat smaller arteries. Towards thinner, radio-opaque devices, tungsten disulfide nanotubes (WSNTs) are studied as potential reinforcing agents of polylactide (PLA). Here, we examine WSNTs as they disperse well in PLA and may conferee radio-opacity to the scaffold similarly to clinical standards. Cytotoxicity assays indicate that WSNTs and PLA-WSNT nanocomposites are well tolerated in vitro. Real time flow-induced crystallization experiments reveal that WSNTs reduce the critical shear stress required to produce thread-like precursors that template oriented PLA crystals. Thus, a relatively small amount of WSNTs (0.1 wt%) dramatically enhances oriented crystallization, which can enable BVSs with greater strength in a thinner profile.

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Wednesday 9:50 Room 305B IN29

Upstream vortex and elastic wave in the viscoelastic flow around a confined cylinder

Boyang Qin[1], Paul F. Salipante[2], Steven Hudson[2], and Paulo E. Arratia[3]
[1]Dept. of Mechanical & Aerospace Engineering, Princeton U, Princeton, NJ 08540, United States; [2]Polymers & Complex Fluids, NIST, Gaithersburg, MD 20899, United States; [3]Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States

The flow of a viscoelastic fluid past a cylinder is a classic benchmark problem that is not completely understood. Using novel holographic particle velocimetry to measure 3D flow fields, we report two main discoveries of the elastic instability upstream of a single cylinder in confined microchannel flow. After the onset of corner vortices upstream of the cylinder, we find that the vortex becomes unsteady and switches between two distinct flow states, leading to symmetry breaking perpendicular to the cylinder axis that is highly three-dimensional in nature. Second, we show that the disturbance of the elastic instability propagates far upstream via an elastic wave and is weakly correlated with that in the cylinder wake. The wave speed and the extent of the instability increase with Weissenberg number, indicating an absolute instability in viscoelastic fluids.

Wednesday 10:15 Room 305B IN30

Flow-induced vibrations of flexible microcylinders due to a viscoelastic flow instability

Cameron C. Hopkins, Simon J. Haward, and Amy Q. Shen
Micro-Bio-Nanofluidics Unit, Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan

In this talk, we present a study of the fluid-structure interaction arising from the flow of a shear-banding wormlike micellar (WLM) solution, past both a single flexible microcylinder, and two flexible microcylinders aligned along the channel mid-width. Using selective laser-induced etching of glass, we have fabricated long cantilevered microcylinders with radii R ~ 20 µm and length L = 1950 µm. The microcylinders are situated in a microchannel embedded in a single piece of glass. The height of the microchannel is H = 2000 µm with its width W = 400 µm. Due to the high aspect ratio of the microchannel (a = H/W = 5), the flow is approximately uniform along the axial direction of the microcylinder. Using high-speed video microscopy, the tip of the microcylinder is tracked, and its trajectory is analyzed with high spatiotemporal resolution. The flow of a Newtonian liquid at low Reynolds numbers (Re) is first studied as a reference state, with the cylinder being displaced in the streamwise direction only, and a measured linear displacement-flow rate relationship is related to the material properties of the microcylinder. In contrast, for the flow of the WLM solution at negligible Re, a purely elastic flow instability occurs above a critical Weissenberg number (Wi), resulting in the fluid flowing preferentially around one side of the post and consequent deflection of the post in both the streamwise and transverse directions. At higher Wi, the flow develops complex spatiotemporal patterns. Similar to the vortex-induced vibrations arising from the inertial instability of viscous flow past a cylinder at high Re, the purely elastic instability of the WLM solution at high Wi results in vibrations of the microcylinder. We present a detailed analysis of these flow-induced vibrations, relate its time-dependence to the properties of the WLM solution and further demonstrate how the fluid-structure interaction couples to a downstream cylinder, resulting in strongly correlated motions.

Wednesday 10:40 Room 305B IN31

Elastic-instability-induced oscillations of a flexible cantilevered beam subject to the microscale and macroscale flow of a viscoelastic fluid

Anita A. Dey[1], Yahya Modarres-Sadeghi[1], Anke Lindner[2], and Jonathan P. Rothstein[1]
[1]University of Massachusetts, Amherst, MA 01003, United States; [2]ESPCI, Laboratoire de Physique et Mécanique des Milieux Hétérogénes, Paris 75005, France

Unlike Newtonian fluids, the flow of viscoelastic fluids can become unstable even at infinitesimal Reynolds numbers due to a purely elastic flow instability occurring at large Weissenberg numbers. We have recently shown that elastic flow instabilities can drive the motion of a number of different flexible structures including sheets and cylinders. The fluctuating fluid forces exerted on the structures from the elastic flow instabilities can grow large enough to result in significant motion of the flexible structure. In this talk, the static and dynamic responses of a cantilevered beam will be presented using two different viscoelastic fluids and length scales. The results of two sets of cantilevered beam experiments- the first, comprising of the flow of a polymer solution past a beam in a microchannel, and the second, comprising of the flow of a wormlike micelle solution past a beam in a macroscale flow cell, will be presented with the goal of understanding the nature of viscoelastic fluid-structure interactions in varying flow conditions. The role of the flexible cantilevered beam in terms of blockage ratio, elastic modulus and type of beam tip conditions will be discussed. The amplitude and frequency of the flexible beam oscillations resulting due to elastic instabilities and the time variation of the flow field will be presented using streak-line imaging, particle image velocimetry and structural tracking techniques.

Wednesday 11:05 Room 305B IN32

Flow of a shear thickening micellar fluid past a falling sphere

Shijian Wu and Hadi Mohammadigoushki
Chemical and Biomedical Engineering, Florida State University, Tallahassee, FL 32310, United States

In this work, we present the first quantitative measurements of a dilute shear thickening micellar solution past a falling sphere. The micellar solution consists of cetyltrimethylammonium bromide and 5-methyl salicylate (CTAB/5MS) in de-ionized water and it exhibits shear thickening behavior beyond a critical shear rate of \dot{\gamma_c}\approx0.4\ (1/s). Davis et al [1] have showed that this CTAB/5MS micellar solution forms un-entangled rod-like micelles at equilibrium. It is found that the drag coefficient for the falling sphere is similar to that of a Newtonian fluid at a vanishingly small Reynolds number (Re = 0.03). However, falling spheres experience a significant drag reduction for conditions that correspond to 0.09 = Re = 9.86. Moreover, an unusually extended wake which spans over a long distance downstream of the sphere is detected by particle image velocimetry (PIV). These unusual results could be rationalized by invoking the phenomenon of flow induced structure (FIS) formation. We hypothesize that strong shear and/or extensional flows around the falling sphere could trigger the aggregation of rod-like micelles into giant worm-like structures. Such worm-like micelles may induce significant sphere drag reduction and extended elastic wakes in the rear of sphere. This interpretation is consistent with the steady shear and transient extensional experiments, whereby a strong shear and elongational thickening have been recovered.

Key words: shear thickening, flow induced structure, rod-like micelles

[1]: Davies, T. S., Ketner, A. M., & Raghavan, S. R. (2006). Journal of the American Chemical Society, 128(20), 6669-6675.

Wednesday 11:30 Room 305B IN33

Shear-induced sedimentation of a sphere in yield stress fluids: A computational study

Mohammad Sarabian[1], Marco Rosti[2], Luca Brandt[2], and Sarah Hormozi[1]
[1]Mechanical Engineering, Ohio University, Athens, OH 45701, United States; [2]KTH Mechanics, Stockholm, Sweden

We numerically investigate the sedimentation of a single sphere subjected to a simple cross shear flow in a complex fluid. The fluid has viscous, elastic and plastic behavior and is well known as elastoviscoplastic (EVP) fluid. Sacramento's constitutive equation is employed to model the EVP fluid (Saramito (2009) [1]). We have recently developed a there dimensional numerical solver to study suspensions of rigid and soft particles and droplets in EVP fluids (Izbassarov et al. (2018) [2]). The solid particle is represented by an immersed boundary method (IBM) with a computationally efficient multi-direct forcing scheme. The main objective of this work is to understand how a cross shear flow affects the drag force on a sphere. We calculate the magnitude of different drag components (viscous drag, form drag, and elastoplastic drag) on the particle and discuss the primary cause of drag enhancement or reduction on the settling of a sphere when a cross shear flow is imposed. We show the dependency of the drag coefficient on plastic and elastic properties of the suspending fluid as well as the nonlinear coupling of the settling flow and the cross shear flow.

[1] Saramito, P. (2009). A new elastoviscoplastic model based on the Herschel-Bulkley viscoplastic model. Journal of Non-Newtonian Fluid Mechanics, 158(1-3), 154-161. [2] Izbassarov, D., Rosti, M. E., Ardekani, M. N., Sarabian, M., Hormozi, S., Brandt, L., & Tammisola, O. (2018). Computational modeling of multiphase viscoelastic and elastoviscoplastic flows. International Journal for Numerical Methods in Fluids, 88(12), 521-543.

Symposium MC
Microfluidic and Confined Flows

Organizers: Sujit Datta and Cari Dutcher

Wednesday 9:50 Room 306A *Keynote* MC1

Development and commercialization of microfluidic flow assurance testing

Tom de Haas
Interface Fluidics, Edmonton, Canada

There are many challenges to overcome when spinning off a company from a university lab. Some of the biggest challenges are finding investors, managing intellectual property, and finding product market fit. Interface Fluidics is a high-growth start-up company that spun out of Prof. David Sinton's Lab at The University of Toronto. We started our company with a focus on flow through porous media and we are in the process of commercializing flow assurance testing (in partnership with Equinor). This presentation will discuss the challenges of commercializing technology from a university and will also outline the advantages of microfluidics-based flow assurance testing. The two types of flow assurance tests that will be the focus of this talk are wax appearance temperature and asphaltene onset pressure. I will discuss the method that we use for these tests, how the results compare to testing in conventional lab equipment, and the challenges of designing laboratory equipment for handling commercial samples rather than model fluids.

Wednesday 10:15 Room 306A MC2

Droplet shape relaxation in confined microfluidic flows for probing the properties of liquid-liquid emulsions

Cari S. Dutcher[1], Shweta Narayan[1], Davis Moravec[2], Andrew Metcalf[3], Daryl Quam[2], and Andrew Dallas[2]
[1]Mechanical Engineering, University of Minnesota-Twin Cities, Minneapolis, MN, MN 55455, United States; [2]Donaldson Company, Inc., Bloomington, MN, United States; [3]Clemson University, Anderson, SC, United States

The presence of droplets suspended in a liquid or gas are known to play essential roles in environmental fields such as hydrology and atmospheric science, as well as commercial applications such as oil-water filtration. Often, the dispersed droplets are stabilized by surface active compounds and surfactants, resulting in complex chemical composition and material properties at the fluid-fluid interface. Microfluidics lends itself to studies of droplet dynamics under confined and unconfined flow fields. Droplet deformation under controlled flow fields can be applied towards measuring interfacial and bulk properties of the liquid-liquid system, including interfacial tension and viscosities of the two phases. In this talk, recent advancements in use of microscale flow fields will be highlighted for measuring properties of multiphase systems with environmental and commercial applications. First, methods for measuring the interfacial tension from droplet deformation in extensional flows will be discussed, with applications to fuel-water/ bilgewater emulsions and atmospheric aerosols. The effect of confinement and continuous phase properties on droplet deformation will be highlighted. Constraints on droplet size relative to the device geometry and microfluidic device materials for accurate interfacial tension measurement will be presented. In a second microfluidic platform, droplets confined at a stagnation point using a hydrodynamic trap are perturbed to induce oscillations in droplet shape. Droplet oscillation frequencies and damping constants are measured. The effect of changing the dispersed phase or continuous phase viscosity on droplet oscillation frequency and damping constant is investigated. This technique finds applications in material property measurement with small sample volumes.

Wednesday 10:40 Room 306A MC3

Coating and crumpling of armored gas filled capsules through confined bubble flow

Charles C. Sharkey, Zixian Cui, and Shelley L. Anna
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Bubbles flowing through the confined geometry of a fluid filled capillary tube are affected by the presence of surface active molecules or particles that modify the interfacial mechanics. Small-molecule surfactants adsorb to the bubble interface and lead to Marangoni stresses that result in changes to the bubble shape. Surface active particles impart significant interfacial elasticity. We investigate the case of bubble flow in a capillary filled with surface active particle-surfactant complexes. Cetyltrimethylammonium bromide (CTAB) surfactant adsorbs to the surface of silica nanoparticles in a glycerol-water suspension to form the surface active complexes. Bubbles are dispensed with varied lengths using a co-flow capillary apparatus. Capillary number is varied by adjusting the bubble velocity and suspension viscosity via the glycerol concentration. Fluid film thickness is measured along the length of the bubble while in the capillary. These measurements are compared with bubble flow through surfactant solutions and with predictions from a Bretherton-type model. The adsorbed particle-surfactant complexes form a rigid layer at the trailing end of the bubble, changing the mechanical properties of the interface. The behavior of the bubble changes with the bubble length, and two critical bubble lengths are observed. Above the first critical length, the film thickness undergoes a sharp transition mid-bubble from a thin film at the leading end to a thickened film at the trailing end. The thickened film arises from the rigid particle layer on the interface. Above the second critical length, the bubble tail cap begins to crumple and collapse. Crumpling occurs soon after the bubble is dispensed into the capillary, and the critical lengths vary with bubble velocity. These results allow us to infer rheological and mechanical properties for the interface associated with the crumpling. We connect crumpling behavior with criteria for the formation of non-spherical, particle coated capsules as the bubbles leave the capillary.

Wednesday 11:05 Room 306A MC4

Microfluidic production of gastro-resistant microcapsules

Mariano Michelon[1], Bruna C. Leopercio[1], Renata V. Tonon[2], Flavia S. Gomes[2], and Marcio S. Carvalho[3]
[1]Mechanical Engineering Department, PUC-Rio, Rio de Janeiro, Rio de Janeiro, Brazil; [2]Embrapa Agroindústria de Alimentos, Rio de Janeiro, Brazil; [3]PUC-Rio, Rio de Janeiro 22451-900, Brazil

We designed a microfluidic process to produce highly hierarchized microcapsules containing an inner oil phase and a gellan-based hydrogel shell. These microcapsules have gained considerable attention in the food industry due to their capacity to protect different active compounds from chemical degradation during their passage through the gastrointestinal system, protecting against acid pH in the stomach and delivering the compounds in the intestine. The microcapsules were obtained through external gelation of the middle phase - composed of aqueous gellan - of an oil-in-water-in-oil double emulsion template obtained using a glass-capillary microfluidic device. The behavior of the structural integrity of microcapsules with different shell thickness were evaluated under the in vitro digestion simulated conditions. The results indicated that microcapsules can be considered resistant to the adverse conditions of the stomach environment. This fact is associated to an increase of hydrogen ions, due to the pH-value condition (pH 2.0) during 2 hours in the stomach step, which promotes the reduction of electrostatic repulsion between gellan pair of double helices, forming a stronger hydrogel network. However, the subsequent intestinal digestion step led to a fragmentation of the microcapsules and the leakage of the inner ingredient. The shell was weakened in intestinal phase due to the lack of available cations to interact with gellan pair of helices and/or due to the erosion of the hydrogel network when exposed to an excess of water after hydrogels swelling in stomach phase. Thus, we observed that an almost complete destabilization of the hydrogel network occurred after 2 h in the intestinal step of the digestion. These results are important in the food field to develop delivery systems to protect a pH-sensitive active ingredient under acid stomach conditions and guarantee its stability for the absorption in the intestine.

Wednesday 11:30 Room 306A MC5

Shearing liquids confined in microfluidic channels at acoustic frequencies without dissipation

Yicheng Zhao, Zehra Parlak, and Stefan Zauscher

Mechanical Engineering and Materials Science, Duke University, DURHAM, NC 27705, United States

Acoustic shear wave resonators (ASWR), which work in the MHz frequency range, have many applications including biomolecular sensing and point of care (POC) diagnostics. However, their performance is significantly inhibited by the large dissipation that results from viscous coupling effects affecting the resonance frequency. We discovered that one can cancel out these viscous effects and thus introduce no dissipation by confining the liquids into microfluidic channels that are coupled rigidly to the ASWR. We used the Finite Element Method (FEM) to simulate our experiments and to understand the underlying physics. To do this, we developed a FE model representation of the device and validated this model through mesh convergence of a series of 2D and 3D FE models. To test the influence of liquid viscosity on the resonance frequency of the ASWR, we subjected liquid samples in the microfluidic channels to viscosity changes up to 40%, while maintaining density constant. Our FEM results confirmed experiments and showed that viscous effects do not play a role in our µ-fluidic ASWR. Canceling viscous effects leads to a near 100 fold increase in the Q-factor of the microfluidic ASWR. Thus, confining liquids in µ-fluidic ASWRs not only cancels out their large dissipation in liquid to levels observed in air/vacuum, but also enables efficient device miniaturization. Combined with the extremely small volume requirements for sensing (~nL), we posit that µ-fluidic ASWRs can overcome current barriers for their widespread use in diagnostic sensing and POC applications. Finally, we show how we can use our µ-fluidic ASWR for liquid viscosity measurements at ultrahigh shear rates.

Symposium AR
Applied Rheology for Pharmaceuticals, Food, and Consumer Products

Organizer: Stephanie Lam and Helen Joyner

Wednesday 9:50 Room 306B AR1

Using rheology to optimize of the chocolate process

Payton Boylston, April Miller, Bailey Schieve, and Matthew J. Armstrong

Chemistry and Life Science, United States Military Academy, west point, NY 10996, United States

The science behind why some chocolates are more appealing than others is based on the optimization of the entire chocolate-making/production process. This process involves cocoa nib processing, mixing, refining, tempering and molding. Proper parameters, such as conch/melanger timing, seed chocolate and temperature, will affect the final taste. Since the appeal of chocolate is based on the chocolate's balance of viscous and elastic behavior, comparing physical properties evaluated from rheological studies can determine the optimal procedures. The Casson model is commonly used to model food dispersions and is commonly used in chocolate manufacturing. The Casson parameters, Casson yield stress and Casson plastic viscosity, define the characteristic chocolate texture and flavor. The Casson yield stress is the minimum stress required to initiate the flow and marks the transition from the solid viscoelastic stage to the liquid stage [1,2,3]. The Casson plastic viscosity is the resistance to flow. These parameters are identified by fitting the Casson Model parameters to the steady state flow curve. Chocolate is a complex multiphase material and the transition from a solid to liquid depends on its evolving, stress dependent microstructure [3,4]. In this study, more contemporary thixo-elastic-visco-plastic (TEVP) rheological models are compared to the traditional steady state Casson model. The TEVP models fit steady and transient data, with a yield stress and plastic viscosity parameters to be compared to the Casson parameters. This research highlights the tempering and refining of the United States Military Academy chocolate making process. Chocolate tempering and refining techniques are studied to determine the impact on the chocolate's complex behavior, yielding optimal rheological parameters.

Wednesday 10:15 Room 306B AR2

LAOS (Large Amplitude Oscillatory Shear) rheological characteristics of non-fat, low-fat, and high-fat yogurt samples

Merve Yildirim and Jozef Kokini

Food Science, Purdue University, West Lafayette, IN 47907, United States

Reduction of fat content in yogurt is a very important nutritional objective. There are three types of yogurts commercially available; these include non-fat, low-fat, and full-fat yogurt. Fat reduction of yogurt is related to loss of the gel-like structure, which affects its creaminess, syneresis and overall viscoelastic properties. LAOS measurements have great potential to mimic manufacturing processes and oral processing during consumption. Information on non-linear rheological properties of yogurt is very limited and is the focus of this research. Predefined LAOS parameters are calculated to characterize the nonlinear rheological properties of yogurt samples with different fat contents.Three different yogurt products were purchased from two different brands including non-fat, low-fat, high-fat yogurts. The cone-plate geometry of the DHR-3 rheometer was used in the strain range of 0.01-200% at a frequency of 10 rad/s.LAOS rheological parameters were obtained using the TRIOS software of TA instruments. Morphological structures of yogurt samples were monitored by Cryo-SEM.For both brands, low-fat yogurts have a weaker gel-like structure compared to full-fat and non-fat counterparts. In the nonlinear viscoelastic region where the applied strain is large, stiffening ratio(S>0) and thickening ratio (T<0) suggests that all of the yogurt samples exhibit strain stiffening and shear thinning behavior. Additionally, all yogurt samples have (?_M^' > ?_L^') intracycle shear thinning, (G_L^'>G_M^') intracycle strain stiffening behavior. Brand 1 has a stronger gel-like structure compared to Brand 2 for all types of yogurts samples based on amplitude and frequency sweeps. Investigation on Lissajous curves of Brand 1 displayed broader non-elliptical elastic trajectories with more dissipated energy; Brand 2 has smaller distorted elliptical viscous

trajectories with less stored energy compared to Brand 1. SEM images also shows that Brand 1 has a dense casein-network compared to Brand 2, which supports the LAOS results.

Wednesday 10:40 Room 306B AR3

Identification of parameters affecting wear behavior of cheese

Fariba Zad Bagher Seighalani and Helen Joyner
School of Food Science, University of Idaho, Moscow, ID 83843, United States

Cheese sliceability and shreddability behaviors are important to both cheese processors and general consumers; these behaviors may relate to cheese wear behaviors. Thus, studying cheese wear, a new dimension of food rheological behaviors, could be a suitable method to characterize or predict cheese processing behavior. Accordingly, the objective of this study was to identify significant factors influencing cheese wear behavior. Hard cheeses with 40, 50, 52 and 54% fat (dry weight) at different aging times (15, 30, 45, and 60 d) were evaluated. Wear measurements were performed using an Anton Paar MCR702 rheometer equipped with a steel twin ball-on-disc system at various normal forces (0.5 and 0.7 N), sliding speeds (30 and 50 mm/s), and temperatures (5, 15 and 25°C). Penetration depth (mm) was recorded and mass loss was measured by calculating differences between sample weights before and after testing. Higher normal force resulted in significantly ($p<0.05$) lower mass loss in all cheeses except for cheese containing 40% fat (dw) at 25°C. Conversely, penetration depth was higher at higher normal force. Mass loss values were significantly different at different temperatures at any given sliding speed and normal force combination. The highest mass loss values occurred at 15°C; mass loss at 5°C and 25°C was significantly lower. Penetration depth was significantly lower at 5°C and increased at higher temperature. Mass loss and penetration depth were greater at higher sliding speeds, which was due to the greater sliding distance during the test; mass loss also increased with aging time. The results of this study provided fundamental information on how processing parameters impacted cheese wear behaviors and can be used to optimize processing parameters for cheese or similar food products.

Wednesday 11:05 Room 306B AR4

Understanding starch swelling behavior and how it impacts rheology and functional properties of food systems

Leslie G. Howarth and Judith K. Whaley
Innovation & Commercial Development, Tate & Lyle, Hoffman Estates, IL 60192, United States

Starches are well-known thickening agents, and the complexities of such soft particle suspensions must be carefully considered during product development. Even in simple systems, textural properties can vary in surprising ways as the swelling of the starch and concentration-in-use change. Therefore, it would be beneficial to have a texture map that allows prediction of food properties based on fundamental aspects of the starch behaviour. In the literature a number of authors have demonstrated that the classical principles of particle interactions can be applied to starch systems. At concentrations below close-packing, the approaches developed for dispersions of hard particles are applicable with viscosity primarily driven by particle excluded volume fraction as modelled by the well-known Krieger-Dougherty equation. Above the concentrations where the granules become close-packed there is a dramatic increase in viscosity but the system does not solidify in the same manner as a hard particle system but remains viscous. As the concentration of starch is increased further there is an increase in elastic behaviour. A crossover occurs at higher concentrations and particle rigidity becomes the dominant factor such that high swelling starches that provide enhanced viscosities at dilute concentrations are less effective at higher concentrations and vice versa. Physical and chemical treatments are applied to starch to control the swelling, as the swelling is reduced the particles become more rigid which gives them tolerance to shear which occurs during food processing. In the current work, we have modelled the effects of swelling volume and concentration on viscous and elastic properties. This has allowed us to create texture maps for thickened starch systems having high predictive power for the effects of starch swelling, concentration and processing upon the textural and sensory attributes of the resulting food products.

Wednesday 11:30 Room 306B *Keynote* AR5

Using in vitro measures to probe the responses of electrospun protein-polysaccharide conjugates to high-shear deformations

Michael W. Boehm[1], Stefan K. Baier[2], Ines Kutzli[3], Monika Gibis[3], and Jochen Weiss[3]
[1]PepsiCo., Purchase, NY, United States; [2]Motif Ingredients, Boston, MA, United States; [3]Univ. of Hohenheim, Stuttgart, Germany

Electrospinning has been used to aid the process of covalent bonding (via the first stage of the Maillard reaction) between protein and polysaccharide by forming high surface-to-volume fibers, which facilitates more efficient heat treatment. The resulting conjugate exhibits improved emulsifying properties, increased solubility, heat stability, pH stability and improvements to taste and reductions in astringency and bitterness, relative to the protein alone. These past efforts have made electrospinning an economically feasible step in the production of protein-polysaccharide conjugates. However, the adoption of electrospun conjugates as beverage additives will require proof that they can positively influence the sensory perception of the beverages to which they are added. We have shown, in past research, how an in vitro approach can be used to elucidate structure-function relationships, relationships that impact sensory perception. In this presentation, we will detail our rheological and tribological techniques, and we will compare the behavior of various protein-maltodextrin conjugates (whey, potato and pea proteins). We will also suggest potential research topics focused on bridging physical property measurements and sensory perception, and we will discuss gaps in existing knowledge.

Symposium GG
Out of Equilibrium Systems: Gels and Glasses

Organizers: Suzanne Fielding, Ran Tao and Rosanna Zia

Wednesday 9:50 Room 306C GG29

Rheology of glass-ceramics for sealing applications

Anne M. Grillet[1], Steve X. Dai[2], and Brenton Elisberg[1]
[1]Engineering Sciences Division, Sandia National Laboratories, Albuquerque, NM 87185, United States; [2]Materials Science Division, Sandia National Laboratories, Albuquerque, NM 87185, United States

Glass to metal seals are commonly used to manufacture hermetic electrical pass-throughs. A common concern is cracking of the glass which can compromise the hermiticity because even smalls differences in thermal expansion coefficient (CTE) can result in large residual stresses in the glass. Glass-ceramics contain an embedded crystalline phase surrounded by a glassy matrix. The crystals form a space filling "gel-like" structure which supports a stress above the melting temperature of the glassy matrix. The morphology, thermal and mechanical properties can be manipulated both by composition and thermal history. In particular, the thermal expansion coefficient can be carefully matched to that of the metals in a sealing application to minimize thermal expansion stresses. This study will focus on a class of lithium silicate glass-ceramics of interest for sealing applications.

The viscoelastic rheology of a traditional glass and the glass ceramic will be presented from room temperature through the matrix glass transition and beyond. The measured mechanical properties of a glass-ceramic are sensitive to the internal microstructure of the glassy and ceramic phases. By varying the cooling rate, the microstructure can be manipulated as evidenced by qualitative changes in the behavior through the glass transition. We will also show additional data on the crystalline phase make up and evidence for dynamic restructuring well below the melting temperature of the glass-ceramic. Measurements of the mechanical properties of the glass-ceramic contribute to continuing efforts to develop and calibrate material models to predict stress development and cracking of glass to metal seals.

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Wednesday 10:15 Room 306C GG30

From rubber-toughening to crazing: How to understand yielding or lack of it in polymer glasses?

Masoud Razavi, Da Huang, S Zhang, and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

We have recently developed a zeroth order molecular picture to explain why some polymer glasses are more ductile than others and what controls the brittle-ductile transition [1]. The new model made it possible to rationalize two counter-intuitive phenomena: (a) plasticizer promotes brittle response [2] and (b) glassy glasses turns brittle upon lowering the rate of drawing [3]. This presentation will show how the rubber-toughening of brittle polymer glasses can also be understood in terms of this molecular level understanding. Moreover, the paradigm of chain networking for molecular mechanics of glassy polymers offers a fresh perspective to explore the physics associated with crazing. Our analysis shows that it is inadequate to correlate the strain softening and hardening characteristics with the brittle and ductile behavior.

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Wednesday 10:40 Room 306C GG31

Photorheology and gelation during polymerization of coordinated ionic liquids

Ria D. Corder and Saad A. Khan
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States

Ionic liquids present a novel and tunable medium for bulk polymerization of vinyl monomers. 1-vinylimidazole (Vim) displays intriguing rheological behavior when mixed with varying amounts of lithium bistriflimide (LiTf2N) to form coordinated ionic liquids (ILs) and then photopolymerized via a free-radical mechanism. Previous work has shown that increasing [LiTf2N] results in faster chemical conversion of monomer during photopolymerization. The purpose of our study is to determine how differences in kinetics are manifested in the development of mechanical properties. We used dynamic oscillatory rheology to non-invasively monitor the *in situ* photopolymerization of coordinated ILs containing varying molar ratios of Vim:LiTf2N. The coordinated ILs were all Newtonian solutions, and the viscosities exhibited a power-law dependence on [LiTf2N]. Polymerization caused large increases in complex modulus (G*) due to the formation of entangled polymer chains below the glass transition temperature. Three distinct regimes were observed with respect to [LiTf2N]: (1) at low [LiTf2N], samples increased in G* faster with [LiTf2N] and behaved as solutions; (2) at intermediate [LiTf2N], G* growth was maximized and samples underwent sol-to-gel transitions during polymerization; (3) at high [LiTf2N], G* growth slowed with [LiTf2N] and samples exhibited viscoelastic behavior. We

attribute gelation to Li+ complexing with imidazole pendant groups to form physical crosslinks. Our samples also exhibited "dark curing", the extent of which increased with [LiTf2N]. EPR spectroscopy performed on a similar photopolymerizing system demonstrates that Li+ can stabilize propagating radicals, leading to enhanced curing following UV exposure. Taken together, these results demonstrate that the rheological behavior of poly(ILs) can be tuned by varying the composition and UV dosage. We then extended the study to observe the effects of other metal salts on the rheology during and after poly(Vim) synthesis from coordinated ILs.

Wednesday 11:05 Room 306C GG32

Gel evolution and collapse in an oil based drilling fluid

Elizabeth Jamie, Andrew Clarke, Louise Bailey, Gerald Meeten, and John Staniland
Schlumberger Cambridge Research, Cambridge CB3 0EL, United Kingdom

While drilling an oil well, the drill-bit produces rock cuttings which are removed continuously to the surface by a drilling-fluid pumped down the drill pipe, through the bit, and returning up through the annulus. This fluid gels sufficiently to prevent the sedimentation of cuttings when pumping ceases. A non-aqueous drilling fluid comprises of a complex formulation of surfactant-stabilized brine-droplets, clays, additives, and particles of a dense weighting-agent, all suspended in the oil-continuous external phase. The drilling operation may fail if these components do not remain well-dispersed throughout the fluid.

In this presentation we explore the evolution of vertical heterogeneity in a model fluid system through results from a selection of sources:
- Formulation stability analyser and X ray tomography
- Conventional rheology
- The T-bar rheological tool (Brookfield), which allows series of torque measurements to be made at increasing depths into a visco-plastic fluid sample, minimally disturbing the material beneath.

The results will be interpreted in the context of recent academic literature, and suggest that the sample undergoes a process resembling delayed gel-collapse rather than a purely sedimentary phase-separation.

Wednesday 11:30 Room 306C GG33

PDMS network structure-property relationships: Influence of molecular architecture on mechanical and wetting properties

Kirill Efimenko, Matthew Melillo, and Jan Genzer
Chemical and Biomolecular Engineering, NC State University, Raleigh, NC 27606, United States

Poly(dimethylsiloxane) (PDMS) is the most common polysiloxane and is frequently referred to as "silicone oil" or fluids, materials, additives, etc., depending on the application. PDMS has found wide use in many industrial applications ranging from lubricants, hydraulic fluids, and electrical insulating materials to foam control agents in food, pulp and paper, textiles and cleaning supplies industries. Specifically, the commercial PDMS formulation known as Sylgard 184 has received much attention in the past two decades due to its application in microfluidics, biological studies, functional coatings, and many others. We would be remiss to argue that model PDMS materials, i.e., not commercial kits, have not been studied in detail. On the contrary, there is a rich literature of various model PDMS systems prepared with precise chemical stoichiometry for specific applications. However, to the best of our knowledge, a systematic investigation that directly compares the dynamic mechanical and dynamic surface wetting properties of Sylgard 184 and model PDMS systems made from various molecular weights and amounts and types of crosslinkers, has not yet been performed. This contribution seeks to fill this void.

Wednesday Afternoon

Symposium AM
Additive Manufacturing and Composites

Organizers: Jon Seppala and Samanvaya Srivastava

Wednesday 1:30 Room 305A AM6

Application of the sequence of physical processes (SPP) framework to the yielding and recovery of conductive pastes for screen printing

Gavin J. Donley[1], William W. Hyde[2], Simon A. Rogers[1], and Florian Nettesheim[3]

[1]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Experimental Station, DuPont, Wilmington, DE 19830, United States; [3]Nutrition and Biosciences, DuPont, Brabrand DK-8220, Denmark

We utilize the recently developed "Sequence of Physical Processes" approach to investigate the yielding and recovery dynamics of two silver pastes that exhibit complex rheology. The SPP framework is unique as it allows insights to be gained regarding yielding and recovery processes on time scales significantly faster than the period of oscillation, with the temporal resolution limited only by the data acquisition time. This resolution allows for the accurate determination of yielding of soft materials under any predetermined pre-shear history, and at time scales that are relevant to the applications of these materials. The SPP approach enables us to resolve rapid material transitions which are inaccessible by steady-state techniques, along with their relative rates and timescales. These results are an important step towards a more comprehensive understanding of the complex behavior of yielding materials used in a variety of applications.

Wednesday 1:55 Room 305A AM7

Viscoelastic characterization in hierarchical fiber reinforced composites

Aaron M. Forster[1], Ran Tao[1], Ajay Krishnamurthy[1], and Erik Thostenson[2]

[1]Material Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, United States; [2]Center for Composite Materials and Dept. of Mechanical Eng., University of Delaware, Newark, DE, United States

Carbon-nanotube (CNT) grafted glass-fiber-reinforced epoxy nanocomposites (GFRP) present a range of stiffnesses (MPa to GPa) and length scales (μm to nm) at the fiber-matrix interface. The contribution of functionalized CNT networks to the local and bulk polymer dynamics is studied here using a combination of torsion dynamical mechanical thermal analysis (DMTA) and neutron scattering (NS) measurements. DMTA measurements highlight a reduction in the storage modulus (G') in the rubbery region and an asymmetric broadening of the loss modulus (G") peak in the a-transition region. NS measurements show a suppressed hydrogen mean square displacement (MSD) in the presence of glass fibers but a higher hydrogen MSD after grafting functionalized CNTs onto fiber surfaces. While NS and DMTA are sensitive to different modes of chain dynamics, the localization of functionalized nanotubes at the fiber interface is found to affect the distribution of polymer relaxation modes without significantly altering the thermally activated relaxation processes. Cure studies show the functionalized CNT layer exhibits different curing profiles compared to the epoxy sample. These differences are investigated using dynamic mechanical measurements during cure.

Wednesday 2:20 Room 305A AM8

Role of flow type on the evolution of semi-flexible fiber orientation

Donald Baird[1], Hongyu Chen[1], and Peter Wapperom[2]

[1]Virginia Tech-Chemical Engineeering, Blacksburg, VA 24061-0211, United States; [2]Mathematics, Virginia Tech-Mathematics, Blacksburg, VA 24061-0211, United States

In order to predict semi-flexible fiber orientation profiles during processing, stress and orientation tensors that reflect their flow behavior are needed. In this presentation we focus on the orientation evolution behavior of long semi-flexible fibers in basic rheological flows as well as squeezing flow which resembles the onset of processing flows. To better reflect slower orientation evolution observed in shear flows, a model was developed with a material constant a which represents the hindrance in orientation evolution due to fiber-fiber interactions. This factor is obtained by fitting to orientation data from simple shear and extensional flows. It was observed experimentally that fiber re-orientation rates are very different in shear and extension and cannot be modeled using a single, constant a. During mold filling the flow types, including extensional, simple shear, rotational flow and mixed flows, have a significant impact on fiber orientation evolution. In this study a flow-type parameter is utilized to locally describe the relative magnitudes of shearing and extension during non-lubricated squeeze flow. As a result, a variable strain reduction factor a is determined locally by the corresponding local flow-type and used in fiber orientation simulation. The application of the variable strain reduction factor in fiber orientation simulations allows the simulated fiber re-orientation rate to be dependent on the local flow type. The predicted orientation results show improved agreement of the profile with the experimental data for non-lubricated squeeze flow. This empirical variable strain reduction factor helps to improve the fiber orientation predictions in complex flows found in processing operations.

Wednesday 2:45 Room 305A AM9

The role of physical structure and morphology on the photodegradation behaviour of polypropylene-graphene oxide nanocomposites

Yuri C. de Oliveira, Leice G. Amurin, Fernanda F. Valim, Guilhermino J. Fechine, and Ricardo E. Andrade
MackGraphe, Mackenzie Presbyterian University, São Paulo, SP 01302-907, Brazil

In this work, polypropylene nanocomposites with different concentrations of graphene oxide (0.1, 0.5, 1.0 and 2.0 wt% GO) obtained by melt mixing via two different methods (solid-solid deposition-SSD and liquid phase feed -LPF), and evaluation of the morphology and structure on photodegradation was studied. Regarding the methods, the LPF method presents smaller particle sizes in comparison to SSD method, where for a high concentration of GO (2% in this case) the SSD present a higher incidence of particles with a surface area of more than 100 µm2. This could be the result of the larger agglomerate of particles SSD premix, since in this method, the GO particles are deposited on the polymer surface and may cause the particles overlap. The nanocomposites were then evaluated regarding their morphology/structure with the photodegradation. It is known that the PP photodegradation origins is the formation of hydroperoxides and carbonyl bands that allows to express a quantitative analysis of photodegradation extent, by calculating the carbonyl index after. The intensities decrease in the nanocomposites bands with GO content increase, indicating that the GO absorbs the UV radiation and reduces the radiation absorbed by the polymer around 35% (stabilizing its molecules), delaying the photooxidative process.

Wednesday 3:45 Room 305A *Keynote* AM10

Materials, systems, and software for thermoplastic additive manufacturing by FDM

Victor Jaker, Tim Diekmann, Jason Nixon, Paul Taylor, Clint Newell, and Adam R. Pawloski
Advanced Materials, Stratasys, Inc, Eden Prairie, MN 55344, United States

Extrusion based additive manufacturing would appear at first glance to be a simple extension of conventional plastics processing. Simply stated, the process follows the conventional operations of melting, extruding, forming into a shape, and setting the shape by cooling. The simplicity of the process unfortunately stops there, due to the added complexity of use in a continuously variable, non-steady state condition.

Additive manufacturing systems are inherently valuable for design freedom, allowing the ability to create nearly arbitrary geometries on demand. For an extrusion-based system, each layer of the geometry will typically have a unique tool path for building the structure from a single extrudate 'bead' of plastic. Because the path is arbitrary, a steady state operation cannot be achieved. Continuous operation is therefore unlike any other conventional plastics process where a steady state (e.g profile extrusion, film extrusion) or cyclical processing (injection molding) can be achieved. The price for achieving flexibility in process and creation of high quality parts (mechanicals and aesthetics) is the precise control of mass and heat transfer processes of viscous plastics on short timescales (micro seconds to tens of seconds). Very significant further complications arise with the control of residual stresses, interlayer bonding, adhesion to secondary support materials, and numerous additional factors required to make a reliable, high quality product.

In this presentation, some of the intrinsic challenges of Fused Deposition Modeling (FDM) will be described from the perspective of integrating the extrusion of thermoplastic materials with system hardware and software.

Wednesday 4:10 Room 305A AM11

In-line rheology of FFF: Process and strength insights

Timothy J. Coogan[1] and David Kazmer[2]
[1]SGR North America, Saint-Gobain Research, Northborough, MA 01532, United States; [2]Plastics Engineering, University of Massachusetts Lowell, Lowell, MA, United States

An in-line rheometer has been incorporated into a fused filament fabrication (FFF) printer by designing a modified nozzle with a custom pressure transducer and a thermocouple for measuring the processed melt temperature. Combining the melt pressure data with the in-line filament velocity provides real-time viscosity data. Additionally, three thermocouples measured the melt temperature, build plate temperature, and environment temperature to enable an in-line transient strength analysis. The melt pressure measurements from the in-line rheometer provide insights into the consistency of the printing process, and the in-line sensors are used to create a real-time predictive strength model that allows users and printer designers to optimize their print process and monitor parts for defects. The implemented system has proven extremely valuable for understanding the FFF process, optimizing quality, and verifying consistency.

Wednesday 4:35 Room 305A AM12

Flow-induced crystallization effects in materials extrusion additive manufacturing

Anthony P. Kotula[1], Jonathan E. Seppala[1], and Claire McIlory[2]
[1]Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8542, United States; [2]School of Mathematical Sciences, University of Nottingham, Nottingham, England NG7 2QL, United Kingdom

Material extrusion additive manufacturing processes force molten polymer through a printer nozzle at high (>100 s^{-1}) shear rates prior to cooling and crystallization. These high shear rates can lead to flow-induced crystallization in common polymer processing techniques, but the magnitude and importance of this effect is unknown for additive manufacturing. Flow-induced crystallization can affect both the crystallization kinetics during printing and the semicrystalline morphology in the final printed part. In this talk, I will present evidence of both effects using polycaprolactone and poly(lactic acid), two semicrystalline polymers common to additive manufacturing. We perform process line Raman

spectroscopy and infrared (IR) thermography measurements in a simplified printing setup to measure the effect of processing conditions on crystallization kinetics. Enhanced kinetics are observed at lower nozzle temperatures and higher shear rates, which we explain via a constitutive model describing polymer deformation in flow and the effect of residual polymer chain stretch on increased nucleation. In the second set of measurements, we examine the distribution of semicrystalline domain sizes in parts printed using a poly(lactic acid) with slow crystallization kinetics. IR thermography captures the fast cooling rate during the printing process, and polarized optical imaging shows no crystalline domains in the printed part. However, a post-print annealing process reveals spherulitic domains with sizes that vary spatially in the printed part. The spherulites decrease in size near the weld zone between two printed layers, which agrees with theoretical predictions.

Wednesday 5:00 Room 305A AM13

Multiscale rheological investigation of highly filled multi-layer filament for Fused Deposition Modeling (FDM)

Shihang Wang, Rebecca R. Ruckdashel, Jay Park, and Javier Vera-Sorroche
Plastics Engineering, University of Massachusetts Lowell, Lowell, MA 01854, United States

Presence of carbon based and/or inorganic fillers in 3D filaments has recently attracted considerable interest from academic and industry to enhance properties of 3D-printed parts. Although 3D-tailored composites have been developed, very little work has been done on the production of advanced 3D filament feedstock for FDM; particularly for highly filled 3D filaments that require (i) high filament strength, (ii) high dimensional accuracy and (iii) superior surface finish. Current FDM filaments rarely exceed filler concentration of 10%, for example, in case of calcium phosphate without sacrificing aforementioned qualities. In this work, a co-axial 3D feedstock filament up to 40% filler concentration has been fabricated via melt spinning; such filament met the desired properties with uniform filler dispersion. We gain further insights on rheological behaviors of such system by performing multiscale flow simulation. On a continuum scale, 2D FEM flow simulations have been conducted to investigate the interfacial instabilities in co-axial flows of dissimilar material. On a mesoscale, we utilize coarse-grained molecular dynamics simulations to predict and investigate the multilayer structure-properties by investigating the effects of i) core/shell layer thickness ratio, ii) filler geometry and concentration, and iii) strain rate.

Wednesday 5:25 Room 305A AM14

The role of rheology in laser sintering of polymer particles

Patrick D. Anderson, Prakhyat Hejmady, Caroline Balemans, Lambert van Breemen, Martien Hulsen, and Ruth Cardinaels
Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands

Merging of particle pairs during selective laser sintering (SLS) of polymers is vital in defining final part properties. Depending on the sintering conditions, polymers can undergo full or partial sintering whereby incomplete sintering results in poor mechanical properties. In the present work, a novel in-house developed experimental setup is used to perform laser sintering experiments on polymer particle doublets while performing in-situ visualisation of the sintering dynamics. Sintering conditions such as heating chamber temperature, laser pulse energy and duration, laser spot size and particle size are precisely controlled and systematically varied. A non-isothermal viscous sintering model, extending the Frenkel model, is developed to qualitatively predict the observed effects of the various parameters. It is shown that the sintering kinetics is determined by a complex interplay between the transient rheology caused by the finite relaxation times of the polymer and the time-dependent temperature profile which also affects the polymer viscosity. The combination of a full material characterisation with sintering experiments under well-defined conditions has resulted in a general understanding of the effects of material and process parameters on laser sintering. Results are compared with a computational model using the finite element method. Firstly, we analysed the viscoelastic flow problem of the sintering process using both the Giesekus model and the eXtended Pom-Pom model to describe the complex behaviour of the polymer. Secondly, we included the temperature-dependent flow behaviour of the system to study the effect of process and material parameters. Finally, we discuss the crystallisation kinetics to predict and tune the morphology of the products.

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Wednesday 1:30 Room 304 SC34

Transition from the viscous to inertial regime in non-Brownian suspensions

Yasaman Madraki[1], Guillaume Ovarlez[2], and Sarah Hormozi[3]
[1]Ohio University, Athens, OH 45701, United States; [2]Physical Chemistry, Universite de Bordeaux, Pessac, Bordeaux 33600, France; [3]Ohio University, Athens, OH 45701, United States

In shear thickening suspensions, viscosity appears to increase when the shear rate increases. In non-Brownian suspensions, different modes of shear thickening behavior have been identified. These modes are attributed to different physical mechanisms such as hydrodynamic interactions among particles, transition from frictionless to frictional rheology, transition from a viscous to an inertial regime, microstructural effects, etc. We have designed a model non-Brownian suspension to study experimentally the viscous to inertial mode of shear thickening behavior. We have developed a series of comprehensive rheometry tests to provide an understanding of the inertial shear thickening mode in detail. We provide a closure for shear stresses in inertial suspensions and we test this closure by studying boundary driven flows of dense suspensions.

Wednesday 1:55 Room 304 SC35

Using acoustic perturbations to dynamically tune shear thickening in colloidal suspensions

Prateek Sehgal[1], Meera Ramaswamy[2], Itai Cohen[2], and Brian J. Kirby[1]
[1]Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, United States; [2]Applied Engineering and Physics, Cornell University, Ithaca, NY 14850, United States

Colloidal suspensions in industrial processes often exhibit shear thickening that is difficult to control actively without changing the physical properties of the suspension constituents. In this work, we present a novel method in which we use acoustic perturbations to actively tune the shear thickening in these suspensions and investigate their dynamics. The key principle underlying our work is that nanoscale acoustic disturbances locally perturb particles and break the force chains responsible for thickening, and thus reduce the suspension viscosity. We apply acoustic perturbations by bonding a piezoelectric element to the bottom plate of the rheometer. We find that the suspension viscosity can be tunably reduced by simply varying the perturbation amplitude, and this tunable dethickening is achieved only at the shear rates corresponding to a thickened state. Additionally, we investigate the suspension dynamics and the temporal evolution of the force chains governing the viscosity using our customized acoustic-rheometer setup. We precisely measure the hysteretic rheological response by cyclically varying the input power. Importantly, this methodology of applying time varying acoustic perturbations can be generally applied in many other soft material systems ranging from polymers and bio-gels to granular materials and emulsions to probe various timescales in play and elucidate mechanisms governing the rheology. The ease with which this technique is applied makes it a powerful method for actively controlling suspension flow properties and investigating system dynamics.

Wednesday 2:20 Room 304 SC36

A new dimensionless number governing dethickening in orthogonally perturbed shear thickened suspensions

Meera Ramaswamy[1], Itai Cohen[1], and Abhishek Shetty[2]
[1]Applied Engineering and Physics, Cornell University, Ithaca, NY 14850, United States; [2]Rheology Division, Anton Paar, Ashland, VA 14850, United States

When concentrated colloidal suspensions are under stress, their viscosity can increase by over an order of magnitude. Previous work has shown that this shear thickened viscosity can be tuned by applying fast oscillatory perturbations orthogonal to the primary shear flows in the system. In this talk, I show that dethickening in the regime where the primary shear flow has fully thickened the suspension, is governed by a single dimensionless parameter - the ratio of the orthogonal shear rate amplitude to that of the primary shear rate. In contrast, a second parameter is required to describe the data in the primary shear flow regime where the suspension is thickening. We also find that larger orthogonal shear rate amplitudes are required to break up force chains at lower volume fractions. Understanding these parameters will enable better strategies to tune the properties of shear thickening suspensions for applications ranging from 3D printing to the processing of cement.

Wednesday 2:45 Room 304 SC37

Pre-shear holds the key to understanding discontinuous shear thickening in dense suspensions

Tabish Khan and Prabhu Nott
Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

The phenomenon of discontinuous shear thickening (DST) of dense particle-liquid suspensions has received a lot of attention in the last few years, and it is now generally believed that the formation of a Coulomb friction-mediated interparticle contact network causes the dramatic rise in viscosity at a critical shear stress. A common feature of most experimental studies is that the suspension is pre-sheared for a long time, typically an hour or more, before conducting the shear rate/stress sweep. However, little is known about what happens during pre-shear, and why is it is needs to be done for such a long duration. Here we report that pre-shear holds the key to understanding DST. By conducting carefully rheometry over long time scales, we show the slow build-up of microstructure that culminates in DST. We show that over the period of pre-shear the suspension goes through continuous shear thickening (CST), then DST, followed by jamming, and finally followed by frictional plastic deformation. We give plausible arguments for why DST occurs after such large strain, and conclude with remarks on what our findings imply for suspension processing.

Wednesday 3:45 Room 304 SC38

The evolving rheology of basaltic lava flows

Arianna Soldati[1], Bruce Houghton[2], and Donald B. Dingwell[1]
[1]Ludwig-Maximilians-Universitat Munchen, Munchen 80333, Germany; [2]University of Hawaii at Manoa, Honolulu, HI, United States

Basaltic lava flows cover the majority of Earth's surface, and pose a threat to human infrastructures. Their emplacement dynamics is primarily controlled by lava rheology. Notably, lava flows are complex multiphase systems whose rheology varies along- and across-flow through both space and time. In a magmatic system at equilibrium, temperature controls crystal fraction and residual liquid composition. These three factors contribute to determining the overall rheological behavior of the flow. However, lava flows are typically emplaced under disequilibrium conditions, which provides an additional layer of complexity to their rheology. So far, the rheological behavior of lava flows has been explored through a limited number of challenging field and laboratory studies. Here we present an overview of the state of the art of rheological studies applied to effusive volcanic eruptions. Specifically, we focus on the case study of the four months-long 2018 Kilauea eruption, for which a wide range of effusion temperatures, bulk compositions, and textures was documented for the 24 eruptive fissures. We investigate the effect of such

parameters on lava flow rheology through high-temperature laboratory experiments. A representative sample suite spanning the compositional range of the erupted lava is considered. Melt-only viscosities are determined for each sample, revealing two distinct trends for lavas emitted during the first and second phase of the eruption. Liquid+crystal rheology measurements are also being conducted at appropriate magmatic temperatures (1020 ?C - 1140 ?C), both under equilibrium and disequilibrium conditions. This innovative, comprehensive approach sets a new standard for the rheological study of a multi-episode effusive eruption. The quantified inter-episode lava rheology heterogeneity provides the right context for interpreting the range of observed flow speeds and emplacement dynamics.

Wednesday 4:10 Room 304 SC39

Deciphering nanocolloid suspension rheology by passive probe rheology simulations

Dinesh Sundaravadivelu Devarajan and Rajesh Khare
Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

Knowledge of the structure-flow-end use property relationships is important for designing practical applications of nanocolloidal suspensions. Recently, we have developed an explicit solvent model of colloidal suspensions that has the ability to capture the effect of the specific colloid-solvent and solvent-solvent interactions on the rheological behavior of nanocolloids. The viscosity and the linear viscoelasticity of these model suspension systems over a range of volume fractions (φ=0.15 to 0.49) as obtained from the non-equilibrium molecular dynamics (NEMD) simulations were found to be in good agreement with the literature theoretical, experimental, and simulation studies. In this work, the use of passive probe rheology simulation technique for determining the viscoelastic properties of the nanocolloidal suspensions was studied. The Brownian motion of the probe is analyzed using the inertial generalized Stokes-Einstein (IGSER) relation. The resulting dynamic moduli (G*) values obtained from passive rheology are in good agreement with those obtained from the active rheology and the bulk rheology simulations. The moduli values obtained from probe rheology will be discussed in the context of the size ratio of the probe and the colloidal particles.

Wednesday 4:35 Room 304 SC40

Rheology and shear-induced structural breakdown in model conductive carbon black suspensions

Julie B. Hipp[1], Jeffrey J. Richards[2], and Norman J. Wagner[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]Chemical & Biological Engineering, Northwestern University, Evanston, IL 60203, United States

The shear-dependent behavior of carbon black suspensions has been widely studied due to their use in many applications where flow is an important aspect as well as their use as a model colloidal suspension for understanding the general behavior of thixotropic suspensions and suspensions of non-uniform particles. In these suspensions, it is commonly understood that shear-dependent properties of interest are directly related to the suspension microstructure. However, direct measurements of this shear-dependent microstructure are lacking, especially at high particle loadings where interactions play a significant role. In this research, the shear-induced microstructure of carbon black suspensions is directly measured by performing Rheo-USANS (Ultra-Small Angle Neutron Scattering) experiments at a range of applied shear rates. The suspensions studied consist of two conductive carbon blacks suspended in either propylene carbonate or mineral oil at a range of volume fractions above the gel point. Therefore, these experiments explore the effects of interaction strength, particle loading, and building block characteristics on the shear-dependent size and fractal dimension of carbon black agglomerates. This structural information is quantified using a hierarchical fractal model and shows a decrease in agglomerate size with increasing shear intensity as well as a volume fraction-dependent agglomerate fractal dimension. This structural information is paired with rheo-electric measurements which show that the extent of structural breakdown is related to the measured shear-thinning behavior and evolution in electrical conductivity. The scaling behaviors of these properties are shown to be system-specific, which points towards a different mechanism by which structures are formed in these systems. This research provides quantitative structure-property relationships for the design of carbon black suspensions for applications such as electrochemical energy storage methods as well as for related suspensions based on particle gels.

Wednesday 5:00 Room 304 SC41

Dynamics and rheology of concentrated suspensions of polarizable particles in an electric field

Siamak Mirfendereski and Jae Sung Park
Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, United States

The rheological behavior of concentrated suspension of ideally polarizable spherical particles in an electric field has been studied using large scale numerical simulations. The particles are assumed to undergo the nonlinear electrokinetic phenomenon termed as dipolophoresis, which is the combination of dielectrophoresis and induced charge electrophoresis. At concentrated regimes, non-trivial suspension dynamics are observed in terms of the hydrodynamic diffusivity, velocity statistics, and number-density fluctuations, where a secondary maximum arises before approaching random close packing. Up to volume fraction of 35%, the particle mobility seems to be hindered by the increase in excluded volume fraction with particle concentration; however, it starts to increase with volume fraction at ?=35% and reaches a local maximum, and then decreases when approaching random close packing. The pair distribution function is also used to examine the local microstructure of the suspensions. The change in the local microstructure, which is known to be strongly correlated to rheological properties of the suspension, can tie into the non-trivial behaviors observed in suspension. In order to quantify the rheological properties of the suspension, the particle stress tensor is calculated. Interestingly, we have seen that normal particle stress in the field direction is predominant over that in other directions, exhibiting a similar trend to the hydrodynamic diffusivity and velocity fluctuation. Lastly, we will discuss the effect of confinement on suspension dynamics and rheology.

Wednesday 5:25 Room 304 SC42

An experimental study on the shear-induced migration of particles in yield stress fluids

Ahmadreza Rashedi[1], Nicolas Lenoir[2], Guillaume Ovarlez[3], and Sarah Hormozi[4]

[1]Mechanical engineering, Ohio University & Universite de Bordeaux, Athens, OH 45701, United States; [2]Laboratory 3SR - UMR 5521, Engineering Institute Univ. Grenoble Alps, Grenoble Cedex nine, Grenoble 38041, France; [3]Physical Chemistry, Universite de Bordeaux, Pessac, Bordeaux 33600, France; [4]Ohio University, Athens, OH 45701, United States

Dense suspensions of solid particles in complex fluids are ubiquitous in many natural and industrial settings. In a nonhomogeneous shear flow, it has been shown that the particles migrate from regions of high shear rates to regions of low shear rates, so-called Shear-Induced Migration (SIM) of particles, which is well studied for Newtonian suspending fluids. However, our knowledge of SIM of particles in complex fluids is limited. The main challenge is that even in the creeping flows, the kinetics of migration not only depends on the shear strain but also depends on the shear rate. Therefore, in order to study SIM in complex fluids, we need to have access to instantaneous distribution of particles in the flow. We have developed a new experimental technique based on X-ray radiography [1] with high spatial and temporal resolutions to study the SIM of particles in complex fluids. We used this technique to study SIM of particles in a yield stress fluid in a wide-gap Taylor Couette geometry. We present our experimental results and refine the recent model framework for the dispersion of solids in yield stress fluids [2].

References:[1] Gholami, M., Rashedi, A., Lenoir, N., Hautemayou, D., Ovarlez, G. and Hormozi, S., 2018. Time-resolved 2D concentration maps in flowing suspensions using X-ray. Journal of Rheology, 62(4), pp.955-974. [2] Hormozi, S. and Frigaard, I.A., 2017. Dispersion of solids in fracturing flows of yield stress fluids. Journal of Fluid Mechanics, 830, pp.93-137.

Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Wednesday 1:30 Room 201 SM35

Molecular origin of strain hardening in blend of ring and linear polystyrene

Anine L. Borger[1], Wendi Wang[2], Qian Huang[2], Grethe V. Jensen[3], Junyoung Ahn[4], Taihyun Chang[4], Dimitris Vlassopoulos[5], and Kell Mortensen[1]

[1]Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark; [2]Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby 2800, Denmark; [3]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, United States; [4]Department of Chemistry, Pohang University of Science and Technology, Pohang 37673, Republic of Korea; [5]Institute of Electronic Structure & Laser, FORTH, Heraklion 70013, Greece

Ring polymers have attracted a great deal of scientific interest due to the lack of free ends which has dramatic consequences on their rheology. Previous studies show that the zero shear viscosity of pure rings is much lower than that of their linear counterparts with the same molecular weight.[1] However, it has been shown that when linear polystyrene is mixed with rings in certain ratios, the zero shear viscosity of the blend is even higher than that of the linear. Uniaxial extensional rheology measurements of the blend show that the maximum stress was enhanced and followed by an unexpected stress overshoot at large Hencky strains. The strain hardening up until the maximum could be relevant e.g. for fiber spinning since strain hardening leads to increased molecular orientation and stretching that again leads to increased fiber strength. In order to study the structural origin of the observed strain hardening, Very Small Angle Neutron Scattering (VSANS) is used in this study.

In the present work, to explore how the rings affect the linear molecules, a blend of 30 % ring and 70 % linear polystyrene molecules (both of molecular weight 185 k and with 10 wt% deuterated linear chains) and a reference sample of pure linear polystyrene (also of molecular weight 185 k and 10 wt% deuterated chains) are used. The samples were prepared by using a filament stretching rheometer at 130C with a constant Hencky strain rate of 0.003 s^{-1}, and quenched at different times. One sample was quenched before the maximum stress where the segments start to be oriented. A second sample corresponds to maximum stress for the blend where the linear chains in the blend are stretched the most with respect to their counterparts in the pure linear. In this way, the level of molecular stretching of the linear component in the blend is quantified and compared with the linear material. Thus, we shine light on the origin of the strain hardening in the linear ring blend.

[1] Pasquino et al., ACS Macro Lett. 2013, 2, 874-878

Wednesday 1:55 Room 201 SM34

Extensional rheology of ring polystyrene melt and linear/ring polystyrene blends

Qian Huang[1], Junyoung Ahn[2], Daniele Parisi[3], Taihyun Chang[2], Ole Hassager[1], Sergey Panyukov[4], Michael Rubinstein[5], and Dimitris Vlassopoulos[3]

[1]Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby 2800, Denmark; [2]Department of Chemistry, Pohang University of Science and Technology, Pohang 37673, Republic of Korea; [3]Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, Heraklion 70013, Greece; [4]P. N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow 117924, Russia; [5]Duke University, Durham, NC 27708, United States

The state-of-the-art understanding of entangled linear polymers is based on the concept of physical network formation from entanglements. The physical network is characterized by a plateau modulus in linear viscoelastic (LVE) measurements. However, linking the two free ends of a linear polymer, thereafter called a ring polymer, has dramatic consequences. For example, non-concatenated rings have much lower zero-shear-rate viscosity compared to their linear entangled counterparts. A plateau modulus is not observed in LVE measurements for ring polymers [1].

Due to the difficulties in synthesis, which leads to very limited amount of samples, well-defined ring polymers have never been studied in extensional flow. In this work, we present the first results of extensional rheology of a ring polystyrene (PS) melt with the molecular weight 185k (Ring-185k). We show that the ring PS is surprisingly strain hardening in extensional flow, and reaches the same extensional steady state viscosity as its linear counterpart (Lin-185k) when the stretch rate is fast enough. We further present the extensional rheology of blends made of Ring-185k and Lin-185k, with weight fraction of 5%, 20%, and 30% of Ring-185k, respectively. We show that in the transient stress-strain responses, stress overshoot is observed for the samples containing 20% and 30% Ring-185k, while the stress overshoot is not observed for the pure Ring-185k and Lin-185k.

The present results shed light into the fascinating flow properties of polymers without free ends, while they also advance the state-of-the-art in polymer physics. At the same time, they open the route for understanding the response of folded proteins and chromosome territories under strong external fields.

[1] Pasquino et al., ACS Macro Lett. 2013, 2, 874-878

Wednesday 2:20 Room 201 SM36

Stress relaxation in ring-linear polymer blends

Daniele Parisi[1], Michael Rubinstein[2], and Dimitris Vlassopoulos[1]

[1]Institute of Electronic Structure & Laser, Foundation for Research and Technology Hellas, Heraklion 70013, Greece; [2]Duke University, Durham, NC 27708, United States

An essential feature associated with the mechanism of motion of linear polymers is the presence of free-ends1. Ring polymers without chain ends exhibit a very different behavior characterized by a power-law stress relaxation2,3, no entanglement plateau and lower viscosity compared to their linear counterparts. A natural question is what happens when linear and ring polymers are blended. We show, by means of rheological experiments, that the addition of rings to an entangled linear polymer melt gives rise to a nonmonotonic variation of the viscosity as a function of the ring polymer fraction. As it was also shown by McKenna and Plazek.4 Interestingly, the viscosity of the blend can even reach values up to two times higher than the pure linear polymer chains because of threading effects of the latter on rings. By adopting the self-consistent model of constraint release of polymer chains5 and accounting for the coherent constraint release of ring polymers mediated by the reptation of linear chains, we show how to describe the linear viscoelasticity of the linear-ring polymer blends in the region of small fraction of rings. In the limit of very large fractions of rings the rheology is extremely sensitive to the presence of linear chains, as also confirmed by simulations6. These results contribute toward the development of a generic picture of polymer blend dynamics.

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Wednesday 2:45 Room 201 SM37

Direct visualization of single ring polymers in the flow-gradient plane of shear flow

Michael Q. Tu[1], Megan Lee[2], Rae M. Robertson-Anderson[2], and Charles M Schroeder[1]

[1]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States; [2]Department of Physics, University of San Diego, San Diego, CA 92110, United States

Ring polymers lack free ends, thereby yielding a unique chain topology that has fascinated polymer physicists and chemists for decades. Despite recent progress, a complete understanding of the dynamics of ring polymer systems remains elusive. Moreover, we generally lack a robust experimental system for interrogating ultrapure ring polymers in shear flow, even in the dilute solution regime. In this work, we experimentally study the dynamics of ring polymers in shear flow using single-molecule imaging. We designed and built a custom shear flow apparatus that is compatible with fluorescence microscopy and allows for imaging of single chain dynamics in the flow-gradient plane of shear flow. In this way, we directly visualize fluorescently labeled ring polymers in shear flow using this custom-built device mounted on an inverted microscope. Using this approach, single chain conformations can be used to understand the contributions of ring polymer molecules to bulk rheological properties such as viscosity and the first normal stress coefficient in shear. We report the steady-state shear fractional extension, orientation angle, and spatial conformation of these ring polymers in dilute solution as a function of dimensionless flow strength (Weissenberg number, Wi) and compare the results to their linear counterparts. We also report observations on tumbling and tank-treading-like behavior of single ring polymers in shear flow. From a broad perspective, these results provide new molecular-level insights into the dynamics of ring polymers in solution.

Wednesday 3:45 Room 201 SM38

Tight-links in extensional flows of nonconcatenated ring polymers

Thomas C. O'Connor[1], Gary S. Grest[2], Ting Ge[3], and Michael Rubinstein[3]
[1]Harry S. Truman Fellow, Sandia National Laboratories, Albuquerque, NM, United States; [2]Sandia National Laboratories, Albuquerque, NM, United States; [3]Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, United States

Non-concatenated ring polymers do not entangle like linear polymers, and they tend to have a much lower Newtonian viscosity than linear melts of similar molecular weight. However, recent experiments show that ring melts are extraordinarily sensitive to extensional flow, exhibiting a large rise in viscosity even for Weissenberg numbers Wi well below 1. Here, we explain the origin of this massive rise in viscosity through thorough molecular dynamics simulations of non-concatenated ring melts in uniaxial extensional flows. Ring melts of three molecular weights are elongated for constant Rouse Wi from 0.1 to 25 and compared to analogous data for linear melts. Simulations confirm that strong extension-rate thickening occurs for all Wi and we find it coincides with the extreme elongation of a minority population of rings that grows with Wi. The large susceptibility of rings to extension is due to a flow-induce formation of "tight-links" that connect two or more rings into supramolecular daisy-chains while flow persists. Links are pulled tight and stabilized by flow and can form spontaneously after flow begins. Once linked, the composite rings act like much larger molecules and experience much larger drag forces than individual rings, driving their strong elongation.

Wednesday 4:10 Room 201 SM39

Long-lived self-entanglements in ring polymers

Beatrice W. Soh, Alexander R. Klotz, and Patrick S. Doyle
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States

The dynamics of entangled linear polymers is well understood in terms of the tube model. A remaining challenge in polymer physics is to fully understand the dynamics of ring polymers, which have no chain ends and lie outside the framework of the tube model. In this work, we perform single-molecule DNA experiments to investigate the dynamics of self-entangled ring polymers. We use electric fields to induce self-entanglements in circular DNA molecules, which serve as a minimal system for studying chain entanglement. Our experimental results show that self-threadings give rise to entanglements in ring polymers and can slow down polymer dynamics significantly. We find that strongly entangled circular molecules remain kinetically arrested in a compact state for very long times, thereby providing experimental evidence for long-lived self-entanglements in ring polymers.

Wednesday 4:35 Room 201 SM40

Rheology of linear and circular DNA molecules

Sourya Banik[1], Dejie Kong[1], Rae M. Anderson[2], Michael J. San Francisco[3], and Gregory B. McKenna[1]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]Department of Physics, University of San Diego, Lubbock, CA, United States; [3]Department of Biological Sciences, Texas Tech University, Lubbock, TX, United States

Rheological experiments on linear and circular(ring) deoxyribonucleic acid (DNA) in solution have been conducted to investigate the dynamics of these different topologies. DNA with molecular weight ranging from 3*10^7 g/mol (45 * 10^3 base pairs) - 3*10^9 g/mol (4.6 *10^6 base pairs) have been used to conduct the experiments. Experiments were conducted on both circular and linear chain samples at different concentrations ranging from semi dilute to the entangled regime up to approximate entanglement densities of 700. The dynamic data suggests that entanglement in the rings is lower than its counterpart linear DNA and a consequent lower rubbery plateau modulus is observed. The damping function h(?) obtained from stress relaxation tests into the large deformation regime conducted on the concentrated samples suggests that the samples were in the entangled regime and similar to the h(?) predicted by the Doi-Edwards model. We also observed that the dynamic results for the circular chains are very susceptible to presence to linear chain impurities. Acknowledgments: The authors would like to thank the National Science Foundation under grant CBET 1603943 and the John R. Bradford Endowment at Texas tech University for support of this work.

Wednesday 5:00 Room 201 SM41

Shear and extensional rheology of large molecular weight cyclic poly(3,6-dioxa-1,8-octanedithiol) (polyDODT)

Dongjie Chen[1], Gregory B. McKenna[1], Judit E. Puskas[2], Carin A. Helfer[2], and Julia A. Kornfield[3]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]Department of Food, Agricultural and Biological Engineering, The Ohio State University, Lubbock, OH 44691, United States; [3]Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Rheology of ring-like or circular polymers remains an area of active research due to the difficulty of making ring polymers of sufficient purity free of linear contaminants. Past work has been limited to rings made in dilute solution and, consequently, have been limited to sizes of approximately 15 entanglements in the linear analog. Furthermore, synthesis in dilute solution results in small amounts of material being available for study. This problem has been overcome by reversible radical recombination polymerization (R3P) recently developed in the Puskas laboratories. R3P synthesis can produce 10-100g scale circular polymer which opens new avenues of research. Here we have studied poly(3,6-dioxa-1,8-octanedithiol) (polyDODT) synthesized by R3P of different molecular weights, solutions of polyDODT as a function of concentration, and cyclic and linear polyDODT mixtures using both shear and extensional rheometry. Of interest is that the largest polyDODT ring investigated to date has a molecular mass corresponding to approximately 297 entanglements in the linear counterpart. The extensional rheology behavior of cyclic polyDODT is compared with that of an emulsion polymerized styrene-butadiene rubber with similar glass transition temperature and entanglement molecular weight. The shear responses of the cyclic polyDODT and of mixtures of cyclic and linear polyDODT are compared with literature results for nominally uncontaminated cyclic polystyrenes. The Department of Energy, Office of Basic Energy Sciences under grant DE-SC0018657 and the John R. Bradford Endowment at Texas Tech University are thanked for their support of this project.

Wednesday 5:25 Room 201 SM43

Macromolecular architecture and complex viscosity

Mona Kanso, Alan J. Giacomin, Chaimongkol Saengow, and Jourdain H. Piette
Chemical Engineering, Queen's University, Kingston, Ontario, Canada

General rigid bead-rod theory [Hassager, *J Chem Phys*, **60**, 4001 (1974)] explains polymer viscoelasticity from macromolecular orientation. By means of general rigid bead-rod theory, we relate the complex viscosity of polymeric liquids to the architecture of axisymmetric macromolecules. In this work, we explore the zero-shear and complex viscosities of 26 different axisymmetric polymer configurations. When non-dimensionalized with the zero-shear viscosity, the complex viscosity depends on the dimensionless frequency and the sole dimensionless architectural parameter, the *macromolecular lopsidedness*. In this work, in this way, we compare and contrast the elastic and viscous components of the complex viscosities of macromolecular chains that are straight, branched, ringed, or star-branched. We explore the effects of branch position along a straight chain, branched-chain backbone length, branched-chain branch-functionality, branch spacing along a straight chain (including pom-poms), the number of branches along a straight chain, ringed polymer perimeter, branch-functionality in planar stars, and branch dimensionality.

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Wednesday 1:30 Room 305B IN34

Shear-induced sedimentation of a sphere in yield stress fluids: An experimental study

Ramin Mehrani[1], Mohammadhossein Firouznia[1], Metzger Bloen[2], Ovarlez Guillaume[3], and Sarah Hormozi[1]
[1]Mechanical engineering, Ohio University, Athens, OH 45701, United States; [2]Aix-Marseille University, Marseille, France; [3]Bordeaux University, Bordeaux, France

We present our experimental results on the flow induced by a settling sphere in yield stress fluids without and with a cross shear flow. The latter gives insight to the understanding of the nonlinear coupling of the simple shear flow and the settling flow. We investigate creeping flows and we use particle image velocimetry and particle tracking velocimetry to analyze the flow and measure the settling velocity. In these set of experiments, we use the Carbapol gel as a test fluid. We show the breaking of the fore-aft symmetry in the direction of gravity which corresponds to the unavoidable elastic properties of yield stress fluids. This feature affects the flow dynamics around the sphere which itself affects the terminal velocity. We provide a closure for the drag coefficient which depends on the Deborah number, Bingham number and the ratio of the cross-flow shear rate to the settling shear rate.

Wednesday 1:55 Room 305B IN35

From PAL to PAL-PSPG: A fast and stable method for viscoplastic flows*

Yannis Dimakopoulos[1], Pantelis Moschopoulos[1], George Makrigiorgos[2], Stylianos Varchanis[1], Alexandros Syrakos[1], Georgios C. Georgiou[3], and John Tsamopoulos[1]
[1]Department of Chemical Engineering, University of Patras, Patras, Achaia, Greece; [2]Department of Chemical & Biomolecular Engineering, University of California, Berkeley, Berkeley, CA, United States; [3]Department of Mathematics and Statistics, University of Cyprus, Nicosia, Nicosia 1678, Cyprus

Simulation of viscoplastic materials has always been a challenging task. The numerical difficulties that originate from the discontinuity at the yielded-unyielded interface require special handling [1]. For this purpose, a modification of the Augmented Lagrangian (AL) method has recently been proposed, namely, the Penalized Augmented Lagrangian method [2] which exhibits smaller computation times and the same accuracy compared to the existing AL methods. At the same time, a new finite element formulation for viscoelastic flows [3] has been proposed that uses equal order of interpolants for all variables along with the classical finite element stabilization techniques, like the PSPG. In this work, we couple the PAL algorithm with the new finite element formulation to present an even faster and stabler method for the computation of viscoplastic flows. The efficiency of the new framework is testified by comparing the numerical results of our method to those of the literature in three benchmark tests: the 2-dimensional flow of a viscoplastic fluid in a square lid-driven cavity, the problem of the steady rise of a bubble in a viscoplastic medium, and the transient filament stretching of a shear thinning, yield-stress fluid. In all cases, we attain the same numerical results, but at a considerably lower computational cost and superior stability. We perform mesh-convergence tests illustrating that both the PAL and the PAL-

PSPG feature an almost 1st order accuracy in space. The mesh-convergence order is limited by the PAL method itself and not from the low-order of interpolants of variables, making the new formulation even more attractive.

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[*] Walters Prize 2018

Wednesday 2:20 Room 305B IN36

Natural and forced convection in Bingham plastic fluids from two differentially heated cylinders in a square duct

Lubhani Mishra[1] and Raj P. Chhabra[2]
[1]Department of Chemical Engineering, Pandit Deendayal Petroleum University, Gandhinagar, Gujarat 382007, India;
[2]Department of Chemical Engineering, Indian Institute of Technology Ropar, Rupnagar, Punjab 140001, India

This study deals with the interaction between two cylinders in vertical arrangement in the natural or forced convection flow conditions inside a square duct to delineate the effects of the cylinder-cylinder and cylinder-wall interactions on the momentum and heat transfer characteristics in Bingham plastic fluids. The governing equations, namely, continuity, momentum and energy equations have been solved using a finite-element based solver, COMSOL Multiphysics (Version 4.3a) within the framework of laminar, steady, two-dimensional and incompressible flow conditions. The first section examines the laminar natural convection from di?erentially heated cylinders in a square duct filled with a Bingham plastic fluid where the vertical arrangement of cylinders at various locations within the duct has been considered for the following ranges of parameters: Rayleigh number (10^4 to 10^6), Prandtl number (10 to 100), Bingham number (0.01 to Bn_{max}) and cylinder diameter-to-duct length ratio as 0.2. Subsequently, forced convection heat transfer has been investigated for a pair of identical circular cylinders in side-by-side arrangement confined in an adiabatic square duct. The cylinders are subjected to the cross-flow of Bingham plastic fluids in the duct with single inlet and outlet ports over the following ranges of the parameters: Reynolds number (5 to 200), Prandtl number (1 to 100) and Bingham number (1 to 100). The numerical results for the velocity, pressure and temperature fields are interpreted in terms of streamfunction and isotherm contours, yield surfaces, local Nusselt number distribution, drag coefficients and average Nusselt number. Predictive correlations have also been developed for the estimation of the heat transfer coefficient in a new application. Thus, the choice for the optimum cylinder arrangement can be made based on the overall values of the drag and Nusselt number determined by a complex interplay between the kinematic and geometric parameters of the system.

Wednesday 2:45 Room 305B IN37

Thixotropic yield-stress fluid drop splash: Testing a dimensionless group across different microstructure classes

Samya Sen, Anthony G. Morales, and Randy H. Ewoldt
Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

We use high-speed imaging to study drop impact and splash behavior of thixotropic yield-stress fluids. Aqueous suspensions of Laponite and Carbopol are both systematically studied, allowing tests of different microstructures against a proposed microstructure-agnostic dimensionless group to identify regime boundaries of stick-splash behavior. The effect of composition, drop diameter, velocity, and coating thickness are studied systematically and specific regimes of impact behavior are identified. The proposed dimensionless group, a ratio of droplet inertia and dissipative flow stresses during the splash event, successfully separates the different impact regime behavior of all fluids studied. Remarkably, we observe a constant critical value of this group for the onset of splashing for all impact conditions and all fluids tested, independent of chemistry or microstructure.

Drop impacts with thixotropically aged fluids give the same outcomes except that 'aged' properties are required for the dimensionless group. However, characterizing flow properties of aged samples is challenging since any deformation inherently rejuvenates and breaks down the microstructure and the rheological properties change, now resembling those of a fresh or 'unaged' sample. Steady-state flow properties are therefore undefined for aged samples, and we propose alternative rheological techniques for characterizing flow properties of aged samples, further using these in dimensionless groups that rationalize the stick-or-splash regime maps.

The results here provide a dramatically simplified understanding of the fluid dynamics of droplet impact of these rheologically complex fluids, with diverse applications including spray coating, painting, and fire suppression.

Symposium MC
Microfluidic and Confined Flows

Organizers: Sujit Datta and Cari Dutcher

Wednesday 3:45 Room 305B MC6

Flows, instabilities and topography driven by supramolecular oscillatory structure forces due to confinement-induced layering of micelles in foam films

Vivek Sharma, Subinuer Yilixiati, Yiran Zhang, and Ewelina Wojcik
Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States

Ultrathin micellar foam films exhibit stratification, manifested as stepwise thinning and coexistence of thin-thick flat regions that differ in thickness by a nanoscopic step size equal to the intermicellar distance. Stratification typically involves the spontaneous formation and growth of thinner, darker, circular domains or thicker, brighter mesas. Mechanistically, domain expansion appears similar to hole growth in polymer films undergoing dewetting by nucleation and growth mechanism that can be described by considering metastable states resulting from a thickness-dependent oscillatory free energy. Dewetting polymer films occasionally phase separate into thick and thin regions forming an interconnected, network-like morphology by undergoing spinodal dewetting. However, the formation of thick-thin spinodal patterns has never been reported for freestanding films. In this contribution, we show that the thickness-dependent oscillatory contribution to free energy that arises due to confinement-induced layering of micelles can drive the formation of such thick-thin regions by undergoing a process we term as spinodal stratification. We visualize and characterize the nanoscopic thickness variations and transitions by using IDIOM (interferometry digital imaging optical microscopy) protocols to obtain exquisite thickness maps of freestanding films for both nucleation and growth mechanism and for spinodal mechanism. We find that evaporation and enhanced drainage in vertical films play a critical role in driving the spinodal stratification process that can occur in both single foam films and in bulk foam. The discovery of this hitherto unreported mechanism of drainage and rupture of micellar foam films that presents unexplored opportunities for understanding and controlling the stability, lifetime and properties of ubiquitous foams.

Wednesday 4:10 Room 305B MC7

The role of molecular elasticity in sprayable yield-stress fluids

Yu-Jiun Lin[1], Jeffrey S. Horner[1], Christine Mourafetis[1], Brandon Illie[2], Matthew Lynch[2], Eric M. Furst[1], and Norman J. Wagner[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]Corporate Functions, Procter & Gamble, Cincinnati, OH 45224, United States

Consumer application attributes are often conflicting, such that molecular engineering can be necessary to yield a successful commercial product. A common example of conflicting attributes is the need for shelf and transportation stability in products comprised of suspensions of emulsions or colloids along with good shear stability, and controllable dissociation. These requirements necessitate rheological properties of a yield stress fluid with low elasticity at high shear rates. Nanostructured fluids where physical interactions provide both this desired yield-stress as well as strong shear-thinning and spayability are required. Rational design of complex fluids at the nanoscale enables formulation of such function-oriented, advanced materials and effective manufacturing processes. In this research, we study engineered, physically associating hydrogels using microfluidics, rheology, and small angle scattering technique to elucidate the role of nanoscale interactions and molecular elasticity in determining the relevant rheological properties. Mixed gums create self-healing and yield-stress structured fluids that are also sprayable. For contrast, a well-characterized, polyethylene oxide solution of varying Mw is similarly studied. An experimental platform composed of microfluidic hyperbolic contraction with pressure sensors probing both shear and extensional properties. Simultaneous microscopy enables flow velocimetry building a connection to the deformation history which can be incorporated into structure kinetic model to study contraction-stimulated alteration. Moreover, bulk rheology and neutron scattering complement the microfluidic flow behavior, providing important insights and connections between molecular structure, bulk properties, and the behavior under more complex flows.

Wednesday 4:35 Room 305B MC8

Active- and transfer-learning applied to microscale-macroscale coupling in modeling of viscoelastic flows

Bruce Caswell[1], Zhen Li[2], Lifei Zhao[3], Zhicheng Wang[4], Jie Ouyang[5], and George Em Karniadakis[3]
[1]School of Engineering, Brown University, Providence, RI 02912, United States; [2]Department of Mechanical Engineering, Clemson University, Clemson, SC 29634, United States; [3]Division of Applied Mathematics, Brown University, Providence, RI 02912, United States; [4]Department of Mechanical Engineering, Massachusetts Institute Technology, , Cambridge, MA 02139, United States; [5]Department of Applied Mathematics, Northwestern Polytechnic University, Xi'an 710129, China

We apply active- and transfer-learning to the multiscale modeling problem of constructing effective constitutive approximations required for viscoelastic flow simulations from a fluid's microscale dynamics, so that its macroscopic rheology is thereby connected to a microstructural model. Our goal is to employ active-learning, based on Gaussian process regression, to adaptively couple the micro and macro scale calculations and run expensive microscale simulations only as necessary. We take the flows of a polymer solution as a model system to demonstrate the proposed multiscale method for the efficient simulation of viscoelastic flows. At the microscale level, we employ dissipative particle dynamics (DPD) to model the fluid as a suspension of bead-spring micro-structures. The fluid is then subjected to steady shear flow which yields the Non-Newtonian viscosity and the first normal stress difference as functions of the shear rate. DPD parameters are set by dimensional scaling relative to experimental steady-shear flow data for a real polymer solution. DPD results at the lowest possible shear rate yield an estimate of the zero-shear rate viscosity

which allows the initiation of the macroscale flow for Newtonian fluid solved by the spectral element method (SEM). The resulting strain-rate field is surveyed to determine additional shear-rate sampling points for the DPD system. This new information allows an initial fit of parameters for a constitutive equation, in this case the FENE-P model whose flow is again solved by SEM. Guided by active-learning Gaussian-process regression a survey of the new strain-rate field determines additional DPD sampling points only as necessary. This process continues to a prescribed endpoint.

Wednesday 5:00 Room 305B MC9

Cross-stream migration of non-spherical particles in a second order fluid – theories of particle dynamics in arbitrary quadratic flows (i.e., pressure driven flows)

Cheng-Wei Tai, Shiyan Wang, and Vivek Narsimhan
Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47097, United States

Cross-stream particle migration in viscoelastic suspensions plays a crucial role in many applications in the biomedical community and the chemical/oil industries. Previous studies in viscoelastic media provided insight on the dynamics of spherical particles in simple shear viscoelastic flows, yet the combined effect of more complex flow profiles and particle shapes on the particle migration is underexplored. In this study, we investigate the dynamics of arbitrary-shaped particles in a second-order fluid, in a flow profile up to quadratic order. For the two model constants ?1 and ?2 (first and second normal stress coefficient) we assume the relationship ?1 = -2?2 under which the flow dynamics will behave as a Stokes flow with modified fluid pressure. The assumption greatly simplifies the mathematical procedure and allows us to capture the fundamental physics of in any slow, viscoelastic flow. We apply multipole expansion approximation to derive the analytical expressions for the polymeric force and torque on an arbitrary-shaped particle. The solutions compared well to previous studies on spheres as well as to our boundary element method (BEM) simulation for arbitrary shaped particles. We apply the derived solutions to study the dynamics of sphere, spheroids (prolate & oblate) and ellipsoid in a quadratic flow of second-order fluid. We examine the particle migration behavior at different positions in a pressure driven flow, as well as the translational and rotational trajectories of the particles. We find that particles tend to migrate towards the flow center and undergo tumbling or alignment with the flow under the influence of polymeric force and torque. Several factors such as flow strength, particle position, shape, and orientation post significant effects on particle motion. Their influences are examined in this work. We summarize by discussing the future directions for experimental studies on particle dynamics as well as for extending current theory towards more complicated systems.

Wednesday 5:25 Room 305B MC10

Experimental investigation of particle electrophoresis in non-Newtonian fluids

Amirreza Malekanfard, Wuzhou Zu, Apollo M. Wolfersberger, and Xiangchun Xuan
Clemson University, CLEMSON, SC, United States

Among the various particle handling approaches in microfluidic devices, electric field is the method of choice because of various advantages. Numerous studies have been conducted investigating electrokinetic particle motion in Newtonian fluids. However, there has been a lack for their non-Newtonian counterparts, despite the fact that many biological and chemical fluids exhibit non-Newtonian characteristics. We present in this work the first experimental observation of polystyrene particles moving towards the walls of a straight rectangular microchannel in the electroosmotic flow of shear-thinning xanthan gum solutions. This phenomenon is on the contrary of that in Newtonian fluids, where particles are repelled from the channel walls and focused towards the center by the wall-induced electrical lift force. We will also present a systematic study of multiple parametric effects on particle electrophoresis in xanthan gum solutions.

Symposium AD
Active and Directed Systems

Organizers: Travis Walker and Arezoo Ardekani

Wednesday 1:30 Room 306A AD1

Magnetically actuated colloidal microswimmers based on elliptical orbits

Sibani Lisa Biswal
Chemical and Biomolecular Engineering, Rice University, Houston, TX, United States

Microscale swimmers are of great interest in a number of scientific and technological applications, from sperm motility to microscale robots. There have been advances in generating mimics for nature's microswimmers, but the swim strokes that can be achieved are limited. We report a novel method for microscale propulsion in which an "arm" particle is directed to orbit near a larger "torso" particle using an eccentric rotating magnetic field, breaking their positional symmetry in a manner that results in the two swimming together in a specified direction. Our results demonstrate how multiple arms and bodies can be reconfigured in situ, allowing us to change the direction and speed of these colloidal microswimmers, as they can intelligently adapt to decrease their drag force. This work provides a new methodology for achieving nonreciprocal motion at low Reynolds number and offers insight into directing the motion of collective active systems.

Wednesday 1:55 Room 306A AD2

Dielectric nanofluids

Jianeng Wang[1], Kevin J. Frankforter[2], Daniel C. Ludois[2], and Daniel J. Klingenberg[1]
[1]Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States; [2]Electrical and Computer Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States

Fluids with high dielectric constant, low conductivity, and low viscosity are needed for electrostatic motors. Adding polarizable particles to a conventional, nonconducting fluid can create a suspension with a high dielectric constant. Electrostatic motors employ large electric fields, and the large field-induced viscosities that arise from the electrorheological effect can be avoided by using Brownian nanoparticles, such that the thermal particle motion overcomes the electrostatic interactions between particles. In this presentation, we will describe experiments and Brownian dynamics simulations aimed at engineering such dielectric nanofluids. Barium titanate particles are synthesized and sterically stabilized to prevent aggregation via van der Waals forces. The particles are dispersed in various nonaqueous liquids. Brownian dynamics simulations are employed to understand the relationships between particle size, concentration, steric layer properties, and electric field strength, and the macroscopic dielectric and rheological properties of the suspensions. Employing particles with diameters on the order of 10 nanometers at a concentration of 25% by volume produces a low viscosity suspension, even in the presence of large electric fields on the order to 10 kV/mm, with a dielectric constant twice that of the suspending liquid.

Wednesday 2:20 Room 306A AD3

Electro-rheology (ER) performance of salt-doped polyurethane thermoset particles dispersed in silicone oil

Robert L. Sammler[1], Brian Nickless[1], Sarat Kuchibhatla[1], David Adrian[2], Justin Walker[1], Willliam Woodward[1], and Thomas P. Clark[3]
[1]Core R&D, Dow, Incorporated, Midland, MI 48640, United States; [2]Dow Performance Silicones, Dow, Incorporated, Midland, MI 48640, United States; [3]DuPont, Midland, MI 48674, United States

Salt-doped polyurethane (PU) thermoset particles dispersed in a non-conducting low-viscosity silicone fluid are under investigation to develop active ("smart") mechanical elements (e.g. clutches, brakes, actuators, control valves, dampers, ...) coupled to sensors triggering the electric field. These stable scalable PU dispersions undergo fast reversible low-current liquid-to-solid transitions at room temperature when subjected to high electric field strengths. The PU dispersions are studied over a range of temperatures (-10 to 120 °C), a range of DC electric field strengths (0 to 4.5 kV/mm), and a range of AC electric-field angular frequencies ω_e (0 to 100 rad/s, $E_0 = 4.0$ kV/mm) while being subjected to either oscillatory or steady shear flows in an annulus. Data interpretation is guided by the electrostatic polarization theory. The ER performance of these salt-doped PU dispersions is found to be dominated by the conductivity mismatch $(\sigma_P-\sigma_C)/(\sigma_P+2\sigma_C)$ between the particles and the silicone oil, and their performance may be elevated with use of AC electric fields with low electric field oscillation frequencies ($\omega_e < 5$ rad/s). The ER performance is strongly temperature dependent, and often exhibits peak ER performance around 37 °C regardless of the applied electric field strength E or oscillation frequency ω_e.

Wednesday 2:45 Room 306A AD4

Exploration of novel responsive and interfacially anchored magneto-capillary gels

Natasha I. Castellanos[1], Sangchul Roh[1], Bhuvnesh Bharti[2], Saad A. Khan[1], and Orlin D. Velev[1]
[1]Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States; [2]Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, United States

We will report how the control of the capillary forces and magnetic interactions can be used to form new smart multiphasic gel systems. We have demonstrated the formation of soft micromagnets composed of polydimethylsiloxane (PDMS) beads, which may have internally embedded chained magnetic nanoparticles. The magnetic-field-directed assembly of the nanoparticles allows for the generation of anisotropic nanostructured PDMS beads. The chain-containing microspheres could have a permanently embedded dipole moment and hence, residual polar magnetization. Once magnetized, their response results in the formation of percolated networks. We have compared gels from these chained beads with PDMS beads with randomly dispersed MNPs from our previous work. We will also describe two types of Magnetically Responsive Capillary Gels (MRCGs). In MRCG Type 1, the magnetic nanoparticles (MNPs) are dispersed in the liquid phase that forms capillary bridges between the silicone microspheres. MRCG Type 2 is constituted of magnetically responsive elastomer microbeads with internally embedded MNPs. We will present the characterization of these gels in terms of rheology, magnetic response, and the ability to self-repair. We proved the tunability of the new chained bead system by conducting magnetization, demagnetization, and re-magnetization experiments that show evidence of the successful reformation of percolating networks. We are currently using magnetic interaction templating to study and manipulate a magnetic response. The direct structure templating could potentially improve the precision of rheological measurements by anchoring the gels to 3D printed patterns. Another potential application of such a gel system could be water filtration. Overall, we have constructed and are developing further a rich toolbox of structures and interactions for making novel magneto-responsive gel networks.

Wednesday 3:45 Room 306A AD5

Hydrodynamic coupling to the electrical response of fluid suspensions of non-Brownian conducting particles

Jeffrey J. Richards and Matthew Snell

Chemical & Biological Engineering, Northwestern University, Evanston, IL 60203, United States

Here, we report on the electrical response of conducting non-Brownian suspensions to applied steady shear. These observations are made in a rheo-dielectric device that tracks the transient and steady electrical response of complex fluids to well-defined deformations. We show using dc-conductivity measurements a shear-rate dependent conductivity that increases both with the shear intensity and the particle volume fraction. The conductivity increases instantaneously upon flow start-up and returns instantaneously and reversibly to the quiescent value upon flow cessation. For volume fractions exceeding 30 vol% microspheres, the ratio of the conductivity under flow to that in the quiescent state can exceed a factor of 10^5. We further examine the origin of this increase using impedance spectroscopy. These measurements reveal a dielectric relaxation feature that is associated with the pair hopping rate of electrons between particles within the suspension. By fitting this dielectric response, a characteristic hopping time can be extracted that is linear with shear rate. These results agree quantitatively with a simple scaling model that approximates the pair-hopping rate of electrons as proportional to the collision frequency of particles within the suspension. This result confirms that the hydrodynamic forces imposed by simple shear couples to the interparticle charge transfer rate. In this way, the electrical response is directly linked to the displacement rate of the fluid. These observations help to reconcile emerging experimental evidence for the role of particle mobility in determining electrical transport in colloidal fluids and suspensions and could provide a basis for new mechano-electric sensing modalities as well as improved electrochemical storage technologies.

Wednesday 4:10 Room 306A AD6

Dynamics of colloids above a bottom wall driven by active torques and forces

Aleksandar Donev

Courant Institute of Mathematical Sciences, New York University, New York, NY 10012, United States

I will describe numerical methods to study the dynamics of suspensions of colloids sedimented above a bottom wall and driven by externally-applied forces (sedimentation) or torques (microrollers). The proximity of the boundary controls the collective dynamics of these active suspensions. Recently a new instability has been observed experimentally and numerically: the fingering of a front of suspended microrollers near a floor. A continuum model shows that this instability is linear and that the size scale selection arises only from hydrodynamic interactions between the particles and the wall. From these fingers, long-lived compact motile structures, called 'critters', can be formed just with hydrodynamic interactions. The presence of a nearby no-slip boundary strongly affects the structures emerging in sedimenting colloidal suspensions. The suspensions first forms a monolayer with a dense traveling front, which can be described using a simple one dimensional nonlocal PDE. The front then transitions into finger-like structures whose width depends on the particle size and height from the floor.

Wednesday 4:35 Room 306A AD7

Particle migration in channel flow of viscoelastic fluids

Amir Hossein Raffiee, Sadegh Dabiri, and Arezoo M. Ardekani

Purdue University, W Lafayette, IN 47907-2088, United States

Particles in a viscoelastic fluid accumulate at discrete set of equilibrium points in a straight microchannel. Evaluation of the governing forces allows us to predict the behavior and equilibrium positions of particles in a microchannel for a wide range of parameters, which is crucial in the design of microfluidic devices for various applications such as such as particle sorting and separation. In this study, we use 3-dimensional computational model to simulate the interaction between the particle and the surrounding polymeric solution using a Giesekus constitutive equation. The results provide an insight into the motion of cells and particles and explain the findings of previous experiments. Furthermore, our results suggest new particle behavior in the range of medium inertia and low elasticity that have not been found before.

Wednesday 5:00 Room 306A AD8

Diffusiophoresis of active colloids in viscoelastic media

Shabab Saad and Giovanniantonio Natale

Chemical & Petroleum Engineering, The University of Calgary, Calgary, AB T2N1N4, Canada

Active colloids (AC) are interesting objects that are able to generate enhanced diffusive motion in the absence of any external fields. Since any biological fluid is viscoelastic in nature, the characterization of active motion in complex fluids is of high relevance for potential drug delivery applications where ACs could act as cargo particles. Here self-diffusiophoretic behavior of a model system made of platinum coated silica Janus microspheres is investigated in presence of hydrogen peroxide in two viscoelastic fluids. Experimentally Janus colloids were dispersed in a dilute Polyvinylpyrrolidone (PVP) water solution and in Polyacrylamide (PAM) water solutions in semi-dilute and semi-dilute entangled regime. PVP is a Maxwell fluid with a single relaxation time whereas PAM behaves as a Jeffrey fluid. These two systems were chosen to probe different relaxation times in the order of $\sim 10^{-3}$ s for PVP to ~10 s for PAM but always smaller than the rotary Brownian motion time scale. Within this regime, we investigate the coupling between the particle dynamics and the viscoelasticity of the medium. Interestingly, we observe in the particles' mean square displacements the competition between the polymer mesh confinement and active motion. These findings are the foundations to understand the collective motion of ACs in complex media.

Wednesday 5:25 Room 306A AD9

Migration of an electrophoretic particle in an inertial or viscoelastic shear flow

Aditya S. Khair and Jason K. Kabarowski
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

The motion of an electrophoretic particle in a weakly inertial or viscoelastic shear flow is calculated. We are motivated by recent experiments reporting cross-streamline migration of spherical charged colloids undergoing electrophoresis in Poiseuille microchannel flow. For a Newtonian fluid, these experiments report that a particle migrates to the center(walls) of the channel when its electrophoretic velocity is in the opposite(same) direction to the Poiseuille flow. Here, we calculate that weak inertial effects lead to a cross-streamline lift force of O($\mu U a Re_s$) in an unbounded simple shear flow, where μ is the fluid viscosity, U is the electrophoretic particle velocity, a is the particle radius, and Re_s is the Reynolds number of the ambient shear. A comparison of our calculations to the above-mentioned experiments is made. Other recent experiments have observed migration of an electrophoretic particle in shear flow of a viscoelastic polymer solution. The migration direction is opposite to what is seen in Newtonian liquids. Here, we calculate that weak viscoelastic effects lead to a cross-streamline lift force of O($\mu U a Wi_s$) in an unbounded simple shear, where Wi_s is the Weissenberg number of the ambient shear. Again, our calculations are compared to the experimental observations.

Symposium TM
Rheometry: Advanced Techniques and Methods

Organizers: Joseph Samaniuk and Michelle Calabrese

Wednesday 1:30 Room 306B TM27

Shear and pressure effects on wax appearance in a waxy oil system

Abdualbaset Ali and Matthew Liberatore
University of Toledo, Toledo, OH 43606, United States

One of the common flow assurance problems in oil industries is the wax solidification in pipelines. Crude oil with a high wax content can result in precipitation and gelation of wax in pipelines. Pipeline blockage leads to safety and economic concerns. In this project, waxy crude oil was modeled using a model system of paraffin wax in mineral oil. The main objective from this work is to construct a wax phase diagram with shear and pressure as independent variables. These samples were used to investigate the effect of shear on the wax appearance temperature (WAT) at ambient pressure and at elevated pressure up to 2000 psi. At the ambient pressure, WAT was measured in the absence of flow (phase study) as well as using rheology. Parallel plate rheology shows that WAT can be altered by shear. Additional measurements using rheo-small angle light scattering will determine if optical or rheological measurements are more sensitive to wax appearance. The high-pressure rheology system combines a mixing cell, high pressure pump, and a pressure cell with rheometer, which has been previously used for heavy oil and hydrate-forming systems. Altering the waxy oils by saturating with methane will likely alter the wax appearance temperature also.

Wednesday 1:55 Room 306B TM30

Effect of SDS on whey protein polymers. Molecular investigation via dilute solution viscometry and dynamic light scattering

Ahmed S. Eissa
Chemical Engineering Department, Cairo University, Cairo 12613, Egypt

Whey proteins are of special importance in formulated foods due to their rich nutritional and functional benefits. Whey proteins form large polymers when heated to a temperature greater than the denaturation temperature. Hydrophobic interactions play an important role in building whey protein polymers. In this study, the effect of Sodium Dodecyl Sulfate (SDS) on whey protein polymers was assessed. Although SDS was expected to dissociate protein polymers into smaller chains, interestingly, polymer molecules got larger upon SDS addition as revealed by both viscometry and dynamic light scattering. Addition of SDS shifted the molecular size distribution of whey protein polymers to higher size and fragmented the bimodal size distribution into trimodal distribution. The study opens a venue for manipulating and enhancing whey protein functional properties by manipulating the hydrophobic interactions via surfactants.

Wednesday 2:20 Room 306B TM31

Rheology as a tool to understand anti-drip properties in flame retardant polycarbonate resins

Manojkumar Chellamuthu[1], Shankar K. Subramanian[1], Zachary Anderson[1], Himanshu Asthana[1], Samrat Sur[2], and Jonathan P. Rothstein[2]
[1]SABIC, Mount Vernon, IN 47630, United States; [2]University of Massachusetts, Amherst, MA 01003, United States

We have investigated the flame resistant properties of a cross-linkable polycarbonate resin by using a dynamic mechanical analysis. A UV curable polycarbonate resin showed a strong rubbery plateau as a function of UV dosage and the amount of UV active end group. The defined threshold value of 9MPa from 160-190°C clearly demonstrates the influence of crosslink density and molecular weight in resisting the flame propagation. Additionally, using a high temperature extensional rheometer, we were able to optimize the effects of long chain branching in polycarbonate resins for improving the anti-drip properties.

Wednesday 2:45 Room 306B TM32

Applications of EMS rheometry from viewpoint of remote sensing

Taichi Hirano, Shujiro Mitani, and Keiji Sakai
Fundamental Engineering, Institute of Industrial Science, UTokyo, Meguro-ku, Tokyo 153-8505, Japan

Recently, we developed an epoch-making methodology of rheometry featured by noncontact manners of torque induction and rotation detection. The system enables accurate and rapid measurement; the accuracy in detecting water viscosity is better than 1% even in low shear rate less than 10 s^{-1}. In addition, owing to the remote driving and sensing technique, a measurement in a sealed container and its disposable usage are possible. The system will be a powerful tool for multi-specimen test of bio-tissues, preventing contamination to/from sample specimens.

The remote torque is induced by our original technique named electromagnetically spinning (EMS) method. In this method, a conductive substance such as aluminum, copper and titanium is used as a rotational probe. A temporally modulated magnetic field causes eddy currents in the probe, and the currents and the magnetic field generates a driving torque through the Lorentz interaction. The rotational speed of the probe is detected by a video-camera device.

In our recent research, we employed a newly developed auto-standing probe, which is versatile for general use of rheological measurement. In the presentation, we would introduce some interesting measurement results obtained using various type of probes; pressure dependence of gas viscosity, two-dimensional rheometry of surfactant monolayer and flow curve measurements of human whole bloods. In addition, we show a commercially available model system of EMS system prepared for the industrial use.

Symposium AR
Applied Rheology for Pharmaceuticals, Food, and Consumer Products

Organizer: Stephanie Lam and Helen Joyner

Wednesday 3:45 Room 306B AR6

Comparison of the behavior and distribution of extension and shear rates in a model sigma blade mixer with a non-Newtonian fluid and their impact on bubble size distribution

Neslihan Bozdogan[1], Sebnem Tavman[2], Seher Kumcuoglu[2], and Jozef Kokini[1]
[1]Food Science, Purdue University, West Lafayette, IN 47907, United States; [2]Food Engineering, Ege University, Izmir, Turkey

The objective of this study is to gain quantitative and predictive insights on the distribution of extension rate, shear rate, ratio of extension rate to shear rate, and effects of extension and shear rate on the bubble size distribution within a sigma blade batch mixer. 3D, and time dependent computational fluid dynamics of a Bird-Carreau type wheat flour dough in a twin sigma blade model mixer (Brabender Farinograph) was performed using the finite element method (Polyflow 19.1, ANSYS Inc). The local distribution of velocity, extension and shear rates and mixing index data were obtained from the simulation. The extension rate magnitudes were numerically estimated using the second and third invariants of the rate of deformation tensors. In order to calculate the bubble size distribution local Capillary numbers were estimated from the necessary flow parameters. Critical capillary number, which is the critical ratio of the viscous forces acting to deform the bubble to the interfacial forces acting to preserve the shape of the bubble, was calculated for different flow types and bubble size distribution through the mixing process was calculated using capillary number, viscosity, and flow strength. Near the barrel walls, which are closely swept by the blades and at the center of the barrel where the two blades clear one another, the highest extension and local shear rate were observed. The counter rotating motion of the blades and the narrow gap between walls of barrel and paddles play critical role in the development of these relatively stronger extension rate fields. The magnitude of extension fields was found to be time dependent. The areas, which are close to the upper boundary of the barrel, show very small or negligible extension and shear rate values. In the regions, where extension and shear rates reach maxima, bubble diameters were smaller and bubble size distribution becomes more homogeneous. In addition, in these regions bubble size values become larger and bubble size distribution becomes non-homogeneous.

Wednesday 4:10 Room 306B AR7

Pinch-off dynamics, shear and extensional rheology, and dispensing of polymer-surfactant complexes

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

The rheological properties of polymer-surfactant mixtures play a significant role in applications ranging from enhanced oil recovery, pharmaceutical and biological fluids, cosmetics, food, soft adhesives and coating. Addition of an ionic surfactant to an aqueous solution of neutral polymer like polyethylene oxide is known to result in a shear rheological response with non-monotonic concentration dependent variation, attributed to association complexes formed by hydrophobic interactions between surfactant monomers and polymers chains, as well as charge effects. Furthermore, the formation of association complexes changes both dynamic and equilibrium surface tension. However, due to a lack of suitable techniques, extensional rheology response of polymer-surfactant mixtures has not been characterized in adequate detail, even though most processing flows, especially those involving drop formation or liquid transfer are influenced by extensional rheology and pinch-off dynamics. In this study, we examine how pinch-off dynamics and the shear and extensional rheological response of polymer solutions are modified by the addition of ionic surfactants. We utilize dripping-onto-substrate rheometry protocols and show that shear and extensional rheology response display contrasting concentration-dependent variation, and we discuss the implications for dispensing of multicomponent complex fluids.

Wednesday 4:35 Room 306B AR8

Embedded droplet printing in yield-stress fluids for pharmaceutical materials manufacturing

Arif Z. Nelson[1], Saif A. Khan[2], and Patrick S. Doyle[3]

[1]Singapore-MIT Alliance for Research and Technology, Singapore 138602, Singapore; [2]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117576, Singapore; [3]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States

We report a method for the formation of uniform pharmaceutical particles through the crystallization of droplets embedded within a yield-stress fluid. Yield-stress fluids are a class of rheologically complex material that are solid-like below a critical stress but undergo a dramatic drop in viscosity and flow above their yield stress. Many current pharmaceutical manufacturing processes consist of outdated grinding and mixing processes which are wasteful, energy intensive, and inflexible. Our method effectively integrates several secondary manufacturing processes which will afford drug products with increased quality control and reduced waste.

Beyond pharmaceutical crystallization, the method we demonstrate constitutes a completely new platform for droplet generation, processing, and experimentation which extends and improves on microfluidic technologies through the use of yield-stress fluid materials. Droplets embedded in specified locations within a bath of yield-stress fluid may be processed for essentially an indefinite period of time with no risk of coalescence or contamination, and with no influence from exterior convective forces or solid boundaries. We investigate fundamental physical aspects of controlling droplet size in a model yield-stress fluid system. In addition to pharmaceutical crystallization, we demonstrate applications of our platform that include biological assays and chemical microreactors.

Wednesday 5:00 Room 306B AR9

Rheological modification of crop sprays for deposition efficiency enhancement

Minghuan Xu, Xiran Li, and John M. Frostad

University of British Columbia, Vancouver, BC V6T1Z3, Canada

Agricultural spraying is widely employed for crop fertilizing and pest management. However, the percentage of these sprays that are delivered to the plant surface is reported to be as low as 8%. Such a low deposition efficiency increases the cost of materials required for effectiveness and can infiltrate and pollute groundwater. Two mechanisms responsible for decreased efficiency are "spray drift" where smaller droplets are carried away in the wind, and low droplet retention where larger droplets rebound, splash, or roll off of plant surfaces. These effects can be modulated by changing the droplet size, but the optimal size is highly dependent on environmental conditions and still may not achieve suitable retention. Instead, we aim to modify the extensional rheology of the spray solution as a means to enhance the retention of larger droplets. Our work builds on prior learnings from single droplet studies with simplified systems where it was demonstrated that splashing and rebounding events are reduced with higher extensional viscosity. Here we examine the potential for increased deposition efficiencies under more realistic conditions with agricultural spray nozzles and fertilizer solutions on both model surfaces and plant surfaces.

Wednesday 5:25 Room 306B AR10

Microrheological characterization of covalent adaptable hydrogel degradation in response to pH changes in the gastrointestinal tract

Nan Wu and Kelly M. Schultz

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

Covalent adaptable hydrogels (CAHs) are synthesized using dynamic covalent chemistry, providing reversible network bonds. This rearrangement occurs when the material is pushed out of equilibrium by external stimuli, such as pH change or external shear. This makes CAHs ideal for biological applications. Of particular interest is CAH use as an delivery vehicle in the gastrointestinal (GI) tract, a pH-dependent process. Our CAH is composed of 8-arm star poly(ethylene glycol) (PEG)-hydrazine that covalently cross-links with 8-arm star PEG-aldehyde. To mimic CAH degradation in pH environments in the GI tract, we use a novel technique μ^2rheology, the multiple particle tracking microrheological (MPT) characterization in a microfluidic device. In MPT, fluorescent probes are embedded in the material and their Brownian motion is measured to relate rheological properties. Our two-layer microfluidic device enables exchange of the incubation fluid around CAH with minimal sample loss to mimic pH changes in the GI tract. First we measure degradation at a single pH (4.3, 5.5, 7.4) to mimic an organ. Next, we measure consecutive degradation at two different pHs (4.3 to 7.4 and 7.4 to 4.3) to mimic degradation through parts of the GI tract. We determine material property evolution is consistent with degradation at a single pH but degradation time can be changed by degradation history. The time scale of pH 7.4 degradation is reduced when the material is first degraded at pH 4.3, but no obvious change when the material is first degraded at pH 7.4 then at pH 4.3. Last, the material is degraded by multiple pH buffers to mimic temporal pH changes through the entire GI tract. We determine both time scale and extent of degradation can be affected by the degradation history. This result indicates that we can tune scaffold degradation by tailoring the material itself, such as changing polymer concentration and ratio of functional groups. This work will inform the design of this material for controlled, targeted oral delivery.

Symposium IR
Interfacial Rheology

Organizers: Javen Weston and John Frostad

Wednesday 1:30 Room 306C *Keynote* IR1

From macro to micro (to nano): Mechanical resonators at all scales for rheology sensing in oilfield fluids

Miguel Gonzalez
Aramco Research Center - Houston, Aramco Services Company, Houston, TX, United States

Real-time monitoring of oilfield fluid rheology is of crucial importance for oil recovery. During various operations such as drilling, production, stimulation, and intervention, the rheology of the fluids being produced or injected into the well need to be monitored to ensure safe operation, or to optimize the process being carried out. However, reliably measuring their physical properties can still pose a great challenge when the fluids are part of a multiphase flow or are complex inhomogeneous fluids, such as emulsions and foams, whose properties can vary in a nontrivial manner with parameters such as temperature, pressure, flow rates, and composition. While specialized commercial instruments that make comparable measurements can be found in other industries, fewer systems tailored to the oil and gas industry exist or are too costly and complex to deploy in every well. In this presentation, I will discuss two examples of viscosity/density sensing systems based on mechanically resonating devices customized to different measurement scenarios in the field. In the first example, I demonstrate a ruggedized tuning fork device for in-line measurements of viscosity and density of non-Newtonian fluids. This instrument is a robust permanent tool for surface installation with applications in quality assessment of drilling mud or other wellbore fluids such as fracturing fluids. I will also discuss techniques currently being explored to extract rheological information from the vibrational damping measured on the resonator. In the second example, I will discuss miniaturized resonators fabricated using micro/nano-machining techniques. These devices can be integrated into small-scale measurement platforms, either for downhole deployment or for lab-on-a-chip platforms useful in portable field viscometry systems.

Wednesday 1:55 Room 306C IR2

Effect of interfacial properties on polymerized high internal phase emulsions

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

High internal phase emulsions (HIPEs) are formed when the volume fraction of the disperse phase exceeds 74%. Polymerized high internal phase emulsions (polyHIPEs) are porous polymers produced through the polymerization of monomers incorporated in the continuous phase of HIPEs. The polyHIPEs have been used as scaffolds, adsorbents, ion-exchange resins, and separation media due to their high porosity and interconnectivity, and low density. The properties of polyHIPEs significantly depend on the properties of the base emulsions, such as composition, stability, droplet size, and especially interfacial properties. The use of surfactants in the polyHIPE formulation is to decrease the interfacial tension and enhance the stability of the HIPEs. The stability of emulsions is related to the viscoelastic properties of the interface in addition to the interfacial tension. Nevertheless, the effect of interfacial properties on the formation of polyHIPEs has not been well understood. In the present work, different surfactant systems are employed to prepare polyHIPEs with different properties. The interfacial rheology of different surfactant systems at the interface of the aqueous and oil phases is investigated to evaluate its effect on the stability of HIPEs and morphology of final polyHIPEs.

Wednesday 2:20 Room 306C IR3

Globular protein stabilized emulsions: Effect of the oil

Jotam Bergfreund and Peter Fischer
IFNH, ETH Zurich, Zurich 8092, Switzerland

Globular proteins, such as beta-lactoglobulin, bovine serum albumin, or lysozyme adsorb to oil/water - interfaces. At the interface, the proteins form a viscoelastic layer by intermolecular interactions. The protein's biocompatibility and nutritional value made them essential in pharmaceutic, cosmetic, food, and industrial emulsions. Further, proteins stabilize oil bodies forming lipid storage containers and interfacial protein films serve as a substrate for cell culture proliferation. Therefore, controlling and understanding the formation of interfacial networks of globular proteins at o/w-interfaces is crucial. Effects of ionic strength, pH, temperature and several pre-treatments are well-known. However, the oil phase has been regarded as exchangeable and its role in the protein adsorption mechanisms, interfacial network formation and emulsion stability behavior has been widely ignored [1]. In our recent work, we investigated the influence of systematically selected oils on interfacial protein layers, and emulsion stability was evaluated. Insights into the interfacial network formation and network strength were gained by measuring adsorption kinetic, dilatational and interfacial shear moduli. Additionally, emulsions were formed and characterized over time. We found that depending on molecular size and polarity of the oils, globular proteins adsorb distinctively. Stronger interactions of polar oils with the hydrophilic exterior of the native protein lead to a decelerated protein unfolding. This results in lower surface pressures and slower formation of viscoelastic networks. In addition, polar oils interact stronger with the protein network by hydrophilic bonding and thereby act as softening agents. The effects of oils on the adsorbed protein layers provide knowledge that promotes higher reproducibility in rheological studies and precise tailoring of interfacial films for an enhanced formation and stability of emulsions in numerous fields.

[1] Bergfreund, J et al. Langmuir 2018, 34 (16) 4929-4936

Wednesday 2:45 Room 306C IR4

Kinetic and thermodynamic control of interfacial localization of silica nanoparticles in cocontinuous polymer blends

Milana Trifkovic[1] and Shohei Yoshida[2]

[1]University of Calgary, Calgary, Alberta T2N 1N4, Canada; [2]Torray Industries Inc, Calgary, Alberta T2N 1N4, Canada

Localization of nanoparticles at the interface of cocontinuous blends provides a way to enhance polymer blend properties but also prepare surface-modified porous materials. In this study, we systematically investigate kinetic and thermodynamic control of interfacial localization of silica nanoparticles in cocontinuous blends of polyethylene (PE) and ethylene vinyl acetate (EVA). We show that bare silica nanoparticles without any functionalization are kinetically arrested at the interface of PP/EVA cocontinuous structure by changing the order of addition of blend components. We achieve comparable morphology and rheological properties with surface functionalized particles, which are thermodynamically driven to pin the interface. We utilize two-color fluorescence microscopy to study the effect of particle functionalization, melt-compounding sequence and mixing times on the morphology of the cocontinuous blends. We estimate the degree of interfacial silica by spatial variation of the nanoparticle fluorescence intensity across the phase domains. We show direct relation between the initial interfacial localization of particles after blending and the characteristic size evolution during coarsening as well as storage modulus obtained by performing time sweep rheological measurements. We find that the same linear relation holds regardless if the particles are trapped kinetically or thermodynamically at the interface. These results present a direct, quantitative, experimental demonstration of the association between the particle interfacial localization and rheological and morphological properties of the cocontinuous blends, and show the premise of deriving surface-modified porous materials without any tuning of particle properties.

Wednesday 3:45 Room 306C IR5

Operation windows for interfacial rheometry

Damian Renggli[1], Randy H. Ewoldt[2], and Jan Vermant[1]

[1]Soft Materials, ETH Zurich, Zurich, Switzerland; [2]Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

The interfacial rheology of liquid interfaces becomes complex if surface active species such as surfactants, particles or proteins are present at the interface. The broad interest in these complex interfaces covers topics from foam or emulsion stability to structural design in food or understanding the behavior of phospholipids as lung surfactants and is still an active area of research. Obtaining confident interfacial rheological data can be very challenging. Confining soft matter to a fluid interface leads to thin monolayers of material, therefore resulting in a very weak mechanical response which might be insufficient to be measured accurately. This inherently soft response combines with other important challenges, including instrument inertia, sample inertia (momentum diffusion), subphase flow (Boussinesq limits), contact line imperfections, and alignment errors. In this work, we study this list of experimental challenges and derive equations for the operating limits of various macroscopic rheometers including the interfacial needle shear rheometer, the double wall ring and the bi-cone geometries. We experimentally investigate the limitations defined intrinsically by the instrument as well as the ones emerging from the properties of the interface of interest. The results provide cautionary examples and guidelines for anyone measuring interfacial rheology with these techniques.

Wednesday 4:10 Room 306C IR6

Experimental and numerical analysis of the pendant drop experiment for complex interfaces

Nick O. Jaensson[1], Patrick D. Anderson[2], and Jan Vermant[1]

[1]Department of Materials, ETH Zurich, Zurich, Switzerland; [2]Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands

Pendant drop experiments are frequently employed to obtain the interfacial or surface tension of liquid-liquid or liquid-gas interfaces. The general approach is to fit the Young-Laplace equation to a drop suspended from a capillary, which yields the surface tension and capillary pressure inside the drop. By performing oscillatory measurements, information about the adsorption/desorption of surface-active entities can be obtained. However, a crucial assumption when applying the Young-Laplace equation is that the interfacial tension is uniform and isotropic, which might not be true for structured, so-called "complex" interfaces. In these type of systems, the non-uniform deformation, combined with elastic properties of the interface, leads to extra and deviatoric surface stresses which are not necessarily uniform nor isotropic. Additionally, in-plane relaxation processes (i.e. viscoelasticity) might be mistaken for transport processes normal to the interface. Applying the Young-Laplace equation to such interfaces might lead to significant errors in the analysis, but is, unfortunately, standard practice. We present a combined experimental/numerical analysis of the pendant drop experiment for complex interfaces. Experiments are performed using carefully selected model interfaces. By estimating the surface stresses in the interface using a direct method, the validity of the Young- Laplace approach can be directly evaluated. For the numerical analysis, the finite element method is employed which solves the complete set of flow- and transport-equations and the interplay with complex interfacial rheology and/or transport processes toward or at the interface. By combining the experimental and numerical results, we delineate the regime where the Young-Laplace approach ceases to be valid, and other approaches for estimating the surface stress become necessary, and we demonstrate one such approach.

Wednesday 4:35 Room 306C IR7

rheo-MAGIK: Investigating interfacial monolayers and their path dependent isotherms via combined neutron reflectivity and interfacial rheology technique

Ying-Heng S. Tein[1], Charles F. Majkrzak[2], Brian Maranville[2], Jan Vermant[3], and Norman J. Wagner[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, United States; [3]ETH Zurich, Zurich, Switzerland

Interfacial structure and rheological properties are critically important in biological (e.g. membranes) as well as many synthetic systems (e.g. emulsions), such that a better understanding how these are correlated can guide the formulation of systems with targeted interfacial properties. Mixed flow fields, typical of classical Langmuir trough experiments, convolute the interpretation of interfacial dilatational rheology for interfacial systems with both finite surface shear and dilatational moduli. Attempts have been made to resolve the anisotropic state of stress into their pure forms, either by multiple measurements in the Langmuir trough [1] or through the use of a radial trough [2]. In this presentation we describe the design and implementation of a new "Quadrotrough" to better approximate pure dilation or shear interface kinematics. The rheological capabilities of this interfacial trough are demonstrated through proof-of-concept experiments on widely studied, model systems. Importantly, this enables more clearly studying the path dependence of interfacial isotherms. Samples investigated include model steric acid insoluble monolayers as well as more complex macromolecules at the air-water interface. We critically test the hypothesis that anisotropic compression will only significantly affect the dilatational rheology for interfaces with finite surface shear moduli. This is important because convolution of mixed flow fields greatly complicates data interpretation. Combining the new Quadrotrough with both Brewster angle microscopy and neutron reflectivity provides detailed structural measurements of the interface at the microscale and nanoscale that elucidates the source of this path dependence. The potential for rheo-MAGIK, will be discussed and future investigations are reflected on for instrument development.

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

Wednesday 5:00 Room 306C IR8

An oscillating liquid bridge to separate interfacial tension and bulk viscosity in simple and complex fluids

James K. Ferri and Robert E. McMillin
Department of Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, VA 23219, United States

The importance of capillary fluid bridges in hydrostatic and hydrodynamic conditions has been recognized in many natural and engineered systems such as the wetting of powders, the destabilization of multiphase fluid systems, and many applications in the formulation of food, consumer, and personal care products. We consider gas and liquid capillary bridges formed between opposing coaxial tubes of radius (a) separated by a gap (h.) We first discuss some static features of fluid-fluid bridges in terms of the curvature (2H), the surface tension (γ), and capillary pressure (Pc) in the bridge. We describe the results of experimental and numerical studies of the dynamics gaseous and Newtonian liquid bridges that result from small amplitude periodic oscillations of the volume of the bridge by injection and withdrawal of fluid through one of the tubes. Under static conditions, the equilibrium shapes of Newtonian or non-Newtonian liquid are governed by the Young-Laplace capillarity equation. The shape (2H) and capillary pressure (Pc) are functions of the aspect ration (a/h) and the Bond number ($\Delta\rho g a^2/\gamma$). Dynamics of infinitesimal perturbations from a static equilibrium configuration depend of the Reynolds number, the Ohnesorge number, and the viscosity ratio between the inner and outer fluids. This paper focuses a summary of the hydrostatic limits and the limiting analytical cases of the hydrodynamics. Analytical limits are compared with experimental results for liquid/liquid and gas/liquid systems and discussion is made as to the potential for simultaneous determination the bulk viscosity and the rheology of the interface in-situ using the capillary pressures measured in each tube.

Wednesday 5:25 Room 306C IR9

Probing structure and dynamics on a particle coated interface using X–ray Photon Correlation Spectroscopy (XPCS)

Charles C. Sharkey[1], Yanxin Li[1], Christine A. Orme[2], Yugang Zhang[3], Andrei Fluerasu[3], and Shelley L. Anna[1]
[1]Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States; [2]Lawrence Livermore National Laboratory, Livermore, CA 94550, United States; [3]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973-5000, United States

Surface active nanoparticles can adsorb to the interfaces of bubbles and droplets. Their arrangement, diffusion, and interactions on the interface can impart elasticity to the bubbles allowing them to resist coalescence. To engineer the behavior of particle coated bubbles, it is essential to be able to correlate nanoparticle structure and dynamics on an interface to the resulting interfacial rheology. Existing techniques to measure interfacial rheology cannot determine particle area fraction, nor their arrangement or interactions. To close this gap, we constructed an X-ray beamline microtensiometer to simultaneously probe interfacial rheology and nanoparticle structure and dynamics on an air-water interface. Silica nanoparticles coated with cetyltrimethylammonium bromide (CTAB) are surface active and used as a model system. The silica - CTAB complexes adsorb and coat the surface of a pinned air bubble, providing a target for an X-ray beam. Coherent X-ray scattering (CHX) and X-ray Photon Correlation Spectroscopy (XPCS) are used to examine nanoparticle microstructure formation, correlations, and kinetics at both static interfaces as well as those that have been compressed and expanded.

Thursday Morning

Symposium AP
Award Presentations

Metzner Award Presentation

Thursday 8:00 Room 304 AP1

Symmetric shear banding and collective swarming of bacterial suspensions

Xiang Cheng
University of Minnesota, Minneapolis, MN 55455, United States

Active fluids are a novel class of non-equilibrium complex fluids with examples across a wide range of biological and physical systems such as flocking animals, swarming microorganisms, vibrated granular rods, and suspensions of synthetic colloidal swimmers. Different from conventional non-equilibrium systems where free energy is injected from boundaries, an active fluid is a dispersion of large numbers of self-propelled units, which convert the ambient/internal free energy and maintain non-equilibrium steady states at microscopic scales. Due to this distinct feature, active fluids exhibit fascinating and unusual flow behaviors unseen in other complex fluids. Here, by combining high-speed confocal microscopy, rheological measurements and biochemical engineering, we experimentally investigate the flow behaviors of E. coli suspensions, a premier example of active fluids. In particular, we show the microscopic dynamics of bacterial suspensions associated with the abnormal rheology and the emergence of collective swarming. Interesting dynamics such as the formation of symmetric shear banding and upstream swimming bacteria are found. Using fluid mechanics and statistical mechanics tools, we develop a quantitative understanding of these unusual behaviors. Our study shows the general organizing principles of active fluids that can be exploited for designing "smart" fluids with controllable fluid properties. Our results also provide new insights into the fundamental transport processes of microbiological systems.

Symposium AM
Additive Manufacturing and Composites

Organizers: Jon Seppala and Samanvaya Srivastava

Thursday 8:40 Room 305A AM15

3D printing of magnets from highly concentrated, plate-like particle suspensions

Alan Shen[1], Xiaoguang Peng[1], Callum Bailey[2], Sameh Dardona[2], Shing-Yun Chang[3], and Anson Ma[1]
[1]Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States; [2]United Technologies Research Center, East Hartford, CT 06108, United States; [3]Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States

A new additive manufacturing method coined "UV-assisted direct write"(UADW) has been developed to produce magnets of arbitrary shapes at room temperature [Additive Manufacturing, 22, 343-350 (2018)]. The UADW method involves mixing magnetic particles with a photo-curable binder to create an ink, which is then extruded through a nozzle and deposited onto a substrate. In this presentation, we will describe how the particle loading and consequently the magnetic strength of 3D printed magnets be maximized through understanding and controlling the rheology of highly concentrated suspensions of plate-like magnetic particles.

Thursday 9:30 Room 305A AM17

Additive manufacturing of gradient index glass optics

Nikola Dudukovic
Lawrence Livermore National Laboratory, Livermore, CA, United States

We present an additive manufacturing approach for fabrication of gradient index glasses for optical applications using direct ink writing (DIW). This multimaterial 3D printing process is based on extrusion of two or more colloidal gels consisting of silica particles and dopants dispersed in organic solvents. The green body is printed with a prescribed gradient in dopant concentration using an active micromixing device, and then thermally treated to form a dense, transparent glass with spatial change in refractive index. The rheological behavior of the materials is crucial to the success of the print, as well as the performance of the final optic. This talk will discuss the relationship between material properties and the phenomena occurring during printing, highlighting the need for rheologically-informed ink design for multimaterial DIW. Three main requirements for successful printing of glass optics will be highlighted: (1) the ability to print void-free monoliths, (2) rheological and compositional compatibility for multimaterial printing, and (3) active micromixing of colloidal materials at high shear.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program 19-ERD-020. LLNL-ABS-774034.

Thursday 10:25 Room 305A AM18

In operando studies of curing dynamics in 3D printed epoxy materials using X-ray photon correlation spectroscopy

Benjamin M. Yavitt[1], Lutz Wiegart[2], Daniel Salatto[1], Zhixing Huang[1], Maya K. Endoh[1], Stanislas Petrash[3], and Tadanori Koga[1]
[1]Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794, United States; [2]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, United States; [3]Henkel Corporation, Bridgewater, NJ 08807, United States

Additive manufacturing (AM), or 3D printing, is a promising method to rapidly process polymeric materials into complex geometries. While AM is widespread and relevant for a range of novel applications, its implementation has outpaced our fundamental understanding of polymer dynamics during the printing process. Characterization and quantification of such dynamics is necessary to optimize final material properties and design new materials for printing. Here we demonstrate a technique to determine in operando dynamics by combining X-ray photon correlation spectroscopy (XPCS) in-line with a 3D printer. Specifically, we investigate the progression of dynamics in a UV curable epoxy during and directly after 3D printing. As the filament is printed and cured, the relaxation processes of the epoxy network are quantified through the autocorrelation function g2(q,t). The characteristic relaxation of the polymer chains in a printed filament is directly related to the intensity of UV light used during curing. The measurement of multi-scale, non-equilibrium dynamics could be used to explain the rheological behavior and further understand the influence of complex flows during 3D printing.

Thursday 10:50 Room 305A AM19

Soft thermoreversible elastomers for additive manufacturing

Shifeng Nian, Zihao Gong, Lauren Weis, and Liheng Cai
Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA 22904, United States

Existing feedstock for additive manufacturing, or 3D printing, is nearly all plastics. These materials are not only mechanically stiff but also fragile, which severely limit their applications where soft, elastic polymers are required to easily comply with the shapes of objects they contact. Here we develop thermoreversible soft elastomers for additive manufacturing. Similar to conventional thermoplastics, our elastomers become a liquid at high temperature, and such temperature triggered solid-to-liquid transition allows the materials for hot direct-ink-writing. However, unlike existing thermoplastics that are very stiff, our elastomers are extremely soft with controllable moduli from 1kPa -100kPa. Harnessing this feature, we use extrusion-based 3D printing to create a complex, hierarchical 3D structure with an exceptional combination of softness and deformability. Our studies provide a new strategy for the development of 3D printable soft elastomers.

Thursday 11:15 Room 305A AM20

Large effect of surface oxide on measurement of liquid metal viscosity

Eric S. Elton, Thomas C. Reeve, Luke E. Thornley, Andrew J. Pascall, and Jason R. Jeffries
Lawrence Livermore National Laboratory, Livermore, CA 94550, United States

The viscosity of liquid metals is increasingly important for metal extrusion and other additive manufacturing techniques. Although molten metals have long been assumed to be Newtonian liquids, recent results have indicated that some metals may shear thin. Here we show that small amounts of oxide on the surface of liquid metals can cause dramatic changes to their measured viscosity. Using a Searle type rheometer, we measured the viscosity of tin and eutectic gallium indium in an argon atmosphere. When either metal is slightly oxidized, the metals display shear thinning behavior and unusually high viscosities. When oxide growth is prohibited by the addition of an active flux on top of the sample, the measured viscosity is Newtonian. These results provide insight into the difficulties of measuring the viscosity of easily oxidized liquids and suggest that liquid metals are Newtonian liquids at all shear rates.

Prepared by LLNL under Contract DE-AC52-07NA27344. IM Release Number LLNL-ABS-772077

Symposium SC
Suspensions, Colloids, and Granular Materials

Organizers: Safa Jamali, Heather Emady and Ehssan Nazockdast

Thursday 8:40 Room 304 SC43

Multiscale dynamics of colloidal particle transport in porous media

Navid Bizmark, Rodney D. Priestley, and Sujit S. Datta
Princeton University, Princeton, NJ 08544, United States

Colloidal particle transport in porous media is commonly encountered in various industrial activities. In particular, there is significant interest to improve oil recovery or aquifer remediation by subsurface injection of surface-active particles. The transport of particles in such systems is complex due to the interplay of particle adsorption, surface erosion, and pore-space advection. Here, we developed a model transparent porous medium that we can image in 3D using confocal microscopy. Through this medium, we observe, for the first time, the interchange between adsorption and erosion events. With these observations, along with a statistical nonlinear model and a continuum model, we demonstrate how different conditions dictate which transport mechanism is dominant. These findings ultimately show how the pore-scale transport dynamics can be controlled to achieve macroscopic aims in oil recovery or aquifer remediation.

Thursday 9:05 Room 304 SC44

Coiling dynamics of semiflexible chains under rotational fields

Steve Kuei and Sibani Lisa Biswal
Chemical and Biomolecular Engineering, Rice University, Houston, TX, United States

In response to external forces, semi-flexible filaments deform, leading to a variety of different dynamical responses. When a rotating force field is used for actuation, these range from simple rotary orbits to complicated non-reciprocal orbits; controllable actuation of these modes has potential for various applications, such as microfluidic scale propulsion and cargo manipulation. In one of these dynamical regimes, tight coils form at the filament ends, and propagate to encompass the entire length. Previous work has hypothesized how this coiling behavior is initiated, but whether the deformation is a result of local or global phenomenon is yet to be determined. Here, we investigate the dynamical formation of these tight coils using a tunable model system consisting of linked paramagnetic particles, to which a rotational magnetic force field is applied, while controlling the persistence length l_p, the contour length l_c, and the strength and frequency of the external driving force. Using a combination of this colloidal experimental model and a bead-spring numerical model, we seek to describe both the initial formation and long-time states of these coils and understand their scaling dependencies.

Thursday 9:30 Room 304 SC45

Parameter determination of the non-local granular fluidity model for wood chips by comparison to well-defined experimental flow systems

Jonathan Stickel[1], Hariswaran Sitaraman[2], and Jordan Klinger[3]
[1]Biosciences Center, National Renewable Energy Laboratory, Golden, CO 80401, United States; [2]Computational Science, National Renewable Energy Laboratory, Golden, CO 80401, United States; [3]Bioenergy Technologies, Idaho National Laboratory, Idaho Falls, ID 83415, United States

Unlike simple liquids and gases, the bulk flow and transport of granular materials remain poorly understood by physicists and pose many problems for engineers in designing and operating bulk-solids handling equipment. Discrete element methods (DEM) are currently considered the state-of-the-art for simulating the flow of granular materials, but DEM is limited in system size to about a few million particles due to high computational costs, even when run on current high-performance computing architectures. Continuum models are needed to simulate the flows of bulk solids in industrial-scale vessels and equipment, e.g., grain silos and coal-ash disposal piles. The focus of this work is the so-called nonlocal granular fluidity (NLGF) model that has been previously shown to reproduce observed nonlocal behaviors that arise when granular phenomena occur on length scales that are near the scale of the system geometry, e.g., the jamming of hopper outlets and the stop-height of piles on inclines [*PNAS*, 110(17), 6730-6735]. We have implemented the NLGF constitutive model in OpenFOAM CFD software, performed simulations of well-defined flow systems, and compared the results to experimental data. Experimental systems include a ring-shear tester, pile formation, flow on an incline, and discharge of a hopper. The tested material was loblolly pine wood chips that were milled and sieved to a size range of roughly 0.05-0.25 inches in diameter. The NLGF model parameters were tuned to achieve reasonable agreement between simulation and experimental results. Further, we evaluate the mapping between measurable material properties (bulk friction angle, particle-particle friction, compressibility, grain diameter, etc.) with NLGF model parameters, some of which have direct analogs (friction parameters and grain diameter) while others are constructs of the model (nonlocal amplitude and timescale of fluidity evolution).

Thursday 10:25 Room 304 SC46

Imbibition and evaporation of droplets of colloidal suspensions on permeable substrates

Truong Pham and Satish Kumar
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55113, United States

When evaporated on a substrate, a droplet containing solutes usually deposits the solutes onto the substrate in a coffee-ring pattern. Recent experiments have shown that substrate permeability can suppress the coffee-ring pattern and promote more uniform solute deposition. Motivated by these observations, we have developed a lubrication-theory-based model to describe imbibition and evaporation of droplets of colloidal suspensions on permeable substrates. The model consists of a system of one-dimensional partial differential equations accounting for the changing droplet shape and depth-averaged concentration of colloidal particles. We also incorporate a precursor film, disjoining pressure, and substrate topography to control contact-line motion of the droplet. Solvent evaporation is described using the well-known one-sided model, and imbibition of solvent by the substrate is assumed to only depend on the excess pressure on the liquid side. The governing equations are solved with finite-difference methods. Our results reveal that solvent evaporation and solvent imbibition have the same qualitative effect on the final particle deposition pattern. For the case where the substrate is smooth, we find that increasing imbibition or evaporation leads to a transition from a cone-shaped deposition pattern to a ring-shaped deposition pattern. For the case where the substrate is rough, the droplet contact line is pinned at a defect on the substrate, and the pinning-depinning transition leads to the bull's-eye deposition pattern often observed in experiments. Finally, we also find that particle adsorption onto the substrate can promote more uniform particle deposition patterns for both smooth and rough substrates, and solvent imbibition can indirectly suppress the coffee-ring pattern by inducing more particle adsorption.

Thursday 10:50 Room 304 SC47

Particle dynamics and structure development during paint drying

Kimberly A. Dennis[1], Scott C. Brown[2], Norman J. Wagner[1], and Eric M. Furst[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]The Chemours Company, Wilmington, DE 19805, United States

Paints are aqueous suspensions of pigments, binders, and rheology modifiers that are designed to be cost effective, stable, and have good flowability while imparting important aesthetic and protective surface properties. The suspension must flow easily at high shear rates during painting and have a sufficient yield stress to stop flowing on the substrate. As the suspension dries, it must form a uniform film that is non-cracking and has good self-leveling properties. Critical final film properties including opacity, rub and stain resistance, and film integrity linked to the structure developed during drying. Modern approaches to measuring structure development involve mechanical rheometers and reflectometry. Mechanical rheometry provides information on system interactions but suffers from artifacts due to the mechanical manipulation of the paint film and is performed under simulated but not actual drying conditions. Reflectometry measurements, on-the-other-hand, are capable of measuring in situ drying processes however, do not convey information on important particle interactions that have the potential to predict final film performance properties. To assess in situ paint drying dynamics, structure development and system interactions, we use diffusing wave spectroscopy (multiple light scattering). The measured light intensity correlation function is interpreted using the Generalized Stokes-Einstein Relation (GSER) to determine the viscous and elastic moduli. We collect reference data for a concentration series of aqueous titanium dioxide suspensions and discuss the relationship to in situ measurements. We then discuss the effects of binder and rheology modifiers on the drying dynamics and structure development of model paint systems.

Thursday 11:15 Room 304 SC48

Vertical film drying of colloidal dispersion using Lattice-Boltzmann method and continuum model

Byoungjin Chun, Tae Hyung Yoo, and Hyun Wook Jung
Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea

Drying of colloidal dispersion is important in many industrial applications, such as catalytic filters, electrodes for lithium ion battery, paint drying, and mineral processing. The film formation of colloidal dispersions requires understanding the combined effects of various factors; the immersed solid particles are driven by both thermal fluctuation of liquid and the flow due to receding gas-liquid interface during evaporation. Sometimes, various external and colloidal forces also play an important role in the formation of colloidal film. The transitional development of concentration gradient of colloids in the vertical direction has been theoretically focused, clearly illustrating the change of microstructure during film formation. One-dimensional continuum and mesoscale models for drying dynamics of wet colloidal film were developed in this study, especially employing a fluctuating lattice Boltzmann method (LBM) which considers both thermal fluctuation and hydrodynamic interactions. The comparison with those of previous theoretical models demonstrates that LBM results well delineate the physically meaningful drying dynamics of colloidal suspensions: uniform distribution across the film ($Pe=O(1)$) and two-dimensional crystal structure of particle accumulation at the gas-liquid interface ($Pe=O(100)-O(1000)$) are observed, respectively. The results also represent that hydrodynamic interactions can be important in the intermediate range of Pe or when colloids are highly confined between gas-liquid interface and the substrate.

Thursday 11:40 Room 304 SC49

Drying colloidal dispersion drops at different orientations

Logesh P. Kumar, Basavaraj G. Madivala, and Sumesh P. Thampi
Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India

Coffee ring formed at the edge of a dried particle laden sessile drop is a result of the migration of particles from the interior towards the three phase contact line of a particulate dispersion. One of the key aspects of such coffee-ring deposits is that it exhibits radial symmetry with respect to the distribution of particles. In our work we have endeavored to break the radial symmetry of the drop shape as well as the particle deposition by orienting the substrate at different angle, rather than drying of drops on a horizontal substrate. Tilting a droplet will lead to the well-known contact angle hysteresis such that the drop is characterized by advancing and receding contact angles. Investigating the deposition patterns resulting from drying particulate dispersions at various orientations revealed that the deposition width and the height have strong relation to substrate orientation and wettability. The time evolution of contact angles, drop height and contact line are monitored to elucidate the physics of formation of different deposit patterns. The calculation of evaporative flux at advancing and receding side of the drop for all possible orientations used in this work indeed show the possibility of biased distribution of particles at the respective positions. Thus by controlling the wettability and the orientation of the substrate we have discovered a way to manipulate the deposition of particles.

Symposium SM
Polymers Solutions, Melts and Blends

Organizers: Sachin Velankar and Evelyne van Ruymbeke

Thursday 8:40 Room 201 SM44

Viscoelastic response of branched polyethylene combs: A molecular dynamics simulation insight

Sidath Wijesinghe[1], Ting Ge[2], K. Michael Salerno[3], Gary S. Grest[4], and Dvora Perahia[1]
[1]Clemson University, Durham, NC, United States; [2]Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, United States; [3]U S Army Research, Aberdeen, MD, United States; [4]Sandia National Laboratories, Albuquerque, NM, United States

Polymers exhibit distinctive rheological behavior depending on their architecture. Addition of small number of branches is sufficient to affect the rheology of polymers compared to their linear counterpart with the same molecular weight. Here, using coarse grained molecular dynamics simulations we resolve the effects of the branch length and branch density on the viscoelastic response of entangled polyethylene (PE) melts with branch lengths above and below the entanglement length. The stress relaxation behavior is measured two ways, following a small step strain perturbation and determined from the stress autocorrelation function using the Green-Kubo relation. The stress relaxation functions were fit to the theoretical expression proposed by Likhtman and McLeish, which self-consistently combines reptation theory with contour length fluctuations and constraint release with. The entanglement molecular weight obtained from theses fits are compared to primitive path analysis. We find that the plateau moduli are sensitive to both branch length and branch density and decreases with decreasing branch length, consistent with reduction in entanglement length and increase in tube diameter. This study contributes to a molecular level insight into long-lived problems in viscoelastic responses of polymers.

We kindly acknowledge NSF DMR 1611136.

Thursday 9:05 Room 201 SM45

Medium-amplitude oscillatory shear (MAOS) predictions for the Johnson-Segalman non-affine deformation model

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

We report our derived medium-amplitude oscillatory shear (MAOS) signatures for the non-affine constitutive equation developed by Johnson and Segalman[1], which assumes that the microscale elements causing stress in the material slip compared to the continuum deformation. Following a recent approach developed by our group[2,3],a Bayesian credibility criterion is used to assess the credibility of this model compared to others, considering both discrete and continuous relaxation spectra, in describing frequency-dependent MAOS data for a polyisoprene polymer melt. The addition of the non-affine deformation model to the set of possible models improves the capability to infer material properties using MAOS.

[1] M. W. Johnson and D. Segalman, "A model for viscoelastic fluid behavior which allows non-affine deformation," J. Non-newtonian Fluid Mech., vol. 2, no. 3, pp. 255-270, May 1977. [2] J. B. Freund and R. H. Ewoldt, "Quantitative rheological model selection: Good fits versus credible models using Bayesian inference," J. Rheology, vol. 59, no. 3, pp. 667-701, 2015. [3] L. Martinetti, J. M. Soulages, and R. H. Ewoldt, "Continuous relaxation spectra for constitutive models in medium-amplitude oscillatory shear," J. Rheology., vol. 62, no. 5, pp. 1271-1298, 2018.

Thursday 9:30 Room 201 SM46

A highly coarse-grained model for dynamics of entangled polymers using transient bonds

Takashi Uneyama
Center for Computational Science, Nagoya University, Nagoya, Aichi 464-8603, Japan

We show a highly coarse-grained dynamics model for entangled polymers which utilize transient bonds and simulation results based on it. In our model, we model a polymer chain as a single particle, as first proposed by Kindt and Briels [P. Kindt and W. J. Briels, J. Chem. Phys. 127, 134901 (2007)]. The dynamic constraints are modelled by introducing dynamically reconstructed transient bonds. The dynamic properties such as the viscoelasticity depends on the density and life time of transient bonds. We apply the idea of the multi-chain slip-spring model [T. Uneyama and Y. Masubuchi, J. Chem. Phys. 137, 154902 (2012)], to construct the effective free energy and the dynamics rule for transient bonds. We show that we can successfully construct a highly coarse-grained model with dynamic constraints (the transient bonds), and our model is statistical mechanically sound [T. Uneyama, J. Chem. Phys. 150, 024901 (2019)]. Simulations based on our model can reproduce the viscoelasticity reasonably, although the diffusion is suppressed.

Thursday 10:25 Room 201 SM47

Efficient sampling of continuous polymer chains through Brownian bridges

Vivek Narsimhan, Shiyan Wang, and Doraiswami Ramkrishna
Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-2100, United States

In materials design of polymeric systems, it is common to describe processes that occur over time scales of O(1-10) seconds and length scales of O(10-10,000) nm. Here, a polymer is treated as a continuous chain, and it is important to develop robust, scalable, and efficient algorithms to sample such configurations in a computer simulation. In this talk, we build upon a mathematical method for sampling polymer chains described by a stochastic differential equation along the polymer's backbone (e.g., Gaussian chains, worm-like chains, etc.). This method is based on the concept of a Brownian bridge, which is a stochastic process whose endpoint is conditioned through the addition of a biasing drift derived from Bayes theorem. We note for a polymer system, one can formulate a Brownian bridge to exclude small Boltzmann weights during sampling, and hence only sample high probability regions in phase space. We implement numerical schemes to generate such bridges for a wide range of applications. The biasing drift needed to create the Brownian bridge is a hitting probability (i.e., entropic barrier), which can be obtained by solving a Backwards Fokker-Planck equation (i.e., a PDE). Thus, through an additional cost of solving a PDE at the beginning of a simulation, we can guarantee our stochastic differential equations will generate efficient configurations of polymer chains. In the latter half of the talk, we outline methods to approximate the biasing drifts needed for the Brownian bridges, which avoids the "curse of dimensionality" when solving the Backwards Fokker-Planck equation. These schemes in principle allow one to scale the algorithms to many polymer chains, and incorporate more detailed physics of polymer backbones such as semi-flexibility, twist, and charge (e.g., DNA, RNA, etc.). We conclude with a discussion on how to incorporate segment-segment interactions (e.g., excluded volume). The ideas developed here open up a wide range of applications in simulating polymer melts, gels, and solutions.

Thursday 10:50 Room 201 SM48

Influence of solvent quality on the entanglement properties of flexible polymers

Carlos G. Lopez and Walter Richtering
Institute of Physical Chemistry, RWTH Aachen, Aachen, NRW 52074, Germany

Scaling models of polymer entanglement predict that the entanglement density in semidilute is a function of the Flory exponent ν. The only two easily accessible solvent qualities for neutral polymers, namely theta solvents (ν=0.5) and good solvents (ν=0.59), 'accidentally' are both theoretically expected to display the same scaling for the entanglement density as a function of polymer concentration. Polyelectrolytes offer a way of exploring a wider range of polymer conformations because in salt-free solvent, the Flory exponent is G ˜ c^2.3. The aim of this contribution is to compare the entanglement properties of polystyrene (PS) in good and theta solvent, with its polyelectrolyte analogue sodium polystyrene sulfonate (NaPSS) in aqueous solution.

Semidilute non-entangled dynamics (diffusion coefficients, longest relaxation times and viscosities) are well described by the Rouse model for both PS and NaPSS. As expected, NaPSS displays longer relaxation times and higher viscosities than polystyrene. The entanglement molecular weight (Me) and the critical molecular weight (MC) of polystyrene exhibit a crossover between MC > Me in the melt to Me > MC in solution. NaPSS in salt-free water displays very low values of the overlap concentration compared to those of the neutral polystyrene, as expected from the highly extended chain conformation resulting from electrostatic repulsion along the chain. Despite the large differences in chain conformation, the entanglement concentration is found to be approximately the same for PS and NaPSS. Our results are compared with scaling models of entanglement formation in solution and the melt.

Thursday 11:15 Room 201 SM42

Internal friction can be measured with the Jarzynski equality

R. Kailasham[1], Rajarshi Chakrabarti[2], and J. Ravi Prakash[3]
[1]IITB-Monash Research Academy, Indian Institute of Technology, Bombay, Mumbai, India; [2]Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai, India; [3]Department of Chemical Engineering, Monash University, Melbourne, Australia

Conformational transitions in polymer molecules lead to a dissipation of energy due to frictional resistance from surrounding solvent molecules, and due to the presence of internal friction within molecules. The latter is linked to configurational rearrangements on an underlying energy landscape. In a rheological context, internal friction is conjectured to lead a shear-rate dependent viscosity, a finite limiting value for the infinite frequency limit of the dynamic viscosity, and to instantaneous stress jumps at the inception of steady shear flow. In a biological context, it is believed to be responsible for the slowing down of the process of protein folding, to influence stretching transitions in single biomolecule force spectroscopy, and to affect the dynamics of intermolecular interactions in intrinsically disordered proteins. The experimental quantification of internal friction has remained challenging. A novel methodology is proposed here for the experimental determination of the internal friction coefficient of polymer chains. Essentially, the average work dissipated as the molecule is stretched repeatedly is calculated by applying the Jarzynski equality, and the internal friction coefficient is then estimated in the hypothetical limit of zero solvent viscosity. The validity of the protocol is established through Brownian dynamics simulations of a single-mode spring-dashpot model for a polymer that incorporates both internal friction and solvent-mediated friction. Single-molecule manipulation techniques, such as optical tweezer-based pulling, can be used to implement the suggested protocol experimentally, and it is argued that the proposed methodology provides a means for the first time of directly estimating the magnitude of the internal friction coefficient in polymers.

Thursday 11:40 Room 201 SM49

Investigation of the controlling factors of tack life on prepreg surface

Hideaki Takahasi[1], Rena Ota[2], and Takashi Ochi[3]

[1]Research and Development Planning Dept., Toray Research Center, Inc., Otsu, Shiga 520-8567, Japan; [2]Materials Characterization Labs., Toray Research Center, Inc., Otsu, Shiga 520-8567, Japan; [3]Composite Materials Research Laboratories, Toray Industries, Inc., Masaki-Cho, Iyogun, Ehime 791-3193, Japan

The prepreg (PPg) is obtained by impregnating a matrix resin composed of an epoxy resin and etc. into reinforcing fibers. To prevent problems such as peeling occurs on the interface of stacked PPg and tack during long-term storage of PPg decreases (*i.e.*, the short tack life), it is important to control the tack life of PPg surface. In this study, to consider the tack life controlling factor, the rheological and tack properties of the matrix resins were investigated.

Two matrix resins coded as "resin S" and "resin L" are prepared. The tack life of PPg with resin L is longer than that of PPg with resin S. The resins are composed of an epoxy resin, a curing agent, and a polymer additive. The main difference between resin S and resin L is the weight fraction of the polymeric additive, about 1% and about 15%, respectively.

On the master curves of the matrix resins at 25°C, as the viscosity of resin S in the angular frequency range corresponding to the sinking phenomenon (J. F. Steffe, Rheological Methods in Food Process Engineering, 2nd Ed., Freeman Press 1997) is smaller than that of resin L. It is surmised that the tack life declines faster because resin S on the PPg surface sinks more quickly, and the effective area for adhesion decreases rapidly.

In the peel tests, for resin S, the elongation of fibrils attached to the plate can be observed prior to breakage. On the other hand, for resin L, only peeling of resin from plate can be observed. With aging at room temperature, fibrillation of resin S was suppressed. The change of peeling mode is suggested, such as from fibril breakage to peeling from the plate. While resin S may become difficult to peel with peeling work amount increase, resin L may become easy to peel with peeling work amount reduction.

From these results, it is suggested that it is necessary to suppress the sinking of the resin and to maintain the appropriate peeling work amount in order to extend the tack life of PPg.

Symposium IN
Flow Induced Instabilities and Non-Newtonian Fluids

Organizers: Hadi Mohammadigoushki and Sarah Hormozi

Thursday 8:40 Room 305B IN38

On well-conditioned methods for modal and nonmodal analysis of Newtonian and viscoelastic fluids

Gokul Hariharan[1], Mihailo R. Jovanovic[2], and Satish Kumar[1]

[1]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55113, United States; [2]Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089, United States

Linear analyses of hydrodynamic flow problems yield useful information about the potential for transition to nonlinear states. Eigenvalues provide information about temporal growth or decay of disturbances, while singular values of frequency responses furnish information about the maximum amplification of disturbances when the system is linearly stable. In this work we compare well-conditioned methods (the ultraspherical and spectral integration methods) with an ill-conditioned method (the spectral collocation method) for modal and nonmodal analysis. We find that even if the method of discretization is well-conditioned, frequency response calculations can be erroneous if singular values are computed as the eigenvalues of a composite system consisting of the regular operator and its adjoint. To address this, we introduce a feedback interconnected system to compute singular values for frequency responses. We apply this method to compute singular values for the inertialess 2D viscoelastic channel flow problem. We find that the stress amplification can be very significant even if there is negligible velocity amplification. This suggests a "silent" nonmodal amplification of stress as a route to elastic turbulence, as even if the velocity fluctuations are observed to decay, the stress fluctuations experience pronounced nonmodal amplification which could trigger nonlinear flow states. Lastly, we find that the Chebyshev spectral integration method has an advantage compared to conventional spectral methods since it does not need a staggered grid when the governing equations are considered in primitive variables.

Thursday 9:05 Room 305B IN39

Turbulence dynamics of dilute polymer solutions: Apparent slip and the effect of slip-inducing surfaces

Ethan A. Davis and Jae Sung Park

Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, United States

The addition of small amounts of long-chain polymers to fluids has long been used for the reduction of skin-friction in shear flows. The behavior of these dilute polymer solutions can differ in many ways from typical Newtonian fluids. One important way in which these complex fluid flows can differ is in their slip behavior at the wall. Polymer solutions are among several classes of complex fluids that display behavior inconsistent with the no-slip assumption. Understanding boundary conditions at the wall plays a vital role in correctly determining the rheology of polymers by allowing for corrections due to slip. Additionally, the presence of surface roughness or low surface energy coatings that are often used for drag reduction can alter these behaviors. Therefore, the current study performs direct numerical simulations to investigate the effect of slip surfaces

(those surfaces which induce a slip velocity at the wall) on dilute polymer solutions in a turbulent channel flow to better understand the dynamics of this class of fluids. Preliminary results indicate an increase in apparent drag when a homogeneous slip surface is included in a dilute polymer solution flow. In this talk, the dynamics of these flows and the underlying mechanisms responsible for their drag behavior will be explored and discussed further.

Thursday 10:25 Room 305B IN41

Megasupramolecular drag reduction: Long end-associative polymers as experimental probes of turbulence

Red Lhota, Hojin Kim, and Julia A. Kornfield
Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

To imitate effects of long-chain polymers while avoiding irreversible cleavage, we employ long end-associative complementary polymers as megasupramolecular experimental probes of turbulence to investigate drag reduction. Since Toms discovered polymeric drag reduction in the 1940s, interaction of long-chain polymers and turbulence has driven developments in energy conservation applications, particularly improving efficiency of pumping petrochemicals through long pipelines. Unfortunately, long-chain polymers suffer from degradation in turbulent flow, requiring reinjection to maintain efficacy. Chain scission of long polymeric drag reducing agents frustrated researchers, too, requiring single-pass measurements in tubes with strenuous requirements for flush-mounting transducers to obtain reproducible results despite flow-induced degradation of the polymer. By forming long linear entities (with extended lengths on the order of microns) through association, flows that would cause covalent bond cleavage in similarly long fully covalent polymers instead reversibly pull-apart the megasupramolecules; individual associative chains remain intact to reform into new entities, allowing repeated cycling of a closed system. Features of the individual units can be controlled to alter the megasupramolecular properties-in this study, we focus on the influence of individual backbone length and end-association strength. The joint effect of backbone length and association strength impacts the length of linear megasupramolecular entities and thus the expected length scales of turbulence interactions. The association strength controls how far a chain can stretch before pulling apart, altering the maximum elastic energy storage in the backbone. Connecting controllable and measurable properties of end-associative polymers to their effects on turbulent flows will enable design of associative polymeric additives for a wide range of applications, from improving pipeline drag reduction to developing specialized flame-resistant lubricants.

Thursday 10:50 Room 305B IN42

Non-linear dynamics of turbulence and re-laminarization of dilute polymer solution jets

Sami Yamanidouzisorkhabi, Gareth H. McKinley, and Irmgard Bischofberger
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Dilute synthetic and biopolymer solutions have been shown to reduce turbulent drag in pipelines and around marine vehicles due to their viscoelasticity. The very low concentrations of polymer employed in drag reduction studies makes direct imaging of the mixing and turbulent flow structures an outstanding challenge and motivates novel experimental techniques to track the spatiotemporal evolution in the dilute polymer solution phase. In this work, we combine particle image velocimetry (PIV) and Schlieren imaging protocols to enable direct velocity measurement and flow visualization of the mixing dynamics and vortical structures that develop in turbulent jets of dilute aqueous polymer solutions injected into quiescent water. At the interface of the viscoelastic jet and water a shear layer develops leading to momentum transfer between the two fluids. This momentum transfer can result in formation of turbulent vortical structures. It is shown that under certain conditions, an increase in viscoelasticity completely eliminates the vortical structures of a turbulent jet resulting in re-laminarization. A comprehensive state diagram is proposed to fully characterize transition to turbulence, turbulence, and re-laminarization based on the viscoelastic properties of the fluid jet. In this state diagram, Reynolds number, elasticity number, and polymer viscosity ratio ($\beta_p = \eta_p / \eta_0$) characterize the interaction between inertial, elastic, and viscous forces. It is shown that the elasticity number criterion suggested by Rallison and Hinch (J. Fluid Mech., 1995) for eliminating the linear modes of instability, together with a high polymer viscosity ratio are necessary and sufficient conditions for re-laminarization. Finally, to illustrate how the viscoelastic properties of the fluid modify the mixing dynamics of the flow, we use the PIV results to compute local values of the Finite Time Lyapunov Exponent (FTLE) characterizing the evolution of material lines in the jet.

Thursday 11:15 Room 305B IN43

Self-sustaining Tollmien-Schlichting waves and elastoinertial turbulence

Ashwin Shekar[1], Ryan M. McMullen[2], Sung-Ning Wang[1], Beverley J. McKeon[2], and Michael D. Graham[1]
[1]Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States; [2]Graduate Aerospace Laboratories, California Institute of Technology, Pasadena, CA 91125, United States

One of the most puzzling and dramatic phenomena in non-Newtonian flow is the substantial reduction of turbulent energy dissipation (drag) that occurs when a small amount of a long-chain polymer is added to a liquid. If the Reynolds number is sufficiently low, a turbulent channel flow will laminarize as polymer concentration increases, but then become turbulent again at higher concentration. Direct simulations of flow in the latter "elastoinertial turbulence" (EIT) regime indicate the presence of localized polymer stretch fluctuations. These observations, along with linear stability and resolvent analyses, show that the turbulent fluctuations resemble Tollmien-Schlichting (TS) modes. Although these are found in Newtonian flows, they do not play a role in fully-developed Newtonian turbulence. In the polymeric case, however, polymer stresses suppress the normal turbulent structures while amplifying the TS modes. Finally, we present results on the existence of a new nonlinear self-sustaining state which we term the lower branch attractor (LBA), which coexists in parameter space with EIT but has very small amplitude. The structure of this flow very closely resembles that of the linear TS mode. A tentative bifurcation scenario describing our observations is presented.

Thursday 11:40 Room 305B IN44

Silicone coatings with nearly matched viscometric properties exhibit distinct pinch-off dynamics, extensional rheology response and processability

Carina Martinez[1], Jelena Dinic[2], Dave Rich[3], Pierre Chevalier[4], Jon DeGroot Jr.[3], and Vivek Sharma[1]
[1]Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States; [2]Institute for Molecular Engineering, University of Chicago, Chicago, IL, United States; [3]The Dow Chemical Company, Auburn, MI, United States; [4]Dow Silicones Belgium, Seneffe, Belgium

Formulation and deposition of coatings to form stable films with desirable thickness, smoothness, homogeneity and high productivity require an understanding of, and control over, highly nonlinear, free surface flows of rheologically complex fluids. Coating flows are the basis of multi-billion dollar industries, and yet the fundamental understanding of the material response to flow fields encountered in coating processes remain long-standing challenges. The torsional shear rheometers lack the range for accessing the requisite deformation rates and flow fields, while the extensional rheometry measurements either require bespoke instrumentation or fail to emulate the deformation history and kinematics representative of coating flows. In this contribution, we characterize and analyze the rheological response exhibited by model silicone coatings in response to capillary-driven flows that mimic the flow parameters encountered in the coating processes using dripping-onto-substrate (DoS) rheometry protocols. The representative silicone coatings, formulated by varying the concentration of a branched polymer additive in an unentangled base polymer melt, display rate-independent, nearly indistinguishable steady shear viscosity values in torsional shear rheometry measurements. We find that the analysis of the radius evolution data obtained using the DoS rheometry yield distinct power law (PL) and elastocapillary (EC) thinning regimes. The existence of PL response implies that pronounced shear thinning influences coating flows at deformation rates higher than those accessible on torsional rheometers. The analysis of EC regime reveals that the addition of branched polymer increases extensional viscosity, extensional relaxation time and degree of strain hardening, which result in reduction in misting, and improvement in coating performance.

Symposium AD
Active and Directed Systems

Organizers: Travis Walker and Arezoo Ardekani

Thursday 8:40 Room 306A AD10

Sculpting vesicles with active particles: Less is more

Hanumantha Rao Vutukuri and Jan Vermant
ETH Zurich, Zurich, Switzerland

Biological cells actively respond to external stimuli, extend protrusions to explore their environment, and experience non-equilibrium fluctuations. Artificial soft matter systems, which mimic various features of biological systems, can help us to understand an abundance of complex cellular phenomena. One of the prominent questions in synthetic biology is whether such soft artificial systems with high local forces, mimicking some aspects of biological cells, can be engineered. One key aspect is to understand how to generate and control shape changes from within. In this talk, we present a simplified biomimetic experimental model system in order to address the question how cells reconfigure their shape and how the membrane responds to a localized point forces from inside, such as those exerted by the cytoskeleton. In our experimental model system, the cell membrane is mimicked by giant unilamellar vesicles of lipid bilayers, and the local internal forces are generated by enclosing self-propelled particles [1]. We demonstrate that the propulsion forces of individual self-propelled particles, as small as ~ 0.1 pN, are sufficient to induce dramatic vesicle shapes and lead to active membrane fluctuations. Microscopic visualization is revealing, strikingly, the formation of tethered, dendric-like structures at low volume fractions and tensions, whereas more global deformations of the vesicle shape are observed for increasing particle loadings. Moreover, the analysis of the mechanical properties of the membrane via shape fluctuation spectra demonstrates a strong deviation from the Helfrich model elucidating the specific role of active non-equilibrium processes. Strikingly - less is more - the most dramatic shape changes are observed at low particle concentrations, as is evidenced by a state diagram. Our results pave a way to better understanding the interplay between active local forces and cell shapes.

Ref. [1]. H.R. Vutukuri, G. Gompper, and J. Vermant, submitted.

Thursday 9:05 Room 306A AD11

Activity-induced fluidization modifies the viscosity of active biopolymer gels

Claudia Dessi[1], David A. Gagnon[1], John Berezney[2], Remi Boros[3], Zvonimir Dogic[3], and Daniel Blair[1]
[1]Department of Physics, Georgetown University, Washington, DC 20057, United States; [2]Department of Physics, Brandeis University, Watham, MA 02453, United States; [3]Department of Physics, University of California Santa Barbara, Santa Barbara, CA 93106, United States

Active kinesin-driven microtubule suspensions are one of the emergent and challenging active systems that have received enormous attention since the last past two decades. The strong chemical-mechanical coupling between bundles of cytoplasmic microtubule proteins and clusters of kinesin molecular motors powered by adenosine triphosphate (ATP), is the main source of internal mechanical work generated in the suspension medium. At sufficient concentrations, large-scale flow dynamics of spontaneous organized flow and active nematic flow have been observed. By

means of a commercial rotational rheometer coupled to a confocal microscope, we investigate the mechanical spectrum of isotropic active suspensions of fluorescent labelled microtubule bundles driven by kinesin molecular motor clusters suspended in a quasi-Newtonian fluid. In particular, steady shear flow experiments in conjunction with flow imaging analysis have been performed in order to quantify the effect of motor-driven activity on the macroscale material properties via changes of measured viscoelastic response. We find that motor-bundle activity coupled with external shear flow induces a non-monotonic resistance to flow of the solvent medium as a function of the applied shear rate, depending on the fraction of microtubule bundles which undergo to shear stiffening. We then propose a simple model based on the timescale competition between the spontaneous motor-bundle coupling and the external applied shear deformation to explain the observed anomalous viscoelastic response in such active systems.

Thursday 9:30 Room 306A AD12

Programming stiffness change in soft materials

Gaurav Chaudhary[1], Ashesh Ghosh[1], Ashwin Bharadwaj[2], Jin Gu Kang[3], Paul Braun[1], Kenneth S. Schweizer[1], and Randy H. Ewoldt[1]

[1]University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Nike Inc., Portland, OR, United States; [3]Korea Institute of Science and Technology, Seoul, Republic of Korea

We demonstrate new paradigms in designing stiffness changing soft materials. Our approach involves combining a semiflexible biopolymer network of fibrin with stimuli-responsive particles, either thermoresponsive microgels of poly(N-isopropylacrylamide) (pNIPAM)[1] or magnetically active iron particles[2]. When exposed to an external stimulus of thermal excitation or magnetic field, the interactions between the embedded particles and fibrin network lead to an unprecedented increase in stiffness by up to 100 times. We hypothesize that the stimuli responsive particles induce local stress in the biopolymer matrix which intrinsically stiffens under stress. For the thermoresponive composite, the drastic deswelling of the microgels deform fibrin filaments, thus leading to stiffening. For the magnetoresponsive composite, the interaction between magnetic dipoles plays an analogous role. Phenomenological models are developed that quantify these hypotheses. The derived predictions are consistent with the experimental data, providing foundational understanding for how to control and engineer dramatic stiffening in these material systems.

[1] Chaudhary, G., A. Ghosh, N. A. Bharadwaj, J. G. Kang, P. V. Braun, K. S. Schweizer, and R. H. Ewoldt, "Thermoresponsive stiffening with microgel particles in a semiflexible fibrin network," Macromolecules, 52 (8), 3029-3041 (2019). http://doi.org/10.1021/acs.macromol.9b00124
[2] Chaudhary, G., Ph.D. Thesis, University of Illinois at Urbana-Champaign (2019)

Thursday 10:25 Room 306A AD13

Hopping and trapping of bacteria in 3D porous media

Tapomoy Bhattacharjee and Sujit S. Datta

Princeton University, Princeton, NJ 08544, United States

Diverse applications, ranging from bioremediation to drug delivery, rely on bacterial migration in 3D porous media; however, how pore-scale confinement alters bacterial motility is unknown. Using a novel experimental platform, we demonstrate that the paradigm of run-and-tumble motility is dramatically altered in a porous medium. Instead, we find a new form of motility in which cells are intermittently and transiently trapped as they navigate the pore space. Moreover, we find that the trapping duration and the length of "hops" between traps together can predict the long-time bacterial translational diffusivity. Our work thus provides a revised picture of bacterial motility in complex media and yields principles for predicting cellular migration over large length and time scales, with implications for healthcare, agriculture, and bioremediation.

Thursday 10:50 Room 306A AD14

Rheology of bacterial suspensions under confinement

Zhengyang Liu, Kechun Zhang, and Xiang Cheng

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

Bacterial suspensions, a premier example of active fluids, show intriguing rheology different from their counterpart colloidal suspensions. While the bulk rheology of bacterial suspensions has been excessively studied, the rheology under confined geometries has not been experimentally explored. Here, by using a microfluidic channel viscometer, we investigate the viscosity of E. coli suspensions under different degrees of confinement. Strong shear thickening is observed at low flow rates, in consistency with a number of previous studies. More importantly, a strong confinement effect is found when the confinement length is comparable to the running length of a single bacterium. The viscosity of bacterial suspensions decreases by a factor of 3, when the confinement decreases from 60 down to 25 microns. By using fast confocal microscopy to study the velocity profiles, we find that upstream swimming bacteria near the confining walls play a key role in the confinement effect. Based on this picture, we formulate a simple model which qualitatively captures this confinement effect. Our study reveals the interplay between the microscopic dynamics and rheology of bacterial suspensions under confinement. Our results provide a benchmark for testing different rheological models of active fluids and are useful for understanding the transport of microorganisms in confined geometries.

Thursday 11:15 Room 306A AD15

Inhomogeneous stresses and the surface tension of active matter

Ahmad K. Omar, Zhen-Gang Wang, and John F. Brady
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Purely repulsive active particles can phase separate into dilute and dense regions, a phenomena that bears a striking resemblance to a traditional liquid-gas phase transition. Despite being far from equilibrium, the pressure of active matter has allowed for the description of a number of phenomena, including the stability limit (the spinodal) of active particles. The success of the active pressure in characterizing this phase behavior makes it all the more puzzling that this very same pressure results in defining a surface tension between the coexistence phases that is extremely negative, sharply contrasting with the observation of a mechanically stable interface. Here, we demonstrate that this contradiction stems from a misinterpretation of the swim stress as a true surface force. Rather, activity manifests in a momentum balance as a body force in the form of a swim force density that balances the traditional surface forces such as those that arise from interparticle interactions and Brownian/momentum diffusion. Upon using these true surface forces we recover a physically plausible surface tension. Just as in the case of a gravitational body force, the swim force density can, in some cases, be absorbed into the definition of stress to define an "equivalent" stress -- the active stress. It is this active stress that has been used in the active matter literature and is the relevant mechanical quantity for a number of phenomena, including phase coexistence.

Thursday 11:40 Room 306A AD16

A touch of non-linearity: Mesoscale swimmers and active matter in fluids at intermediate Reynolds numbers

Daphne Klotsa
Applied physical sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3050, United States

Living matter, such as biological tissue, can be seen as a nonequilibrium hierarchical assembly of assemblies of smaller and smaller active components, where energy is consumed at many scales. The remarkable properties (e.g. functionality and versatility) of such living or "active-matter" systems make them promising candidates to study and synthetically design. While many active-matter systems reside in fluids (solution, blood, ocean, air), so far, studies that include hydrodynamic interactions have focussed on microscopic scales in Stokes flows, where the active particles are <100μm and the Reynolds number, Re <<1. At those microscopic scales viscosity dominates and inertia can be neglected. However, what happens as swimmers slightly increase in size (say ~0.1mm-100cm) or as they form larger aggregates and swarms? The system then enters the intermediate Reynolds regime where both inertia and viscosity play a role, and where nonlinearities in the fluid are introduced. In this talk, I will present a simple model swimmer used to understand the transition from Stokes to intermediate Reynolds numbers, first for a single swimmer, then for pairwise interactions and finally for collective behavior. We show that, even for a simple model, inertia can induce hydrodynamic interactions that generate novel phase behavior, steady states and transitions.

Symposium MC
Microfluidic and Confined Flows

Organizers: Sujit Datta and Cari Dutcher

Thursday 8:40 Room 306B MC11

Vortex trapping of particles in xanthan gum solutions

Di Li[1], Adam J. Kummetz[1], Xiangchun Xuan[1], and Mahmud K. Raihan[2]
[1]Clemson University, CLEMSON, SC, United States; [2]Mechanical Engineering, Clemson, Clemson, SC 29634, United States

Inertia-induced vortex trapping of particles has been extensively studied in the flow of Newtonian fluids over confined micro-cavities. It has also been utilized to isolate rare cells for significant biomedical applications. However, the effects of fluid rheological properties on vortex trapping have yet to be explored. In this talk, we will present our recent experimental results on the vortex trapping of spherical rigid particles in the flow of shear-thinning xanthan gum solutions through a planar expansion-contraction microchannel. The effects of particle diameter, cavity size and polymer concentration on particle trapping are examined.

Thursday 9:05 Room 306B MC12

Lubrication solutions of Herschel-Bulkley flow in channels and tubes

Pandelitsa Panaseti[1], Georgios C. Georgiou[1], Iasonas Ioannou[2], and Lorenzo Fusi[3]
[1]Department of Mathematics and Statistics, University of Cyprus, Nicosia 1678, Cyprus; [2]Department of Mechanical and Process Engineering, ETH Zurich, Zurich 8092, Switzerland; [3]Dipartimento di Matematica e Informatica Ulisse Dini, Università degli Studi di Firenze, Firenze 50134, Italy

Lubrication solutions are derived for the flows of a Herschel-Bulkley fluid in long asymmetric channels and also in long, linearly converging or diverging tubes extending a recently proposed method, which avoids the lubrication paradox approximating satisfactorily the correct shape of the yield surface at zero order. The method is applicable in a range of Bingham numbers where the unyielded core extends from the inlet to the outlet plane of the channel or tube. Both the consistency index and the yield stress are assumed to be pressure-dependent. In the case of the asymmetric channel, the walls of which are described by two arbitrary functions h1(x) and h2(x) such that h2(x)>h1(x) and h1(x)+h2(x) is linear. Under the

lubrication approximation, the pressure at zero order is a function of x only, is decou-pled from the velocity components, and obeys a first-order integro-differential equation. The two yield surfaces defining the asymmetric unyielded core are given by s1(x)=-h1(x)/2n+(1+1/2n)h2(x)-C/2 and s2(x)=h1(x)+h2(x)-s1(x), where n is the power-law exponent and C is a constant that depends on the Bingham number and the consistency-index and yield-stress growth numbers. An interesting feature of the asymmetric flow is that the unyielded zone moves not only in the main flow direction but also in the transverse direction. The two velocity components in both the yielded and unyielded regions are calculated by means of closed-form expressions in terms of the calculated pressure and the two yield surfaces. The case of tubes with a linearly varying radius h(x), which is far more complicated, will also be analysed and discussed and representative results demonstrating the effects of the Bingham number and the consistency-index and yield-stress growth numbers will be presented.

Thursday 9:30 Room 306B MC13

Flow-induced near-wall depletion layer dependence on RBC aggregation

Yeng-Long Chen and Chih-Tang Liao
Institute of Physics, Academia Sinica, Taipei, Taipei City 11529, Taiwan

Flow-induced particle migration in microflow leads to near-wall particle depletion layers, resulting in non-linear viscosity dependence on shear rate and particle concentration. Typically, shear thinning is found as the depletion layer thickness increases with shear rate. For red blood cells (RBC), the depletion layer thickness also depends on whether the cells aggregate. Using lattice Boltzmann method, we investigated how attractive interactions between RBC affect aggregation, flow-induced migration, and depletion layer thickness. For very attractive RBC, we found a regime where the depletion layer thickness decreased with increasing shear rate, resulting in shear thickening.

Symposium AR
Applied Rheology for Pharmaceuticals, Food, and Consumer Products

Organizer: Stephanie Lam and Helen Joyner

Thursday 10:25 Room 306B AR11

Rheological assessment of sensory attributes of skin-care products

Andrei Potanin, Joey Lu, Brajesh Jha, and Christine Boyke
Colgate-Palmolive, Piscataway, NJ 08855-1343, United States

Complex behavior of commercial skin care lotions and liquid facial cleansers was investigated in order to identify correlations between rheological measurements and sensory attributes of these products. Sensory attributes were evaluated by trained panelists. In particular, sensory attributes pertaining to appearance, pick-up and rub-out were assessed for lotion products; whereas for facial cleanser the focus was primarily on the lather attributes. In both cases statistical correlations were established between instrumental measurements and sensory attributes which can be used to engineer a product with certain desired properties.

Thursday 10:50 Room 306B AR12

A new pressurized Couette cell for rheological characterization

Amit Ahuja[1], Reginald Lee[1], Alina Latshaw[1], Maik Nowak[2], and Peter Foster[1]
[1]TA Instruments, New Castle, DE 19720, United States; [2]BASF SE, Ludwigshafen am Rhei, Germany

Despite the relevance of pressure in several industrial processes, the impact of pressure on the rheological properties has been less explored in comparison to the effects of temperature. This is mostly due to the challenges to develop a high sensitivity pressurized rheological geometry. The contributions from mechanical bearings and high-pressure mechanical seals can severely limit the sensitivity of the measurements, particularly for low torque measurements. The inherent baseline friction from a conventional mechanical bearing can be as large which typically restrict low torque measurements to 100 µN.m. Using a Couette geometry which utilizes a novel design (patent pending) to provide material pressurization (up to 5 bar) without conventional bearings and mechanical seals improved low torque sensitivity (1 µN.m in oscillatory and 10 µN.m in shear flows). This pressure cell allows testing in both steady shear and dynamic oscillatory flow modes over a range of testing conditions (-5°C to 150°C) simulating extreme processing, usage, and storage conditions, to characterize shear and viscoelastic properties for a variety of materials ranging from low viscosity to structured complex fluids. First, the novel design features of this pressure cell will be discussed which will be followed by examples involving two potential applications. Particularly, in the food industry, most food products undergo extreme processing conditions of high temperature and pressure and the measurements of sample behavior above 100°C is extremely difficult due to water-based formulations. By using Xanthan gum solution in water as a model system, it will be demonstrated that testing in this pressurized Couette cell suppresses boiling of the volatile components from the formulation, allowing to characterize the structure of the sample in the right processing conditions. The second example utilizes a commercial shaving foam from a pressurized container and discusses the stability and pressure-induced changes on the foam rheology.

Thursday 11:15 Room 306B AR13

Rheo-physical characterization of concentrated surfactant solutions

Eduard Caicedo-Casso[1], Seth Lindberg[2], and Kendra Erk[1]
[1]School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States; [2]Corporate Engineering, The Procter & Gamble Company, West Chester, OH 45069, United States

Manufacture of concentrated beauty care and cleaning products using conventional production methods without increasing the input energy or altering the material's microstructure is challenging. Compared to diluted feed stocks, concentrated raw materials can have very different rheological properties including the localization of strain that manifests as shear bands and wall slip. This study describes processing-relevant relationships between the microstructure and flow behavior of concentrated surfactant solutions using a combination of basic rheometry, ultrasonic velocimetry, X-ray scattering, and flow birefringence measurements. The objective was to evaluate the quality of data that can be obtained from a flow curve experiment performed in a rotational rheometer. Sodium laureth sulfate was used to recreate the different microstructural arrangements that are typically found in consumer care products. It was discovered that common features of flow curves - such as power-law shear thinning - can result from a wide variety of material responses including wall slip in spherical micelle solutions and plug flow in solutions of hexagonally packed cylindrical micelles and lamellar structures.

Thursday 11:40 Room 306B AR14

Development and validation of a viscoelastic model for photovoltaic module encapsulants

Ashley M. Maes, James Y. Hartley, and Christine Roberts
Sandia National Laboratories, Albuquerque, NM 87185-0346, United States

Encapsulant layers in photovoltaic (PV) modules bind the module laminate layers together, while providing protection of the electrical components from water and environmental contaminates. The development of material models was motivated by the desire to include viscoelastic behavior of the encapsulant layer in thermal-mechanical finite element models (FEMs) of full scale PV modules developed to study component stress states and predict failures. This presentation will summarize the steps taken to populate Sandia's Universal Polymer Model for two commercial encapsulant polymers: crosslinked poly(ethylene vinyl acetate) and polyolefin elastomer. Experimental methods used include dynamic mechanical analysis, to measure the viscoelastic response, and thermal mechanical analysis to measure thermal expansion and relaxation. Results from cantilever beam experiments on glass-encapsulant laminates will also be presented as validation of the material model parameters. FEM results of stress profiles during simulated thermal and/or mechanical load cycling will be included.

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

Symposium IR
Interfacial Rheology

Organizers: Javen Weston and John Frostad

Thursday 8:40 Room 306C IR10

Interfacial layer formation of clay particles with surfactants

Joung Sook Hong[1] and Peter Fischer[2]
[1]Institute of Chemical Processes, Seoul National University, SEOUL, Select From List 08826, Republic of Korea; [2]IFNH, ETH Zurich, Zurich 8092, Switzerland

The combined addition of clay and surfactant stabilizes or destabilize the emulsion depending on interfacial interaction of clay and surfactant. In order to investigate the interaction of clay and surfactant at the interface, the interfacial layer formation of clay particles at the oil-water interface was studied through interfacial rheometry under the regulated flow of surfactant-aqueous solution. Also, it was compared with the observation of the interfacial localization of clay in a model emulsion (single droplet) with surfactant. The interfacial diffusion of surfactant mostly destroyed the formation of particulate interface by stronger interfacial adsorption of surfactant than clay. However, if there is a strong interaction between clay and surfactant, interfacial modulus of the oil-water interface with particles and surfactant was increased rapidly and also it abruptly decreased with a further addition of surfactant. It means that clays remain at the interface and rather generate a strong complex interface with a small amount of surfactant. As surfactant diffuses to the interface more, it enhances desorption of particles. The interfacial layer formation of clays with surfactant was significantly determined depending on the competition between the stronger interfacial adsorption of surfactant and the interaction between clay and surfactant, as well as the content. For the limited condition of surfactant, surfactant enhanced localization of clay and increased interfacial modulus due to complex structure formation between clay and surfactant.

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Thursday 9:05 Room 306C IR12

Viscoelasticity of a carbon nanotube-laden air-water interface

Shing-Yun Chang[1], Sahil Vora[1], Charles Young[1], Abhishek Shetty[2], and Anson Ma[1]
[1]Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States; [2]Rheology Division, Anton Paar, Ashland, VA 14850, United States

Two different methods have been used to characterize the viscoelasticity of an air-water interface decorated by carbon nanotubes (CNTs). The first method involves applying sinusoidal deformation to the CNT-laden interface by oscillating the barriers of a Langmuir-Pockels (LP) trough laterally and measuring the corresponding surface pressure changes via a Wilhelmy plate. In the second method, the LP trough was modified and then coupled with a torsional rheometer equipped with a bicone test fixture. Surface moduli and viscosities obtained from these methods are compared, revealing the challenges associated with using these measurement methods.

Thursday 9:30 Room 306C IR11

Real-time absolute measurement of particle contact angle at an oil/water interface

Md Anisul Islam[1], Gordon Christopher[1], and Craig Snoeyink[2]
[1]Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]Mechanical and Aerospace Engineering, University at Buffalo, Buffalo, NY 14213, United States

Contact angle has an important role in determining the stability and interfacial viscoelasticity of the interface. However, contact angles are not fixed for any particular interface. A better understanding of how the distribution of contact angles varies in response to surface coverage, particle-particle interactions, and even particle shape will improve our understanding of the physical behavior of these interfaces. Direct measurement of contact angle is very difficult due to the small length scales and as a result, contact angle is calculated in terms of height of the particles center of mass above the interface. However, traditional measurement techniques such as freezing or gelling may affect the particle locations and dynamic behavior of interface. Holographic microscopy is useful for multiple particles only if the particles are widely spread at the interface. We will present a new method for measuring the absolute three-phase contact angles of statistically robust populations of interfacial particles, without hampering the interfacial dynamics. This method utilizes dual-color Bessel Beam Microscopy, a high-resolution 3D particle tracking system to determine both the location of the interface and the contact angle of particles adsorbed to it. The interface height is determined by localizing blue fluorescent nanoparticles adsorbed to the interface while the micron-sized particles of interest are red fluorescent. Localizing particles with vastly different sizes poses unique is useful in many different contexts but poses unique challenges. This talk will discuss the new methodologies developed to make this possible as well as results of real-time absolute particle angle distribution measurements of interfacial polystyrene particles.

Thursday 10:25 Room 306C IR13

A mesoscale computational study of momentum transfer across complex fluid-fluid interfaces

Felipe Paiva[1], Shaghayegh Khani[1], Arman Boromand[2], Argimiro Secchi[3], Veronica Calado[3], and Joao Maia[1]
[1]Case Western Reserve University, Cleveland, OH, United States; [2]Mechanical Engineering and Material Sciences, Yale University, New Haven, CT 06511, United States; [3]Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

Studying the effect of an applied shear flow field is important for fine-tuning material microstructure. This is relevant mainly at interfaces with increasingly complex microstructures as they dictate the equilibrium and nonequilibrium rheological properties of multiphase nanomaterials. Very recently, Molecular Dynamics simulations and experimental efforts have shown that momentum transfer plays an important role in generating dynamic heterogeneities and stretched exponential relaxation at complex interfaces. Hence, in this study, we perform a mesoscale Dissipative Particle Dynamics (DPD) computational study of how efficiently momentum is transferred across increasingly complex fluid-fluid interfaces with symmetric surfactants of different architectures and stiffnesses. This is also done with different thermostating schemes, namely the regular DPD thermostat, which is intrinsically linked to low gas-like Schmidt numbers, and the Lowe-Andersen thermostat, which allows for increased Schmidt numbers in DPD simulations. Hence, this study encompasses both an investigation of how numerical computational tools affect results from momentum transfer studies and of how surfactant architecture/stiffness affects momentum transfer across complex interfaces. This is important in many applications where multiphase flow is present, such as food processing and cosmetic applications.

Thursday 10:50 Room 306C IR14

Predicting shear rheology of soft interfaces

Aditya Raghunandan[1], Nicholas E. Debono[1], Juan M. Lopez[2], and Hirsa H. Amir[1]
[1]M, Rensselaer Polytechnic Institute, Troy, NY 12180, United States; [2]Mathematical and Statistical Sciences, Arizona State University, Tempe, AZ 85287, United States

Predicting non-Newtonian shear responses of soft matter systems at fluid-fluid interfaces has been restricted by using linear (Newtonian) constitutive equations to determine rheological properties. Predicting this nonlinear behavior is integral to comprehending many biophysical processes and the development of engineered products. Here, we present a non-Newtonian constitutive equation for interfaces under steady shear where the interfacial shear viscosity is generalized to be a function the imposed shear-rate. We introduce non-Newtonian material properties that control nonlinear and linear shear responses of an interfacial system. Combining flow field predictions and experiments in a knife-edge surface viscometer, we recently demonstrated that monolayers of DPPC - the primary constituent of mammalian cell walls and pulmonary surfactant - are shear-thinning at near-physiological surface packing over six decades of shear-rate. Here, we extend this framework to capture the interfacial

rheology of adsorbed protein films (insulin). We show that interfacial rheology can be used as a non-invasive probe to detect and monitor shear-induced protein aggregation and subsequent fibril formation at interfaces.

Thursday 11:15 Room 306C IR15

Rheology of a carboxylic acid at water/oil interface

Isabela F. Soares[1], Marcio N. Souza[2], Mônica F. Naccache[1], and Gerald G. Fuller[3]
[1]Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22451900, Brazil; [2]Chemical Engineering, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941909, Brazil; [3]Chemical Engineering, Stanford University, Stanford, CA 94305-4125, United States

In the oil industry activities, oil/water emulsions are commonly found, and the interfaces formed lead to physical-chemical adsorption phenomena. Among the natural interfacial activity species, naphthenic acids act as a major surfactant capable of form calcium and sodium naphthenates. The dissociated fractions of naphthenic acids can react with metal ions present in aqueous solutions, forming rigid structures known as metallic naphthenic molecules. Metallic naphthenate deposits are a major issue in the oil industry. This work studies the interfacial rheology of a model naphthenic acid, a carboxylic organic (stearic) acid, in the presence of monovalent and divalent salts, and high pH. Dilatational and shear experiments were performed for oil/water and oil/brine systems. Dilatational tests were done using the pendant drop method, whereas the du Nöuy ring was used for the interfacial shear rheology. The results show that the interfacial dilatational modulus increases with time and salt concentration. The interfacial moduli with monovalent cations were greater than that of pure deionized water. The same trend was observed for both salts, but the films form faster and are more rigid in the presence of Na+, due to differences in the acid/salt complexes that are formed. Dilatational results for divalent cations showed an increase on the interfacial moduli, especially for large salt concentrations. We also obtained the interfacial shear rheology of the stearic acid film for different salts and concentrations. Time sweep tests were carried out to evaluate the aging time of the stearic acid with different bulk solutions. It was observed that sodium ions induce a more elastic and rigid interface compared to calcium ions. The results also showed that higher salt concentrations lead to higher elastic modulus, although for the calcium chloride this increase is stronger, possible due to the local complex interactions between the cations in the aqueous phase and the dissociated molecules of the carboxylic acid at the interface.

Thursday 11:40 Room 306C IR16

Linear and non-linear rheology of liquid metals

Alan R. Jacob, Michael D. Dickey, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Gallium and its alloys react with oxygen to form a native oxide that encapsulates the liquid metal with a solid 'skin'. The viscoelasticity of this skin is leveraged in applications such as soft electronics, 3D printing and components for microfluidic devices. In these applications, rheological characterization of the oxide skin is paramount for understanding and controlling liquid metals. Here, we provide a direct comparison of the linear and non-linear viscoelastic properties for gallium-based liquid metals and illustrate the effect of different subphases. The Du Noüy ring is used to investigate the interfacial rheology of oxide skins formed by gallium-based liquid metal alloys. The results show that the oxide layer on gallium, eutectic gallium indium, and galinstan all form similar elastic layers. In the linear regime, the storage modulus of the oxide layer decreases when exposed to water. Large amplitude oscillatory shear is used to investigate the dynamic yielding properties of liquid metals in air and water interface. Fourier transform analysis and intra cycle non-linearity are quantified for the liquid metals in both subphases. These studies provide guidance on selecting liquid metals as well as methods to tune their rheological behavior for future applications.

Poster Session

Symposium PO
Poster Session

Organizers: Alan Jacob and Vivek Sharma

Wednesday 6:30 Ballroom on 4th floor PO1

Remote sensing of coagulation process by electro-magnetically spinning system

Keiji Sakai[1], Maiko Hosoda[2], and Yoshikazu Yamakawa[3]
[1]Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan; [2]Tokyo Denki University, Saitama, Japan; [3]Triple Eye Co., Ltd, Kyoto, Japan

Recently, we succeeded in improving Electro-Magnetically-Spinning(EMS) viscometer system for remote sensing of the coagulation process of fluid samples. In the measurement by EMS method, a thin metal disk is used as a probe rotor, which is set on the surface of the layered sample with thickness of 0.5mm. The system applies rotating magnetic field to the rotor and induces current in it. The Lorentz interaction between the magnetic field and the current drives the rotor to follow the rotation of the magnetic field. Viscosity and its dependence on shear rate can be obtained from the relation between the rotational speeds of the magnetic field and the probe. Non-Contact, sealable, disposable and safe measurements are possible, which is useful features especially for the medical field treating bio-hazardous materials. The coagulation can be detected as the appearance of elasticity, which is detected as the restoration of the deformation of samples under the alternative torque. In the presentation, we introduce a new video analysis system, which gives quantitative measure for the sample elasticity.

Wednesday 6:30 Ballroom on 4th floor PO2

PIV analysis of the vane in cup flow of a viscoplastic microgel

Esteban F. Medina-Bañuelos[1], Benjamín M. Marín-Santibáñez[1], and José Pérez-González[2]
[1]SEPI-ESIQIE, Instituto Politécnico Nacional, Ciudad de México 07738, Mexico; [2]Laboratorio de Reología y Física de la Materia Blanda-ESFM, Instituto Politécnico Nacional, Ciudad de México 07738, Mexico

The vane in cup flow of a Newtonian fluid and a model yield-stress fluid, a 0.12 wt.% Carbopol® 940 microgel, with slip at the cup were analyzed in this work using particle image velocimetry (PIV). The velocity distributions for the Newtonian fluid indicate that the fluid trapped in between two adjacent blades rotates as a rigid body along with the vane up to a radial position smaller than the radius of the vane R_V, and such radial position was found to be independent of the vane rotational speed. Also, for radial locations, r, greater than that at which rigid body-like motion ends, the tangential velocity exhibits a maximum, which is located at a radial position smaller than R_V and is also independent of the rotational speed. In the region between the radius of the vane and the cup, the tangential velocity profiles resemble those observed between two concentric cylinders. This observation suggests that a Couette analogy may be applied to analyze the vane in cup flow of Newtonian fluids provided that an equivalent radius, R_{eq}, is defined, being R_{eq} the radius of a virtual inner cylinder of a Couette geometry. Regardless of how it is determined, R_{eq} remains constant for all Newtonian fluids in a given vane and cup geometry. However, the velocity profiles of the viscoplastic microgel showed that both, the radial position at which the rigid body-like motion ends and that where the maximum is located, change with the flow conditions. This result suggests that R_{eq} will depend on the flow conditions for a non-Newtonian fluid in a vane in cup geometry and that it will be different for different non-Newtonian fluids. Consequently, there is not a definite method to determine the value of R_{eq} for non-Newtonian fluids, which precludes the use of the vane in cup geometry as a rheometer for complex fluids.

Wednesday 6:30 Ballroom on 4th floor PO3

Using non-lubricated squeeze flow to determine empirical parameters for modeling long fiber injection molded thermoplastics

Kennedy Boyce, Greg Lambert, and Donald Baird
Chemical Engineering, Virginia Tech, Blacksburg, VA 24060, United States

Polymer fiber composites provide a solution to the demand for lighter and stronger materials. Injection molding is likely to be the most common method for part production and chopped long fibers such as glass and carbon are used to reinforce thermoplastics. The mechanical performance of the parts is dependent on the length and orientation of the reinforcing fibers. Models have been designed to predict the orientation evolution of the fibers during injection molding. The models require a set of empirical parameters. In order to improve the design process, a method for determining these material and flow dependent parameters has been developed. Mold filling is a combination of shear and extensional flows. Research has shown that neither simple shear nor simple extensional flow can be used to accurately represent the suspension behavior. Non-lubricated squeeze flow (NLSF) provides a combination of flows. The flow generated in NLSF is simple enough for investigation but complex enough to induce fiber bending and includes the effects of shear and extensional flows. Glass fiber reinforced polypropylene parameters have been calculated and verified using this technique. Further verification is being conducted to determine if non-lubricated squeeze flow can be used to rheologically determine the parameters for different composites using a carbon fiber reinforced nylon 6,6.

Wednesday 6:30 Ballroom on 4th floor PO4

Medium amplitude parallel superposition (MAPS) rheology

Kyle Lennon[1], James Swan[1], and Gareth H. McKinley[2]
[1]Chemical Engineering, MIT, Cambridge, MA 02139, United States; [2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

A new mathematical representation for nonlinear viscoelasticity based on the Volterra series expansion of the nonlinear functional relationship between shear stress and strain history is presented. We develop the theoretical and experimental framework for this representation, which we call medium amplitude parallel superposition (MAPS) rheology, and reveal a new material property, called the third order complex modulus. This material property describes completely the weakly nonlinear response of a viscoelastic material to an arbitrary homogenous shear deformation history. We show that the third order complex modulus is a super-set of the properties measured in medium amplitude oscillatory shear (MAOS) and parallel superposition (PS) measurements. A straightforward method for visualizing the third order complex modulus in theoretical and experimental studies is then proposed, which exploits symmetries of the response function to reduce it to a minimal domain. The third order complex modulus is computed and plotted for a few phenomenological constitutive models to illustrate the richness of the MAPS framework. Finally, an experimental protocol is presented, which allows high-throughput direct measurements of the third order complex modulus using commercially available rheometers, and this protocol is applied to measurements of nonlinear viscoelasticity in a model material.

Wednesday 6:30 Ballroom on 4th floor PO5

The role of elasticity in thixotropy: Elastic stress during parallel superposition

Jiho Choi and Simon A. Rogers
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Materials that display thixotropy, or time-dependent viscosities, are ubiquitous in industry, the environment, and consumer products. Despite the wide-spread use and importance of thixotropic materials, theoretical descriptions still fail to accurately describe the complex behaviors exhibited in transient flows. Here, we employ a series of complex transient tests to experimentally probe those complex dynamics. We use flow cessation tests [1] to identify transient elastic stresses during stress jump tests which are commonly used to identify thixotropy. It is shown that the evolution of the elastic stress closely follows that of total stress in the series of stress jump tests, indicating that elasticity is a significant contributor to thixotropy. This laborious experimental method of obtaining elastic stress is compared to calculations of the elastic stress from a rapid and novel analysis of parallel superposition tests based on the sequence of physical processes (SPP) [2] framework. In the SPP framework, the elastic stress is calculated via integration of the SPP modulus, which echoes the importance of elasticity in thixotropy, in that it also follows the shape of total stress in parallel superposition. Therefore, we can obtain the elastic stress using the SPP framework significantly quicker than by a series of flow cessation tests. While parallel superposition tests have previously been analyzed by dividing the stress into steady and oscillating components, the SPP framework treats all stress equally, and enables us to obtain accurate viscoelastic metrics for parallel superposition. These results show that we can extend the utility of the SPP approach to the study of thixotropy and parallel superposition, which has so far been limited to large amplitude oscillatory shear studies only.[1] Dullaert, K., and J. Mewis, "Stress jumps on weakly flocculated dispersions," J. Colloid Interface Sci. 287, 542-551 (2005).[2] Rogers. S. A., "In search of physical meaning," Rheol. Acta. 56, 501-525 (2017).

Wednesday 6:30 Ballroom on 4th floor PO6

Tribological characterization of polymer brush-grafted substrates with varying elastic moduli

Christopher M. Serfass and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Recent studies show that surfaces grafted with polymer brushes attain extremely low friction coefficients and increased wear resistance. These types of engineered surfaces mimic natural lubrication and are increasingly important in applications such as self-cleaning and anti-fouling. Our goal is to investigate the steady state and transient tribological response of substrates of varying elastic moduli grafted with polymer brushes. Here, we employ atom transfer radical polymerization (ATRP) to grow polyzwitterionic and polyelectrolyte brushes from hard silicon (E~10^11 Pa) and soft poly(dimethyl siloxane) (PDMS) substrates (E~10^6 Pa). This grafting-from process grows monomers one unit at a time from initiators attached a priori onto the surfaces. Tribological characterization of native and polymer-grafted surfaces is performed using a ball-on-three-plates geometry attached to a stress-controlled rheometer, in which the surfaces are fully immersed in a liquid medium. Preliminary studies using tribopairs of native PDMS and brush-grafted silicon immersed in deionized water show a reduction in friction of two orders of magnitude compared to native silicon.

Wednesday 6:30 Ballroom on 4th floor PO7

Tribology of solid- solid interfaces – selecting test fixture materials to optimize measurement sensitivity and reproducibility

Sarah K. Cotts and Jada Evers
TA Instruments, New Castle, DE 19720, United States

Over the past several years, rheometers' tribology testing capabilities have been used in an increasing number of applications. The primary area of focus is on lubricity of complex fluids, especially in the personal care and food industry. This characterization has proven relevant to sensory properties such as texture and mouthfeel, expanding beyond standard rheological measurements. Tribology instrumentation can also be used to

measure friction between solid surfaces absent any lubricating material. Studying solid surface friction is relevant to many applications. Materials for industrial applications may require a low Coefficient of Friction for moving parts, or a high Coefficient of Friction to prevent slip. In addition to bulk materials, a coating may also be formulated to optimize the surface friction to achieve a desired texture or feel.

Previous tribology testing has demonstrated that the testing fixture material has significant effects on the measurement. Modification to the fixture to mimic skin for personal care products or mimic the tongue for food has proven effective for quantifying desirable properties between products compared to measuring with standard steel fixtures. The work presented will focus on "ring on plate" and "3 balls on plate" tribology configurations utilizing a wide range of materials for the upper fixture, including thermoplastics, elastomers, skin-substitutes and others. Different test fixture materials will be compared to show reproducibility and differentiation for example applications.

Wednesday 6:30 Ballroom on 4th floor PO8

Capillary RheoSANS: Measuring the rheology and nanostructure of complex fluids at high shear rates

Ryan Murphy[1], Zachary Riedel[2], Marshall Nakatani[3], Javen Weston[4], Paul F. Salipante[5], Yun Liu[1], Steven Hudson[6], and Katie M. Weigandt[1]

[1]NIST Center for Neutron Research, Gaithersburg, MD 20899, United States; [2]Clemson University, Clemson, SC, United States; [3]George Washington University, Washington D.C., DC, United States; [4]Chemical Engineering, University of Tulsa, Tulsa, OK 74104, United States; [5]Polymers & Complex Fluids, NIST, Gaithersburg, MD 20899, United States; [6]NIST, Gaithersburg, MD 20899, United States

Complex fluids containing surfactants, polymers, nanoparticles, or proteins can change when subjected to flow at high velocity and within confined geometries. These extreme flow environments can generate high shear rates and forces that damage materials during purification, formulation, and application. To better understand these flow-induced effects at high shear rates, a new Capillary RheoSANS (CRSANS) device combines capillary rheometery positioned within small angle neutron scattering (SANS) instruments to simultaneously measure the rheology and nanostructure. Currently, CRSANS measures pressure drops up to 500 bar, shear rate-dependent viscosity up to 1000 mPa-s, and generates apparent wall shear rates up to 10,000,000 s-1. The device recycles relatively small sample volumes (1-2 mL) to facilitate SANS measurements on biological and deuterated samples. Current device capabilities are demonstrated with various model systems, including worm-like micelles, concentrated silica suspensions, lipid bilayers, and the NIST monoclonal antibody. Ongoing work aims to improve measurement precision, lower shear rate boundaries, temperature control, and to enable measurement of higher viscosity samples such as polymer melts, pastes, and slurries.

Wednesday 6:30 Ballroom on 4th floor PO9

Closed boundary shear rheology: An alternative to existing methods for high shear rate testing of filled polymer products

Alina Latshaw[1], Thomas Rauschmann[2], and Sandeep Reddy[2]

[1]TA Instruments, New Castle, DE 19720, United States; [2]TA Instruments, Wetzlar, Germany

Fully characterizing the flow behavior of materials across a wide range of shear rates is imperative for the optimization of industrial processing operations. Specifically, elevated shear rate ranges are linked to processing behavior exhibited in pipe flow, molding processes, and extrusion, among other applications. For many polymeric systems, steady state viscosity measurements at high shear rates are difficult obtain on open boundary rheometers due to elasticity-induced sample fracture. Other measurement techniques such as conversion of complex viscosity through the Cox-Merz relation or commercial products such as capillary devices or the cone and partitioned plate may be used as alternatives, but still pose their own challenges. The Cox-Merz relation has proven to be an empirical relationship that is robust for homopolymers, but loses accuracy for complex blends, especially those with particulate fillers. Capillary rheometry requires a large volume of material for testing and additional corrections must be applied for accurate measurements. The cone and partitioned plate is a useful tool for performing steady shear measurements on open boundary rheometers, however it simply delays the onset of edge fracture. In this poster, we explore the measurement of steady shear viscosity at elevated shear rates using a steady state methodology in a closed boundary rheometer that overcomes many of the aforementioned challenges and provides a viable path to direct measurements for processing elastomer compounds.

Wednesday 6:30 Ballroom on 4th floor PO10

A sequence of physical processes in time-resolved powder rheology

Gavin J. Donley[1], Abhishek Shetty[2], and Simon A. Rogers[1]

[1]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Rheology Division, Anton Paar, Ashland, VA 14850, United States

The behavior of powders under flow is relevant to a wide range of industrial processes, from pharmaceuticals to additive manufacturing. As the flow properties of powders, which are dictated by complex inter-particle interactions, are very sensitive to small changes in environmental parameters such as air flow rate, temperature, and humidity, the ability to obtain accurate and meaningful rheological data has been challenging. Here, we demonstrate the viability of a rotational air-bearing rheometer with a powder flow cell that enables rotational and oscillatory testing of powders. The setup is augmented with a mass flow controller which allows oscillatory testing of powders from sub-fluidized to completely fluidized states. We perform large amplitude oscillatory shear (LAOS) on soda lime glass spheres using a range of air flow rates that act to soften the powders, and analyze the response with the recently-developed Sequence of Physical Processes (SPP) approach. We show that the powders behave as nearly ideal elastoplastic materials with air flow-rate-dependent yield stresses. By phenomenologically describing the responses as simple elastoplastic responses with a constant yield strain and modulus, we show how entire amplitude sweeps can be described with only a few material parameters.

Wednesday 6:30 Ballroom on 4th floor PO11

Rheo-NMR velocimetry of large amplitude oscillatory shear

Jayesha S. Jayaratne[1], Rehab N. Al-Kaby[2], Sarah L. Codd[2], Timothy I. Brox[3], Josephine A. Maley[2], Petrik Galvosas[3], and Joseph D. Seymour[1]

[1]Chemical and Biological Engineering, Montana State University, Bozeman, MT 59717, United States; [2]Mechanical & Industrial Engineering, Montana State University, Bozeman, MT 59717, United States; [3]Victoria University of Wellington, Wellington, New Zealand

In many processing and application environments large amplitude and oscillatory shear forces are applied to materials. This, and the potential for greater understanding of material microscale response, has led to the development of large amplitude oscillatory shear (LAOS) rheometry methods [1,2]. In this study, 1D velocity profiles for fluids subject to large amplitude oscillatory shear (LAOS) were measured across a 1mm fluid gap in a concentric cylinder rheo-NMR [3] shear cell. Fluids exhibiting a range of rheological responses, from yield stress 0.2 wt.% carbopol, ketchup and drinking yogurt, to shear thinning 0.6 %w/v xanthan gum were measured and compared against Newtonian fluids (water and 1,000 cSt silicone oil) in order to establish what information the spatial velocity provides under LAOS flow conditions. Given the novelty of the data, various analyses are presented including oscillatory spatial velocity profiles, time dependent velocity profiles at fixed gap locations and a modified form of Lissajous curves. The experimental results demonstrate the extension of rheo-NMR velocimetry to characterize flow behavior under LAOS.

[1] K. Hyun et al. "A review of nonlinear oscillatory shear tests: Analysis and application of LAOS", Progress in Polymer Science 36(12) 1697-1753 (2011). [2] Simon Rogers, "Large amplitude oscillatory shear: Simple to describe, hard to interpret", Physics Today 71(7) 34-40 (2018). [3] P.T. Callaghan, "Rheo-NMR: nuclear magnetic resonance and the rheology of complex fluids, Reports on Progress in Physics 62 599-670 (1999).

Wednesday 6:30 Ballroom on 4th floor PO12

Combined FT rheology and thermal surface analysis for complete mechanical testing

Valerian Hirschberg[1], Manfred Wilhelm[2], and Denis Rodrigue[1]

[1]Department of Chemical Engineering, Universite Laval, Quebec City, Quebec G1V 0A8, Canada; [2]Institut for Technical Chemistry and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe 76128, Germany

Dynamic mechanical testing of High Density Polyethylene (HDPE) and Polyamide 6 (Nylon 6) was performed at different frequencies (?$_1$/2p = 5 Hz and ?$_1$/2p = 0.2 Hz) under Large Amplitude Oscillatory Elongation (LAOE) conditions. The stress response was analyzed via Fourier transform (FT) and the surface temperature was followed via a thermal camera. The thermal analysis results showed that a clear thermoelastic coupling (TC) effect exists as well as intrinsic heating during a test. Under LAOE, TC leads to a sample temperature decrease during the loading half-cycle and a temperature increase during the unloading half cycle. Under static tension for strain rates comparable to the testing frequency, an increase in the maximum surface temperature (Tmax) was observed for Nylon 6 in contrast to HDPE due to some plastic deformation effects. Under LAOE and low frequencies (?$_1$/2p = 0.2 Hz), plastic deformation is important which can be correlated with characteristic changes in the shape of the Lissajous curves and consequently in the behavior of the stress higher harmonics. In particular, the $I_{2/1}$ intensity was found to rapidly increase with increasing plastic deformation. The thermoelastic coupling and T_{max} as a function of the cycle number changed due to plastic deformation, from a sinusoidal shape with the frequency of the deformation to one with twice the applied deformation frequency. Decomposition of T_{max} via FT during the first 15 cycles after the initial cycle revealed, beside the fundamental harmonic T_1, higher harmonics T_2 and T_3 at twice and trice the fundamental frequency. The higher harmonics in T_{max}, T_1, T_2 and T_3 were also found to respectively scale linearly (T_1 a $e_0$1), quadratically (T_2 a e_0^2) and cubically (T_3 a e_0^3) with respect to the applied strain amplitude e_0.

Wednesday 6:30 Ballroom on 4th floor PO13

Probing nonlinear rheology layer-by-layer in interfacial hydration water

Wonho Jhe

Physics & Astronomy, Seoul National University, Seoul 08826, Republic of Korea

Viscoelastic fluids exhibit rheological nonlinearity at a high shear rate. Although typical nonlinear effects, shear thinning and shear thickening, have been usually understood by variation of intrinsic quantities such as viscosity, one still requires a better understanding of the microscopic origins, currently under debate, especially on the shear-thickening mechanism. We present accurate measurements of shear stress in the bound hydration water layer using noncontact dynamic force microscopy. We find shear thickening occurs above ~10^6 s-1 shear rate beyond 0.3-nm layer thickness, which is attributed to the nonviscous, elasticity-associated fluidic instability via fluctuation correlation. Such a nonlinear fluidic transition is observed due to the long relaxation time (~10-6 s) of water available in the nanoconfined hydration layer, which indicates the onset of elastic turbulence at nanoscale, elucidating the interplay between relaxation and shear motion, which also indicates the onset of elastic turbulence at nanoscale above a universal shear velocity of ~1mm=s. This extensive layer-by-layer control paves the way for fundamental studies of nonlinear nanorheology and nanoscale hydrodynamics, as well as provides novel insights on viscoelastic dynamics of interfacial water.

Wednesday 6:30 Ballroom on 4th floor PO14

Correlation of rheological data and optically visible sample effects during measurements

Tobias Nill
Anton Paar Germany GmbH, Ostfildern 73760, Germany

Many optically visible sample effects such as edge fracture, sagging, stringing, necking degradation, slip, gap emptying and phase transitions can occur during a rheological measurement in a dynamic shear rheometer. Very often, these are undesired effects which affect the measurement results in a significant way and therefore should be avoided. On the other hand, it may also be a goal to investigate these effects in more detail in order to better understand the rheological behavior of materials. The occurrence of these effects is dependent on many influence factors like the type of measuring system and test parameters (e.g. shear rate, frequency, strain amplitude and temperature). This contribution will present a way to investigate the sample behavior and the influence factors of these effects and to help with the interpretation of measurement results by observing and recording the optically visible real-time sample behavior and by correlating it with the rheological data. It will highlight applications which show significant effects of optically visible sample behavior on rheological data. Furthermore, these optical data can add valuable information to the post-measurement analysis, validate measurement results and help to optimize the test parameters in order to avoid undesired sample behavior during the measurement. The investigation is enabled by the use of a camera setup for a high temperature oven with integrated illumination mounted on a Modular Compact Rheometer from Anton Paar. With this optical system sharp real-time pictures and videos of the sample behavior during the measurement can be recorded and correlated directly to the measuring points at which they were recorded. Optical investigations can be performed over a temperature range of -160 °C to 600 °C and with a field of view of 50 mm diameter, allowing to observe a wide sample area.

Wednesday 6:30 Ballroom on 4th floor PO15

Enhancing material characterization through the Rheo-Raman techniques

James P. Eickhoff and Javier Lanauze
Rheology, Anton Paar USA, Ashland, VA 23005, United States

The combination of rheology with Raman spectroscopy offers a wide range of possibilities for further characterizing both the physical as well as chemical changes in a system in-situ. Such areas of interest where this technique may be important is studying the onset of crystallization, shear breakdown, as well as thermal curing/degradation. The Raman signature can be directly related to the various rheology changes in the sample, presenting an additional capability for understanding a material response. A series of samples were tested using a Rheo-Raman configuration to show the additional information which can be obtained through such studies.

Wednesday 6:30 Ballroom on 4th floor PO16

Correlation of rheological parameters between laboratory and online rheometers

Azadeh Farahanchi and Kevin Criag
Dynisco Instruments LLC, Franklin, MA 02038, United States

The growing tendency towards productivity, efficiency, and sustainability among manufactures and recyclers in the plastics industry arises the necessity of timely control of the process and quality while eliminating the waste amount. Online rheometers have increasingly been used in variety of extrusion lines in order to have continuous data stream of rheological properties and real-time information on the process without any delay for the laboratory testing. A newly designed online rheometer has been developed to duplicate the test conditions of laboratory rheometers, continuously provide information on the melt flow rate (MFR), shear viscosity, intrinsic viscosity, and extensional viscosity of in-process extrudate materials. The present work aims to describe how this online rheometer has been designed on an extruder to accurately control the amount of volumetric flow rate and driving pressure while considering the effect of reservoir pressure, entrance pressure drop, and capillary diameter. As a result, this online system continually measures various rheological parameters which closely match those from a laboratory melt indexer, capillary rheometer, and extensional rheometer. Moreover, through calculation of activation energy for a specific material and introducing a temperature correlation, it has been investigated how this online rheometer considers the temperature dependency of material`s rheological properties and accurately measures these parameters at various operating temperatures.

Wednesday 6:30 Ballroom on 4th floor PO17

Insights from recovery rheology applied to step-strain and start-up of shear flows

Piyush K. Singh, Johnny Ching-Wei Lee, and Simon A. Rogers
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Material functions are at the core of every rheological study. It is through the presentation of material functions that we describe the physics that dictate the behavior of soft materials. Traditional rheological metrics such as moduli and viscosities are defined in the official nomenclature of the Society of Rheology in terms of the total strain and the rate at which the total strain changes, respectively. Recent works have shown significant benefit in distinguishing between the total strain and the recoverable strain, even in strain-controlled tests [Lee et al, Phys. Rev. Lett. (2019); Lee et al, AICHE J (2019)]. It has been shown that elastic moduli that are defined in terms of the recoverable strain and viscosities that are defined in terms of the rate of acquisition of unrecoverable strain can be clearly correlated across a range of linear and transient nonlinear rheological tests. In this work, investigating a well-studied system of wormlike micelles, we further apply the ideas of recovery rheology to two of the most common experiments in rheometry, step strain and start up of shear. We show that quantities defined in terms of recoverable and unrecoverable strains, especially for these transient flows, are remarkably consistent across distinct flow types. Furthermore, such quantities yield the same information across test conditions. For example, despite the micellar solution being known to be shear-thinning under steady-state flow, we show that at early times under a wide range of nonlinear shear rates that the same (zero-shear) viscosity is observed. Our results have strong implications for fundamental questions such as how we define moduli and viscosities under transient flow conditions, as well as how we define useful dimensionless groups such as transient Deborah and Weissenberg numbers.

Wednesday 6:30 Ballroom on 4th floor PO18

Investigation of non-linear coarsening mechanism in co-continuous polymer blends via confocal rheology

Rajas Sudhir Shah, Steven Byrant, and Milana Trifkovic
University of Calgary, Calgary, Alberta T2N 1N4, Canada

Co-continuous polymer blends offer synergistic effect on mechanical properties and have also found applications in conductive plastics, membranes, etc. However, their morphology is thermodynamically unstable due to the excess local free energy stored in their highly curved interfaces which leads to coarsening of these microstructures upon annealing. Hence, it is important to understand the coarsening mechanism of these blends in-order to determine the optimum melt-processing conditions for such blends. The interdependence of viscoelastic properties of polymer blends and their micro-structures have been widely studied and it is reported that they depend on blend composition, interfacial tension and viscoelastic properties of components. In general, there are two regimes of coarsening, first linear growth regime and second non-linear regime with a slower rate which ultimately plateau-out at very long times. The linear growth regime is well understood, extensively studied and modelled in literature and a few attempts have been made to explain and model the late coarsening regime. However, the explanation of the microstructural changes that occur during the transition from linear to the non-linear regime is still lacking. Primarily, this gap is because almost all morphological measurements are done discretely and independently to rheometry. In this study, laser scanning confocal microscopy (LSCM) is coupled by rotational rheometry of polymer blend melts to simultaneously probe their coarsening dynamics in-situ and understand the interplay between viscoelasticity and morphology. Using LSCM, coarsening is characterized by imaging the 4D (3 spatial and 1 temporal dimension) evolution of the microstructure while the oscillatory shear response of the blend provides data on viscoelastic dynamics. We have studied the effect of interfacial tension between the components on the onset of transition and nature of annealing in the late coarsening regime and evaluated the findings with the available mathematical models.

Wednesday 6:30 Ballroom on 4th floor PO19

Can we predict viscosity of electrolytes? Simple theories versus molecular dynamics simulations with LiTFSI in acetonitrile

Yilin Wang[1], Hossam Farag[2], Yang Zhang[2], and Randy H. Ewoldt[1]
[1]Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]University of Illinois at Urbana Champaign, Urbana, IL, United States

We collect experimental viscosity data for LiTFSI salt in acetonitrile solvent using a microfluidic channel flow viscometer (Rheosense, mVROC) over a range of concentrations (0 to 0.7 M) and temperatures (293 to 333 K). The experimental data is used to calibrate and test various methods of predicting the viscosity of this electrolyte system, motivated by the design and engineering of liquids for redox flow battery systems. We assess the trade-off between model complexity and model accuracy with a simple theory and molecular dynamics simulation. The simple theory is based on the Jones-Dole equation and Eyring's theory, a semi-predictive model that requires calibration of model parameters to some experimental viscosity data points. For comparison, molecular dynamic (MD) simulations were conducted to make a priori prediction of the viscosity, though the potential field model also requires calibration to some (non-viscosity) experimental data. Here the forcefield used is the optimized potentials for liquid simulations (OPLS) - all atom force field, modified based on our mp2 quantum chemistry calculations for atomic partial charge and geometry. The partial atomic charges for coulombic interactions are rescaled by a calibrated fraction (80%) to mimic the average charge screening due to polarization and charge transfer effects. In order to predict zero-shear viscosity from atomic trajectories, we use the Green-Kubo relations, integrating the time auto correlation function of the off-diagonal stress tensor elements. Predictions from both models are compared to the experimental data which shows the relative trade-off between model complexity and model accuracy in predicting transport properties in these small molecule complex fluids.

Wednesday 6:30 Ballroom on 4th floor PO20

Improving the estimation of the zero-shear-rate viscosity

Montgomery T. Shaw
Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, United States

The zero-shear-rate viscosity, η_0, is a quantity that is well defined but often very difficult to measure directly. As a result, most investigators will estimate η_0 by extrapolation using data gathered at more accessible shear rates or frequencies. At times, the extrapolation appears alarmingly risky and the value obtained will be quite uncertain or even worthless. The purpose of this work was to find ways to improve the estimate of η_0 without requiring a huge change in the experimental effort. To check on the proposed methods, three polymer melts - PDMS, PIB, PViBE - were evaluated experimentally over five decades of frequency. Using truncated data sets, attempts were made to determine η_0 using various extrapolation equations including 19 well-known GNF empiricisms. The modes of the distribution of η_0 results was examined as possible "best estimate." While interesting, there is admittedly little basis for this technique, although it appeared to give favorable results for the tested polymers.

Wednesday 6:30 Ballroom on 4th floor PO21

Flow of transiently networked FENE and Hookean dumbbell mixtures

Lucas E. Quintero[1], Lin Zhou[2], and L. Pamela Cook[1]
[1]Mathematical Sciences, University of Delware, Newark, DE 19716, United States; [2]Mathematics, New York City College of Technology, CUNY, Brooklyn, NY 11201, United States

Flow characteristics of poly disperse mixtures of transiently attached FENE and Hookean dumbbells are examined. Both constant breaking rates and dumbbell stretch dependent breakage rates are considered in the mesoscale stochastic model. Using a semi-implicit Predictor-Corrector method similar to that suggested by Somasi et al [1], the FENE spring law can be accurately computationally captured. The analysis includes tracking of omputational error. The goal is to understand macro scale viscoelastic properties such as shear thickening and shear thinning and their dependence, both in time and in space, on local conditions and parameters.

[1] M. Somasi, B. Khomami, N.J. Woo, J.S. Hur, E.S.G. Shaqfeh, Brownian dynamics simulations of bead-rod and bead-spring chains: numerical algorithms and coarse-graining issues, JNNFM 108 (2002) 227-255

Wednesday 6:30 Ballroom on 4th floor PO22

Intermolecular hooking in unentangled semidilute polymer solutions under extensional flow

Charles D. Young and Charles E. Sing
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Polymer solution dynamics and rheology are relevant to a wide range of processing methods. Developing an understanding of the polymer conformational dynamics and the emergent material properties is challenging because of the interplay of hydrodynamic interactions (HI), excluded volume (EV), and topological constraints driven by concentration and polymer architecture. This is particularly true when extensional flow is introduced, which strongly deforms the polymers from their equilibrium conformations. Using a new technique for rapid Brownian dynamics (BD) simulation, which we call the iterative conformational averaging (CA) method, we investigate the dynamics and rheology of linear, comb, and ring polymer solutions at concentrations increasing from the dilute limit to the entanglement crossover point. We apply a step strain rate planar extensional flow to the equilibrium solution and quantify the dynamics in startup, at steady state, and after flow cessation via conformational distributions and the polymer contribution to extensional viscosity. We show that flow enhances intermolecular HI and topological interactions, resulting in transient intermolecular entanglements and concentration dependent rheology below the overlap concentration c*. Interestingly, each polymer architecture exhibits unique molecular conformations. We characterize this molecular individualism as a function of polymer concentration, strain rate, and molecular weight. We establish connections between entangled populations and the ensemble average conformational distributions and solution stress. We also compare to scaling theories, which predict the coexistence of coiled and stretched conformations on the basis of conformation dependent HI.

Wednesday 6:30 Ballroom on 4th floor PO23

Validating predictive models of the modulus change for polymers due to outdoor exposure

Christopher C. White, Donald Hunston, LiPiin Sung, and Adam Pintar
Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States

The NIST service life prediction program has demonstrated success in producing validated predictions for the property change resulting from outdoor exposure for a range of polymer systems including Epoxy, Polyethylene, Polyester, Polyethylene terephthalate, and Polyurethane elastomers. These predictions, of which are based on ASTM 1850, have included uncertainty calculations. In each of these systems, a predictive model grounded in laboratory exposure data is validated with outdoor exposure data. Two complications in the widespread adoption of these methods are the requirement that samples of the formulations must be degraded in a reasonable amount of time and the limited availability of the NIST developed environmental exposure equipment. Both complications can be addressed with the development of commercially viable exposure equipment based on NIST developed technology. Efforts to incorporate this new equipment into the ASTM 1850 protocols will be detailed.

Wednesday 6:30 Ballroom on 4th floor PO24

Linear and nonlinear shear rheology of pure ring polymers using cyclic poly(phthalaldehyde)

Michael Q. Tu, Johnny Ching-Wei Lee, Simon A. Rogers, and Charles M Schroeder
Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Ring polymers have fascinated polymer chemists and physicists for decades, yet achieving a complete understanding of the dynamics of pure ring polymer systems has remained a grand challenge due to experimental ring polymer systems suffering from linear polymer contamination. Even with recent advances in purification methods, existing ring polymer samples are thought to contain trace amounts of contaminant linear polymers, which have been shown to greatly affect the rheological response of these samples. In this work, we approach understanding the rheology of ring polymer systems by utilizing cyclic poly(phthalaldehyde), a low-ceiling temperature polymer whose metastable chemistry results in kinetically-trapped cyclic polymers above -40°C. Above this temperature, any linear chains present will degrade from free ends, resulting in a system comprised of highly pure and stable ring polymers. The synthesis is facile and can be performed at the multi-gram scale. Due to the self-immolating nature of linear chains at room temperature, no additional purification after synthesis is needed to separate linear and circular chains. We report

the linear and nonlinear viscoelastic properties of highly concentrated cPPA samples (>70 wt%) of various molecular weights. The transient nonlinear start-up shear responses shows stronger shear-thinning than a previously-reported polystyrene ring melt, but exhibit drastically reduced scaling behavior in the overshoot viscosity and strain with respect to shear rate. We attribute these differences to the fact that the molecular weights of our samples are high (Mw > 200 kDa) and our samples are highly pure with respect to ring/linear purity. Overall, these results give experimental insight into the dynamics of ring polymer systems with unprecedented purity.

Wednesday 6:30 Ballroom on 4th floor PO25

Fundamental study of polymer compatibility of polymer blends and their effects on melt spinning process and fiber/nonwoven properties

Imon Khan
Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, NC 27606, United States

Understanding the compatibility of traditional polymers in blends and their role on fiber formation process is very important as well as challenging in many aspects. Blends of one PP and LLDPE with two different types of compatibilizers were studied to investigate the effect of compatibilizers on blend properties. Rheological behavior and morphology of the blends were investigated.

Wednesday 6:30 Ballroom on 4th floor PO26

Rheology and compatibility of bioplasticizers in PVC

Sara Reynaud[1] and Zuzanna Donnelly[2]
[1]Analytical & System Research, Arkema, King of Prussia, PA 19406, United States; [2]Hydrogen Peroxide, Arkema, King of Prussia, PA 19406, United States

The substitution of phthalate esters used in the poly(vinyl chloride) industry with more eco-friendly plasticizers has been a topic of interest for almost two decades due to the high toxicity and the harmful health effects resulting from phthalate exposure. However, blending bioplasticizers in plastisol to achieve optimum gelation characteristics can be challenging and compatibility issues can negatively affect the mechanical properties, mainly flexibility and impact performance, of the final article. In this work, we present a fundamental study of epoxidized oils and esters plasticizers to compare with commercial plastisizers of different types used in plastisol formulations. Dynamic Shear Rheology and Dynamic Mechanical Analysis were employed in the investigation of plastisol curing kinetics (solvation, gelation and fusion), prediction of bioplasticizers compatibility and hence final plastisol properties while ensuring good processability.

Wednesday 6:30 Ballroom on 4th floor PO27

A novel analytical model to predict the dynamics of polymer chains in dilute solutions in an arbitrary flow

Indranil Saha Dalal[1] and Ronald G. Larson[2]
[1]Chemical Engineering, IIT Kanpur, Kanpur, Uttar Pradesh 208016, India; [2]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

We present a new analytical model, the "FENE-mode" model, to predict the dynamic behavior of dilute polymer chains in any given flow field. The model uses pre-averaged equations for the normal modes of the chain coupled with an appropriate representative spring constant, making it orders of magnitude faster than BD simulations. We compare the predictions of the FENE-mode model with those from BD simulations of uniaxial extension and steady shear, as well as a planar mixed flow between planar extensional and simple shear and another between shear and pure rotation. For all cases, we find an excellent agreement with BD simulations for the transient behavior of chain stretch and stress and the final steady state stresses.

Wednesday 6:30 Ballroom on 4th floor PO28

Nonlinear shear rheology of isotactic polypropylene melts

Daniele Parisi, Jiho Seo, Aijie Han, and Ralph Colby
Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, United States

Strong flow fields are inevitable components of polymer processing. When semicrystalline polymers are involved, such conditions might induce conformational changes and ordering. This phenomenon is known as Flow Induced Crystallization (FIC). These flow-induced modifications in the polymer crystallinity and crystalline morphology strongly affect the mechanical properties of the final product, attracting broad interest. In this experimental work, we investigate the nonlinear rheological response under shear flow of a set of seven isotactic polypropylene (iPP) melts with different molecular characteristics (158 kg/mol < Mw < 627 kg/mol and varying molar mass distribution). Experiments were all performed at 170 °C, slightly above the melting temperature. By combining different rheological techniques such as dynamic oscillatory shear, start-up shear experiments with a cone partitioned plate (CPP) and capillary rheometry, we have obtained flow curves that cover many decades in shear rate. The well resolved shear thinning region, nearly unaffected by flow instability, allowed us to detect the effect of FIC on the mechanical response, along the line of a previous experimental work on the same samples. Results are then compared with flow curves obtained with parallel plates combined with polarized optics using a transparent bottom plate and a reflecting top plate. The visual observation of the sheared systems allows a direct detection of the crystalline structures induced by the flow and at the same time, how this phenomenon depends on edge fracture (which is significantly present in plate-plate geometry) and on the molecular structure of the strictly linear iPPs.

Wednesday 6:30 Ballroom on 4th floor PO29

Rheological scaling of semidilute polymerized ionic liquids in ionic liquid solutions

Atsushi Matsumoto and Amy Q. Shen
Micro-Bio-Nanofluidics Unit, Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan

Polymerized ionic liquids (PILs) are a special type of polyelectrolytes with ionic liquid moieties covalently attached to a polymer backbone. PILs are considered as an ideal class of solid-state polymer electrolytes due to the suppressed electrostatic interaction, resulting from the sterically hindered and charge delocalized ions. Existing studies show that electrostatic interactions play a dominant role in determining the viscoelastic properties of ordinary polyelecrolytes [1]. However, the effect of the suppressed electrostatic interaction on the rheological properties of PILs is not well understood. Recently, we found that the charge underscreening effect, in which the screening length increases with the increasing ion concentration, led to expanding PIL chains at high ion concentrations in the dilute regime [2]. In this study, we investigate the effect of charge underscreening on the rheological properties of PILs in the semidilute unentangled regime by using a model system consisting of a PIL (PC$_4$-TFSI: the poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide)) in a mixture of an ionic liquid (BmimTFSI) and a non-ionic solvent (DMF). The ionic liquid BmimTFSI acts as both a solvent and a source of salt ions to regulate the electrostatic screening. We observe: i) both specific viscosity η_{sp} and relaxation time λ are initially constants at low ion concentrations c_s and then decrease with increasing c_s at an intermediate c_s. ii) both η_{sp} and λ increase with increasing c_s, similar to the trend observed in the dilute regime. This result indicates that the charge underscreening effect is still dominant in the semidilute unentangled regime. We further capture the experimental results by proposing and validating a modified scaling law accounting for the dependence of the correlation length on c_s.

[1] Dobrynin, et al., Macromolecules, 1995 [2] Matsumoto et al., Macromolecules, 2019

Wednesday 6:30 Ballroom on 4th floor PO30

Color, rheology, and microstructure of bottlebrush diblock copolymer solutions

Matthew A. Wade[1], Johnny Ching-Wei Lee[1], Elizabeth Kelley[2], Katie M. Weigandt[3], and Simon A. Rogers[1]
[1]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]NIST, Gaithersburg, MD, United States; [3]NIST Center for Neutron Research, Gaithersburg, MD 20877, United States

The formation of structure-property-processing relations is crucial to designing energy-efficient processes and defect-free products. We present the results of a comprehensive study that combines data from imaging, rheometry, and scattering techniques to holistically describe the color, rheology, and microstructure of a solution of bottlebrush diblock copolymers under steady shearing conditions. Studies were carried out on a 16.8 wt% solution of poly(norbornene-g-poly(lactic acid)$_{60}$)$_{200}$-b-poly(norbornene-g-poly(styrene)$_{45}$)$_{200}$ polymers suspended in toluene. Rheo-small angle neutron scattering (rheo-SANS) measurements were performed in the velocity-vorticity (1-3) and velocity gradient-vorticity (2-3) planes over shear rates ranging from 0 to 100 s^{-1}. The resulting scattering patterns indicate the presence of lamellar stacking along the velocity gradient direction under quiescence and low shear conditions (0.01 s^{-1}), distortions of the lamellae at intermediate shear rates, and the formation of leek-like structures along the velocity direction at high shear rates. These changes in microstructure closely mirror the striking changes in sample color with shear in which the sample appears green under quiescent and low shear conditions and transitions to teal and blue at higher shear rates. The correlation between sample color, microstructure, and rheology presented here lays the groundwork for understanding the complex interplay between structure and function that dictates the success of additive manufacturing using bottlebrush diblock copolymers.

Wednesday 6:30 Ballroom on 4th floor PO31

The time-averaged extension of a FENE dumbbell in an oscillatory planar extensional flow

Shivam Sahu and Aditya S. Khair
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Recent studies have demonstrated a non-zero time-averaged (mean) polymer extension in an oscillatory planar extension flow that has zero mean extension. Motivated by this surprising finding, we predict the non-zero mean extension of an elastic dumbbell in oscillatory, planar extension. We utilize the Warner spring (finitely extensible nonlinear elastic) force law to describe the elasticity of the dumbbell. Specifically, the end-to-end distance $\boldsymbol{R}$ of the dumbbell is described by a probability density function $\psi(t,\boldsymbol{R})$ that satisfies a conservation equation in physical space, where t is the time. We first address the weakly nonlinear flow limit $Wi << 1$, where the Weissenberg number, Wi, is the ratio of the rate of deformation to rate of relaxation of dumbbell and characterizes the strength of the flow. We derive an asymptotic expression for $\mathbf{S}=2<\boldsymbol{RR}>$, which represents the ensemble-averaged mean-squared extension of dumbbell at small Wi via a regular perturbation expansion. From this asymptotic solution, we compute the time-averaged polymer extension, which is an inherently non-linear effect arising from the non-oscillating component of $\mathbf{S}$ at $O(Wi^2)$, irrespective of flow type. Next, we seek an asymptotic solution to the constitutive model in the singular limit $Wi >> 1$, where the rate of deformation is much larger than the rate of relaxation of dumbbell, and $Wi/De >> 1$, where De is the Deborah number representing the non-dimensional frequency of oscillation of flow.

Wednesday 6:30 Ballroom on 4th floor PO32

Novel numerical simulations of the debonding process of pressure sensitive adhesives

Stylianos Varchanis, Yannis Dimakopoulos, and John Tsamopoulos
Department of Chemical Engineering, University of Patras, Patras, Achaia, Greece

Debonding mechanisms during stretching of pressure sensitive adhesives (PSAs) start from cavitation and growth of cavities, continue with fibril formation and extension, and terminate with fibril breakage [1]. How the competing viscous, viscoelastic and elastic forces determine the growth of cavities, the shape and tack properties of a stretched adhesive is predicted from the transient solution of the equations of mass and momentum conservation along with a constitutive law for an incompressible material. We use the RoliePoly [2] tube model to describe the rheological response of PSAs. The governing equations are solved numerically via a novel 3-dimensional stabilized Lagrangian FEM numerical scheme. This new algorithm accelerates dramatically the simulations because it uses linear interpolation functions for both the position vector and pressure and does not require the storage of the deformation history of the material. One of the configurations that we study, assumes the presence of a cluster of cavities with multiple moving contact lines on the bottom substrate. These are initially growing spherically, later like mushrooms and finally they are elongated axially forming fibrils or a foamy network. Their deformation and interaction are very important and affect significantly the debonding energy of the material.

[1] H. Lakrout, P. Sergot, C. Creton, J. Adhesion 69, 3-4, 307-359 (1999). [2] A. E. Likhtman, A. E., and R. S. Graham, J. Non-Newtonian Fluid Mech., 114, 1-12 (2003).

Wednesday 6:30 Ballroom on 4th floor PO33

A thermodynamic method for constitutive equation

Kwang Soo Cho

Department of Polymer Science and Engineering, Kyungpook National University, Daegu, Republic of Korea

We developed a systematic thermodynamic method for the development of constitutive equation by using the Liu procedure and a simple assumption that stress is decomposed to equilibrium and dissipative parts. We modified the Liu procedure, which is a rigorous mathematical method to determine entropy flux and entropy production rate, in order to apply it to the thermodynamic space consisting of classical state variables and internal variables. It is remarkable that the resultant constitutive equation is equivalent to that obtained from the GENERIC formalism. It is remarkable that our approach is much simpler in mathematical manipulation as well as is more intuitive in physical sense of thermodynamics than the GENERIC formalism.

Wednesday 6:30 Ballroom on 4th floor PO34

Are GNF and FENE-P models appropriate to model the flow of polymer solutions?

Indranil Saha Dalal, Raghav Kumar, and Shruti Rawat

Chemical Engineering, IIT Kanpur, Kanpur, Uttar Pradesh 208016, India

In this study, we examine the suitability and accuracy of the FENE-P and GNF (Generalized Newtonian Fluid) models for flow problems involving polymer solutions. We test the models for both external and internal flows and compare the trends with experimental observations. The FENE-P, developed decades ago by Bird and coworkers, models the polymer solution by a nonlinear spring immersed in a background Newtonian fluid. However, owing to their simplicity, the GNF models are extremely popular for CFD simulations of polymer solutions. Among these, we select the Carreau-Yasuda model, which can fit the viscosity - shear rate function for all ranges of shear rates. All studies are performed with the FENE-P and its "equivalent" GNF model i.e. with parameters tuned to match the viscosity variation with shear rate. Our results show that these equivalent models provide similar results for internal flows. However, for external flows around objects, the trends are quite different. For such flows, the results with the FENE-P qualitatively agree well with the experimental observations, while the GNF models completely fail to capture the velocity and stress fields. Our results raise serious doubts on the validity of GNF models for polymer solutions, especially for external flows.

Wednesday 6:30 Ballroom on 4th floor PO35

Molecular considerations for ductility ($T < T_g$) and drawability ($T > T_g$) of semicrystalline polymers

Masoud Razavi and Shi-Qing Wang

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

We make oversimplifications to construct a tractable molecular model for mechanics of semicrystalline polymers that takes into account of the mechanical interplay between crystalline and amorphous regions connected by tie chains. The idea can be reformulated to address the origin of yielding or breaking in semicrystalline polymers that form spherulites. Our goal is to understand the brittle failure of fully crystallized glassy polymers such as PLA and PET and whether or not various semicrystalline polymers are highly drawable above their glass transition temperatures.

Wednesday 6:30 Ballroom on 4th floor PO36

Single molecule dynamics of symmetric 3-arm star polymers in dilute solution

Shivani Falgun Patel and Charles M Schroeder

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

Branched polymers play a key role in modern technology and advanced materials. Despite their increasing importance, our current understanding of the non-equilibrium dynamic behavior of these topologically complex polymers is limited. Owing to their complex molecular architectures, these polymers exhibit rich dynamic behavior that is not fully understood at the molecular level. To address this, we study the dynamics of branched polymers with precisely controlled architectures using single-molecule fluorescence microscopy. In this work, we use a hybrid enzymatic-synthetic approach to synthesize DNA-based controlled branched polymers such as symmetric 3-arm star polymers suitable for direct visualization using single molecule techniques. These star polymers provide the perfect model architecture for studying the impact of precisely-controlled branching points along a linear backbone. We directly study the steady state and transient stretching dynamics of these polymers in planar extensional flow as a function of flow strength and compare them to the dynamics of linear polymers in ultra-dilute solutions. Interestingly, we see marked differences in the molecular individualism exhibited by star polymers during the stretching process leading to a more diverse set of transient stretching pathways compared to their linear counterparts. We also observe unequal stretching of the individual arms at steady state in extensional flow. Overall, this work aims to bridge the gap in our understanding of the molecular-scale origins of rich rheological behavior exhibited by topologically complex polymers.

Wednesday 6:30 Ballroom on 4th floor PO37

Macromolecular architecture and complex viscosity

Mona Kanso, Alan J. Giacomin, Chaimongkol Saengow, and Jourdain H. Piette
Chemical Engineering, Queen's University, Kingston, Ontario, Canada

General rigid bead-rod theory [Hassager, J Chem Phys, 60, 4001 (1974)] explains polymer viscoelasticity from macromolecular orientation. By means of general rigid bead-rod theory, we relate the complex viscosity of polymeric liquids to the architecture of axisymmetric macromolecules. In this work, we explore the zeroshear and complex viscosities of 24 different axisymmetric polymer configurations. When non-dimensionalized with the zero-shear viscosity, the complex viscosity depends on the dimensionless frequency and the sole dimensionless architectural parameter, the macromolecular lopsidedness. In this work, in this way, we compare and contrast the elastic and viscous components of the complex viscosities of macromolecular chains that are straight, branched, ringed, or star-branched. We explore the effects of branch position along a straight chain, branched-chain backbone length, branched-chain branch-functionality, branch spacing along a straight chain (including pom-poms), the number of branches along a straight chain, ringed polymer perimeter, branch-functionality in planar stars, and branch dimensionality.

Wednesday 6:30 Ballroom on 4th floor PO38

Temperature dependent stress relaxation of neutral and ionic dynamic polymers

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

Dynamic polymer networks with an associative bond exchange process, also called vitrimers, are a promising route to recyclable and self-healing materials. We have developed silicone vitrimers containing a controlled density of dynamic boronic ester bonds which can be made either neutral or ionic. These networks provide an ideal model system due to the high thermal stability, low glass transition temperature, and negligible water uptake of the silicone polymer. At room temperature, the stress relaxation of these networks is independent of the dynamic bond density, which we attribute to fast segmental dynamics and a reaction kinetic limited exchange process. Stress relaxation measurements conducted over a wide temperature range show that these materials display the Arrhenius temperature dependence expected for vitrimers, but only at high temperatures. In colder regimes, a pronounced non-Arrhenius dependence emerges regardless of the molecular weight between crosslinks. Frequency sweeps and time temperature superposition indicate that the flow is thermorheologically simple. Finally, we have studied the impact of systematically changing the dynamic bonds into an anionic form by the addition of NaOH. With increasing ionic content, the network modulus decreases while the stress relaxation time increases compared to our analogous neutral network. Additional self-healing tests demonstrated that the ionic systems also heal faster than the neutral. Our studies point to the importance of measuring vitrimer properties over a broad temperature window and understanding ionic effects in dynamic networks.

Wednesday 6:30 Ballroom on 4th floor PO39

Concentration dependence of extensional relaxation time and FENE constant in aqueous PEO solutions using a microfluidic rheometer

Seo Gyun Kim and Heon Sang Lee
Chemical Engineering, Dong-A University, Busan, Republic of Korea

The measurement techniques based on capillary-thinning such as capillary breakup extensional rheometer (CaBER) and dripping onto substrate (DoS) rheometry are available for the measurement of the short extensional relaxation time below 1 ms. Both CaBER and DoS have a merit in their simplicity, since just one drop of solution is required for the measurement. However, they have weak points that measurable range of extension rate in a single concentration of solution is limited, and the time to maintain the constant extension rate is too short to reach the steady-state. In our previous works, we proposed a differential pressure extensional rheometer (DPER) that would maintain a constant extension rate for a long time. We also suggested a method extracting the steady-state extensional viscosity, relaxation time distribution, and finite extensible non-linear elastic (FENE) constant (b) for a semi-dilute PEO solution using the DPER. In this study, we present the concentration dependence of the extensional relaxation time and b for dilute and semi-dilute PEO solutions. The linear average of extensional relaxation time distribution is consistent with that reported by CaBER or DoS rheometry. The b in the semi-dilute regime is about 10.3 times greater than that in the dilute regime. The b has the same value in the semi-dilute unentangled PEO solutions.

Wednesday 6:30 Ballroom on 4th floor PO40

Thermally activated slide-ring networks

Karan V. Dikshit[1] and Carson J. Bruns[2]
[1]Materials Science and Engineering, University of Colorado Boulder, Boulder, CO 80309, United States; [2]Mechanical Engineering, University of Colorado Boulder, Boulder, CO 80309, United States

This work explores the viscoelastic properties of thermoresponsive slide-ring gels. These gels are made from polyrotaxanes (PRs), which are mechanically interlocked molecules (MIMs) of a polymer and macrocycles. Synthesis of slide ring gels was inspired by a 1999 paper by Pierre Gilles de Gennes. He proposed the existence of sliding gels - multiple ionic polymers held together by a central cationic molecule. Simplification of this idea led to the concept of slidable cross-links threaded on a polymer chain. Soon after de Gennes' paper, the polyrotaxane community synthesized the first ever slide-ring hydrogel, known then as a topological gel. Literature shows these gels possess a characteristic low modulus and high swelling ratio. We demonstrate thermal actuation of these materials by chemically modifying the rings. The modification yields a thermoresponsive hydrogel, which could potentially be used in a range of applications including drug delivery and tissue engineering.

Wednesday 6:30 Ballroom on 4th floor PO41

Linear rheology of an associative covalent adaptable network

Bassil El-Zaatari and Julia Kalow
Department of Chemistry, Northwestern University, Evanston, IL 60208, United States

Vitrimers are an emerging class of thermosetting polymers containing dynamic covalent bonds that undergo associative exchange processes. Under elevated temperatures, these bonds can rearrange, modifying the topology of the material without changing the crosslink density. These materials, while covalently crosslinked, can act as viscoelastic fluids at higher temperatures, enabling characteristics such as recyclability and self-healing. The relationship between molecular exchange chemistry and network properties remains poorly defined. By taking advantage of conjugate addition-elimination reactions of thiols with various crosslinkers at the molecular and polymer level, we aim to understand how the molecular exchange kinetics affect both vitrimer kinetics stress relaxation and bulk properties. We show that these materials can be modeled using an ideal Maxwell model at long timescales. Finally, we examine if and when vitrimers are thermo-rheologically simple materials through applying time-temperature superpositions.

Wednesday 6:30 Ballroom on 4th floor PO42

The molecular origins of viscosity in the liquid state and Thomas Kuhn

Thomas W. Theyson
TensTech Inc, Matthews, NC 28105, United States

The author has, over the last 30+ years, accumulated a large data base covering the viscosity of low to intermediate molecular weight lubricant materials. This presentation will review the normal rheological behavior associated with these materials along with the intermolecular forces that have been traditionally viewed as being responsible for the viscosity in the liquid state. However, the presentation will concentrate on examples of what appears to be unexplained rheological phenomena: inflection points in viscosity-molecular weight curves and viscosity outliers. In the latter area, examples will be presented where the viscosity is >10-fold higher than or <1/10th of the "normal value" predicted based on the viscosity-molecular weight curves for standard lubricant materials. The literature provides only limited guidance on these issues and where there are attempts to explain the observed differences, they generally revert to correlative physical properties rather than providing an explanation based on fundamental molecular interaction forces. This makes us wonder if we really do understand the nature of the intermolecular forces that generate viscosity in the low to intermediate molecular weight, organic liquids and the impact this might have on our broader understanding of rheology. Finally, we discuss possible intermolecular interactions that might provide the basis for explaining some of these observed phenomena and then touch briefly on Thomas Kuhn's premise: that it is in struggling with anomalous data that a science advances its understanding of the paradigm within which the practice of "normal science" is carried out.

Wednesday 6:30 Ballroom on 4th floor PO43

Extensional rheology of aqueous polymer solutions in filament thinning and microfluidic contraction flows

Athena E. Metaxas[1] and Cari S. Dutcher[2]
[1]Chemical Engineering and Materials Science, University of Minnesota-Twin Cities, Minneapolis, MN 55455, United States;
[2]Mechanical Engineering, University of Minnesota-Twin Cities, Minneapolis, MN, MN 55455, United States

Methylcellulose (MC), a methoxy- substituted cellulose ether, is used in a variety of food, pharmaceutical, construction, and consumer applications due to its solubility in water at low temperatures. In addition to its solubility at low temperatures, MC reversibly transitions to a turbid hydrogel upon heating or upon the addition of NaCl to the solution. The gelation phenomenon in aqueous MC solutions is due to the formation of a fibrillar network. While the small amplitude oscillatory and large amplitude oscillatory shear rheological behavior has been characterized for MC solutions, the extensional flow behavior has not been reported. Capillary breakup extensional rheometry (CaBER) can be used to characterize larger molecular weight MC solutions. For MC solutions with lower molecular weights, and therefore lower viscosities, CaBER cannot successfully resolve extensional properties such as the extensional relaxation time and extensional viscosity. Filament stretching using a cross-slot microfluidic channel is a promising method to resolve extensional properties of MC solutions at varying NaCl concentrations. The elastocapillary regime, which determines the extensional relaxation time and viscosity, emerges with the presence of NaCl. This behavior is attributed to the presence of fibrils in the MC solutions containing NaCl annealed at room temperature. The study of the extensional behavior of this already commercially relevant polymer enables new ways to process MC, such as fiber spinning and extrusion.

Wednesday 6:30 Ballroom on 4th floor PO44

Rheological and optical properties of photocurable organic coatings for outgas-free flexible display

So Hyun Kim, Junki Oh, Kevin I. Jung, Joona Bang, and Hyun Wook Jung
Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea

Organic light emitting diode (OLED), which is a core part of flexible displays, is protected by inner layers due to its weakness to moisture and oxygen. Organic and inorganic layers are alternatively stacked using thin film encapsulation (TFE) technology. In contrast to the case of inorganic

layers, various properties and photo-curing features of organic layers have not been extensively studied, although organic layers play a key role in effectively preventing outgas problem. For the outgas-free layer, the remaining unreacted monomers in the cured organic layer should be reduced by optimally tuning the crosslinking density during the photo-curing process. In this study, we have developed a new initiator system, based on 2-isopropyl thioxanthone, to minimize outgas emission and form high crosslinking density in the organic layer. Basic rheological properties and surface tension of curable coatings were measured to understand the applicability on the inkjet process. To monitor temporal evolution of crosslinking density during photo-curing operation, real-time rheological behavior of various initiators was investigated using a rotational rheometer equipped with UV device. Also, the optical properties such as transmittance and refractive index, and outgas amount of the cured organic film were analyzed for the applicability to flexible display fields. Finally, the optimal UV curing conditions for producing organic layers were established by correlating real-time curing dynamics and post-cured film properties.

Wednesday 6:30 Ballroom on 4th floor PO45

Role of polymer physics on the formation of "beads on a string"

Dylan R. Chase and Michael Cromer
School Of Mathematical Sciences, Rochester Institute Of Technology, Rochester, NY, United States

When a viscoelastic material is stretched between two surfaces, the interaction between elastic and capillary stresses leads to the formation of a "beads-on-a-string" structure where between drops, thin and stable filaments form. Under certain conditions, small "satellite" drops can form between the main droplets. In application, such as in inkjet printing, the emergence of these satellite drops are cause for concern, thus it becomes important to understand what properties lead to their formation. In this work we consider the capillary thinning of polymer solutions via a thin film approximation and implementing various constitutive models. The non-linear system of partial differential equations is solved numerically using a unique numerical solver, in particular, the use of a weighted upwind discretization scheme on the convective terms. The scheme is weighted locally via the velocity: in regions of slow flow, a central differencing is used, however, as the velocity increases, the weighting moves closer to a pure upwind differencing. Using a fully implicit time-stepping scheme, the method is highly stable, allowing large time steps and (relatively) fast simulation times. Using this method, we investigate the effects that certain polymer properties have on drop formation. In particular, we consider several polymer models (e.g., FENE-P, Giesekus, Rolie-Poly) to determine the roles played by polymer stretch, anisotropic drag, entanglement, and convective constraint release. All of these unique properties are examined while also testing the effects of changing different fluid properties, such as the Deborah number, Ohnesorge number, and viscosity ratio. Phase diagrams reveal specific values for which satellite droplets form regarding these physical properties.

Wednesday 6:30 Ballroom on 4th floor PO46

Facing the facts: A look at the Society of Rheology's history

Megan S. Anderson[1] and Gareth H. McKinley[2]
[1]American Institute of Physics, College Park, MD, United States; [2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

From the creation of plastics to the Digital Revolution, the past century of scientific discovery has impacted society in profound ways. This history is crucial to understanding and appreciating the current state of the physical sciences, and a significant portion of it is preserved through the American Institute of Physics (AIP) and the AIP member societies. My work this past summer focused on preserving the history of the Society of Rheology through biographies on Bingham Medalists. I researched and wrote forty of these biographies, gaining insight on the individuals who have shaped the rheology community. By documenting the faces behind scientific facts, we can better appreciate our past and look forward to the future.

Wednesday 6:30 Ballroom on 4th floor PO47

MEEPT: A flowable redox-active organic with a charged state that remains flowable at concentrations of at least 0.5 M

Yilin Wang[1], Malsha T. Suduwella[2], Zhou Yu[3], Lei Cheng[3], Lu Zhang[3], Susan A. Odom[2], and Randy H. Ewoldt[1]
[1]Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Department of Chemistry, University of Kentucky, Lexington, KY, United States; [3]Argonne National Laboratory, Lemont, IL, United States

We report viscous flow properties of N-[2-(2-methoxyethoxy)ethyl]phenothiazine (MEEPT), a new redox active molecule (ROM), with molecular weight 388.2 g mol^{-1}, that has been evaluated as an active charge-storage material in redox flow batteries for electrochemical energy storage systems. To study a broad spectrum of concentrations without requiring significant amounts of sample, we employed a microfluidic viscometer (Rheosense mVROC). Using this technique, we measured the viscosity of both the pure liquid state and variably concentrated solutions of neutral (MEEPT) state, and measured variably concentrated solutions of the charged cation state (MEEPT-BF_4) - a solid material - both in the non-aqueous solvent acetonitrile at concentrations up to 0.5 M. Experiments confirm that the pure MEEPT substance is flowable, but with a large Newtonian viscosity (412 mPa s^{-1} at room temperature), a value approximately 1,000x larger than acetonitrile. By contrast, MEEPT / acetonitrile solutions have significantly lower viscosities. At concentrations up to 0.5 M, the viscosity increased by less than a factor of two compared to the solvent. It is notable that higher-order concentration effects are generally negligible and there is no sharp increase in viscosity up to 0.5 M for all ROM systems, including acetonitrile solutions containing both uncharged and charged forms of this ROM, as well as solutions containing supporting salts at concentrations of 0.5 M - in this case LiTFSI or TEABF_4. Here the viscosity versus concentration exhibited a nearly linear trend, which was used to determine intrinsic viscosity and molecular hydrodynamic diameter. The hydrodynamic diameter ranges from 9.4 - 11.6

Å, with the diameter of the neutral ROM being smaller than the charged form. Inclusion of supporting salt does not significantly change the hydrodynamic diameter. Further, for all compositions studied here, we observed the Newtonian constant viscosity over shear rate 5000 to 30000 s^{-1}.

Wednesday 6:30 Ballroom on 4th floor PO48

Viscoelastic identification of PLA/PBAT blends by use of relaxation time spectrum

Hyunkyu Jang and Kwang Soo Cho
Department of Polymer Science and Engineering, Kyungpook National University, Daegu, Republic of Korea

Since polylactic acid (PLA) and polybutylene adipate-co-terephtalate (PBAT) are well-known biodegradable polymers, it is important to understand linear viscoelasticity of their blends. For this purpose, we applied fixed point iteration method to the calculation of the relaxation spectra of the blends at various PLA contents. The weighted relaxation spectra of the blends clearly indicate the structural changes due to PLA contents. We compared the spectra with the corresponding TEM images.

Wednesday 6:30 Ballroom on 4th floor PO49

Modeling flow effects on polymer crystallization

Jiho Seo[1], Anne Gohn[2], Alicyn Rhoades[2], Richard Schaake[3], and Ralph Colby[1]
[1]Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, United States; [2]School of Engineering, Penn State Behrend, Erie, PA 16563, United States; [3]Engineering and Research Centre, SKF, Nieuwegein, The Netherlands

When a semicrystalline polymer melt is subjected to intense shear flow before crystallization, the crystallization rate is accelerated, referred to as flow-induced crystallization (FIC). In this study, the FIC behaviors are investigated with commercial poly(ether ether ketone) under well-defined shearing conditions using a rotational rheometer. With the FIC kinetics, a flow-induced nucleation model is suggested based on Flory's entropy reduction model and the isothermal nucleation model of Hoffman and Lauritzen. The flow-induced nucleation model agrees relatively well with the rheological data demonstrating good trends for the influence of specific work. These results imply that only ~1% of mechanical energy is contributed to reducing the entropy-relevant free energy due to the dominance of friction and relaxation effects. Aside from the specific work, this model introduces the idea of a critical nucleation volume that is similar in size to the volume of a Kuhn monomer.

Wednesday 6:30 Ballroom on 4th floor PO50

Rheological response of polyelectrolyte complexes under the effect of salt and temperature

Siqi Meng, Jeffery M. Ting, Hao Wu, and Matthew V. Tirrell
Pritzker School of Molecular Engineering, The University of Chicago, Chicago, IL 60637, United States

When oppositely charged polyelectrolytes mix together in water, they tend to phase separate into a polymer-poor supernatant phase and a polymer-rich phase known as polyelectrolyte complexes (PECs), driven by the electrostatic attraction and the entropy gain from the release of counterions. Depending on the balance of water, polymer, and solution salinity, the physical states of PECs can span from glass-like solids to low viscosity liquids. Multiple studies have demonstrated that the transition between these two states can be readily achieved through changing the salt concentration and temperature condition. However, how the dynamics of PECs evolve during this process have been rarely studied. To fill this gap, we herein investigate the rheological response of PECs under different salt and temperature condition. We first employed aqueous reversible addition-fragmentation chain transfer (RAFT) polymerization technique to develop a model PEC system, whose morphology would shift from glassy solid-like state to viscoelastic liquids by fine-tuning the solution salt concentration. Next, we conducted oscillatory shear measurements and steady-state flow sweep measurements to examine the linear viscoelastic response and chain relaxation behaviors under the effect of salt and temperature. These findings reveal how PECs change between different states, thereby enhancing our capabilities in predicting and controlling the properties of this intriguing polymeric material.

Wednesday 6:30 Ballroom on 4th floor PO51

Mechanisms of wax deposition: Rheological study of different thermal and flow histories

Conor Harris and Ronald G. Larson
Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

Wax deposition occurs in a waxy crude oil due to wax crystals precipitating in solution after a waxy oil mixture has fallen below its relative wax appearance temperature T_{wat}. The gel structure introduces complex rheological behavior, such as a yield stress, that is dependent on the thermal and flow history during cooling. A current development of heat and mass transfer model of wax deposition for pipeline flow assurance has been proposed by Luqman et. al [Luqman Hakim Ahmad Mahir, T. K. H. S. F., Vilas Bôas Fávero; Larson, R. G. Mechanism of Wax Deposition on Cold Surfaces: Gelation and Deposit Aging (To be published). 2018]. Currently, the model lacks a phenomenological approach to quantify the amount of precipitated wax C_{pi} that occurs at the front of a growing wax oil gel, which is dependent on the yield stress σ. Yield stress values for a n-paraffin wax in oil mixture are investigated as a function of different cooling rates and flow histories. We present two yield stress measurements, a stress ramp and an amplitude sweep. For stress ramp measurements, we consider a temperature sweep under constant stress, $\sigma = 1$ Pa, with varying cooling rates $\dot{T} \in \{0.3,0.4,0.5,0.6,0.7\}$ ° C min^{-1} from a temperature above the T_{wat} to one final temperature, $T_f = 20$ ° C. The oscillatory measurements are completed under the same thermal histories while under a constant strain, $\gamma = 1\%$. Results indicate that for steady shear flow conditions, σ_y increases as a function of both wait time t_w and cooling rate $\dot{T}$. Oscillatory measurements show an opposite trend as σ_y

decreased with decreasing cooling rate $\dot{T}$, indicating that during cooling, the strain γ exhibited on the waxy oil disrupts the crystallization process. The results from this study reveals a complex crystallization process within waxy oil systems that is dependent on the combination of both thermal and flow histories.

Wednesday 6:30 Ballroom on 4th floor PO52

Stratification in foam films made with polymer-surfactant complexes

Chenxian Xu, Carina Martinez, Patrycja Kotwis, Chrystian Ochoa, and Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States

Ultrathin freestanding films exhibit stratification due to confinement-induced structuring and layering of small molecules in simple fluids, and of supramolecular structures like micelles, lipid layers and nanoparticles in complex fluids. Stratification proceeds by the formation and growth of thinner domains at the expense of surrounding thicker film, and results in formation of nanoscopic terraces and mesas within a film. Thickness variations in stratifying films can be visualized and analyzed with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms) using interferometry, digital imaging and optical microscopy (IDIOM) protocols we developed recently. We have shown before that topographical changes including nanoridge & mesa growth, and the overall stratification dynamics in micellar foam films, can be described quantitatively by nonlinear thin film equation, amended with supramolecular oscillatory surface forces. In this contribution, we utilize IDIOM protocols to characterize and analyze the influence of a neutral water-soluble polymer on step-wise thinning, domain expansion dynamics and nanoscopic topography of stratifying thin films. The complex interplay of capillarity, disjoining pressure and viscoelasticity leads to fascinating drainage kinetics, and requires consideration of structure and rheology of polymer-surfactant complexes.

Wednesday 6:30 Ballroom on 4th floor PO53

Shear-induced microstructure and mechanical characterization of composite organocolloid-hydrogels

Lauren Kass, E. Daniel Cárdenas-Vásquez, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Thermoresponsive nanoemulsions that contain a bridging polymer are known to self-assemble into colloidal gel structures above the critical gel temperature. We incorporate thermoresponsive nanoemulsions into composite single (SN) and double network (DN) hydrogels by using ultraviolet (UV) light to photopolymerize the liquid precursor. The oil-in-water nanoemulsions consist of fluorescently dyed poly(dimethyl siloxane) (PDMS) droplets suspended in a continuous phase of poly(ethylene glycol) diacrylate (PEGDA) as the crosslinker and first network, and sodium alginate as the second hydrogel network. Steady shear experiments of the precursor show a shear thinning behavior at temperatures higher than the gel point, and temperature ramp rheology of the precursors shows that the gelation temperatures are T_{gel} = 29 and 33 ºC for SN and DN hydrogels, respectively. The characteristic length scales of the colloidal microstructure are quantified using confocal microscopy and cryo-SEM. The results show that local gradients in shear rates could be used to deliberately introduce microstructural variations in the manufacturing of composite soft materials, with applications such as hydrogel membranes and microfluidic platforms. Additionally, we perform tensile mechanical measurements, which show that the incorporation of a second hydrogel network in the system increases the rupture stress, fracture energy and Young's modulus in DN hydrogels when compared to SN hydrogels.

Wednesday 6:30 Ballroom on 4th floor PO54

Wormlike micellar gels: Linear and nonlinear rheology

Ronak Gupta, Rodrigo S. Mitishita, Gwynn J. Elfring, and Ian Frigaard
Mechanical Engineering, University of British Columbia, Vancouver, British Columbia V6T1Z4, Canada

Long chained zwitterionic surfactants are extensively used in the oil industry for fracturing and gravel packing operations. These materials display characteristics favourable for gravel suspension, and enable turbulent drag reduction due to their viscoelasticity (Goyal et al., 2017). In this study, we characterize a commercial surfactant for gravel packing by carrying out linear and non-linear rheology experiments. We show that the surfactant+water system exhibits gel-like behaviour at room temperature, similar to the surfactant studied in (Kumar et al., 2007). It undergoes a gel-sol transition with increase in temperature. The results also quantify how the relaxation time of the solution and elastic modulus of the gel state depend on surfactant concentration and temperature. Further, we investigate the yielding characteristics of such micellar gels using creep and amplitude sweeps, and study the phenomenon of shear driven fluidization to better quantify the solid-liquid and yielding transitions in wormlike micellar gels.

Goyal, Gaurav, Elfring, Gwynn J & Frigaard, Ian A 2017 Rheology and flow studies of drag-reducing gravel packing fluids. Rheologica Acta 56 (11), 905-914.
Kumar, Rakesh, Kalur, Gokul C, Ziserman, Lior, Danino, Dganit & Raghavan, Srinivasa R 2007 Wormlike micelles of a c22-tailed zwitterionic betaine surfactant: from viscoelastic solutions to elastic gels. Langmuir 23 (26), 12849-12856.

Wednesday 6:30 Ballroom on 4th floor PO55

Engineered transparent emulsion to optically study the flow in yield stress fluid suspensions

Ahmadreza Rashedi[1], Guillaume Ovarlez[2], and Sarah Hormozi[3]
[1]Mechanical engineering, Ohio University & Universite de Bordeaux, Athens, OH 45701, United States; [2]Physical Chemistry, Universite de Bordeaux, Pessac, Bordeaux 33600, France; [3]Ohio University, Athens, OH 45701, United States

We have engineered a model suspension consisting of rigid particles and yield stress fluids. The suspending fluid is an emulsion with adjustable density, rheological behavior, and refractive index. We explain the design procedure in detail. The optically transparent emulsion opens the possibility of exploring Particle Tracking/Image Velocimetry (PIV/PTV) techniques in studying dynamic flows involving particles in complex fluids. As a proof of concept, we have performed PTV to provide accurate measurements of solid volume fractions for the dispersion of particles in a Taylor-Couette cell.

Wednesday 6:30 Ballroom on 4th floor PO56

Rheology of THF hydrate slurries at high pressure

Paulo R. de Souza Mendes, Mônica F. Naccache, and Paulo H. de Lima Silva
Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22451900, Brazil

One of the main issues in the area of drilling and production in deep and ultra-deep water in the oil industry is the formation of natural gas hydrates. Hydrates are crystalline structures resembling ice, which are usually formed in conditions of high pressure and low temperature. Once these structures are formed, they usually agglomerate and form plugs that completely block the production line, causing huge financial losses. This work analyzes the rheological behavior of hydrate slurries formed by a mixture of water and tetrahydrofuran (THF, C4H20) under high pressure and low temperature conditions, similar to the ones found in deep water oil exploration. The THF hydrates form structures similar to the ones found in the hydrates formed in the water-in-petroleum emulsions in the presence of natural gas at extreme conditions of high pressure and low temperature. The research revealed important issues that need to be taken into account in rheological measurements. Flow-curve and oscillatory tests have been performed at different pressures, temperatures and THF concentrations. Among other findings, the results obtained show that the hydrate slurry viscosity, yield stress and elasticity increase with pressure.

Wednesday 6:30 Ballroom on 4th floor PO57

Foam films and liquid bridges formed by aqueous sodium naphthenate solutions

Chrystian Ochoa[1], Shang Gao[2], Jelena Dinic[3], Samanvaya Srivastava[2], and Vivek Sharma[1]
[1]Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States; [2]Chemical Engineering, University of California at Los Angeles, Los Angeles, CA, United States; [3]Institute for Molecular Engineering, University of Chicago, Chicago, IL, United States

Sodium Naphthenates found in crude oils can act as surfactants and self-assemble in aqueous solutions to form micelles and liquid crystals. Understanding and controlling the drainage kinetics of thin films is an important problem that underlies the stability, lifetime and rheology of petroleum foams and emulsions. Here, we show that foam films formed by aqueous solutions of sodium naphthenates exhibit step-wise thinning or stratification. We utilize Interferometry, Digital, Imaging, Optical Microscopy protocols, previously developed by our group, to investigate the drainage and stratification in micellar foam films (< 100 nm) with high spatial (thickness < 10 nm) and temporal resolution (< 1 ms). We determine how the concentration of added sodium naphthenates influences the nanoscopic topography, stratification kinetics and step size of foam films. Finally, we show that visualization and analysis of capillary-driven thinning and pinch-off dynamics of the columnar neck in an asymmetric liquid bridge created by dripping-onto-substrate (DoS) of sodium naphthenate solutions can be used for characterizing the change in shear viscosity, extensional viscosity and microstructure in such surfactant solutions.

Wednesday 6:30 Ballroom on 4th floor PO58

Rheology of concentrated emulsions with adhesive and repulsive droplets

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

High internal phase emulsions (HIPEs) can be produced when the volume fraction of the dispersed droplets is higher than 74%. HIPEs can be used as a template to synthesize porous materials, known as polymerized high internal phase emulsions (polyHIPEs). The adhesive and non-adhesive concentrated emulsions have different rheological behaviors due to differences in the interdroplet interaction. However, the effects of droplet size on the rheological properties of attractive and repulsive emulsions have not been compared and discussed in the literature. Therefore, in the present work, we investigate the yield stress, dynamic moduli, and shear thinning of the attractive and repulsive HIPE systems with different droplet sizes. In addition, the degree of adhesiveness/repulsiveness of droplets obtained from the morphology of the HIPEs and the resulting polyHIPEs are studied for the rheological analysis.

Wednesday 6:30 Ballroom on 4th floor PO59

Destabilizing emulsions to enable oil removal processes

Eduard Caicedo-Casso[1], Cole Davis[1], Seth Lindberg[2], Patrick Stenger[2], John Howarter[1], Carlos Martinez[1], and Kendra Erk[1]
[1]School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States; [2]Corporate Engineering, The Procter & Gamble Company, West Chester, OH 45069, United States

Marine vessels routinely collect considerable amounts of soiled wash water known as bilge water. Strict environmental regulations forbid vessels from discharging the bilge water into the ocean without first reducing the level of oil to less than 15 ppm. Currently, emulsified oils and suspended solid particles are removed using water filtration treatment techniques; these processes are costly to operate, so there is a great motivation to innovate new ways to remain compliant. Researchers at Purdue University and the Procter and Gamble Company have partnered to provide science-driven strategies to treat bilge water. This partnership focus on experimentally determine the impacts of surfactant chemistry and mechanical processing on the formation and instability of oil-in-water emulsions. Destabilizing the emulsion will be critical to enable traditional filtration processes. This poster presents the rheological and physical characterization of model oil-in-water emulsions that represent bilge water formulas. These emulsions are based on ingredients present in shipboard operations: sodium laureth sulfate (SLES), alcohol ethoxylates (AEs), sodium chloride (NaCl), calcium chloride (CaCl2), silica nanoparticles (SiO2), iron oxide (Fe3O4), and heavy mineral oils. Surface tension, creaming rate, dynamic aging and emulsion stability data show the dominant contribution of anionic surfactants (SLES) over other contaminants. These results, coupled with the energy input imparted to emulsions, will be used to better predict emulsion stability and guide the development of affordable bilge water treatment options.

Wednesday 6:30 Ballroom on 4th floor PO60

Particle image velocimetry for evaluating the flow profiles of thermoresponsive nanoemulsions

Kristine M. Smith, E. Daniel Cárdenas-Vásquez, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

High shear processing of colloidal nanoemulsions are commonly encountered in instances of fiber spinning, 3D printing and vial filling. When an attractive interaction is present between the colloidal nanodroplets at elevated temperatures, a gel network forms. An imposed shear flow on the gelled networks result in the development of structural heterogeneity that correlates with the overall applied shear rate. In order to quantify the influence of shear on the shear-induced structures, we report velocity profiles of thermoresponsive nanoemulsions through glass capillaries using particle image velocimetry. Fluorescent microbeads are imaged with a high-speed confocal microscope to map the impact of local shear rates on colloidal gel microstructures. This velocity profile will be compared to a theoretically-derived velocity profile computed from the Navier-Stokes equations and the Herschel-Bulkley fluid model. We find that the experimental velocity profile reveals instances of wall slip and shear banding which are not captured in the theoretical velocity profile.

Wednesday 6:30 Ballroom on 4th floor PO61

Foamability of aqueous solutions of charged surfactants and of surfactant-polymer mixtures

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

Dynamic adsorption of a freshly created interface is intimately linked with the rate of mass transfer of surfactant from liquid sub-phase to the interface, and this adsorption-limited kinetics is said to impact the stability of the newly formed interface. Addition of polymer to a surfactant solution affects the dynamic adsorption and the rheological response due to the formation of association complexes. Dynamic surface tension refers to the time dependent variation in surface tension, which is related with the rate of mass transfer of a surfactant from liquid sub-phase to the interface. Dynamic surface tension measurements carried out with conventional methods like pendant drop analysis, Wilhelmy plate, etc. are limited in their temporal resolution. In this study, we apply the method of maximum bubble pressure tensiometry for the measurement of dynamic surface tension effects at extremely short (1-50 ms) timescales. We discuss the overall adsorption kinetics of charged surfactants and the influence of added polymer on dynamic surface tension. Finally, we examine how pinch-off dynamics and rheological properties are modified in the presence of added polymers by including a critical examination of shear and extensional rheological responses.

Wednesday 6:30 Ballroom on 4th floor PO62

Rheology of concentrated nanoemulsions with different volume fractions

Hamed Salimi-Kenari, Zahra Abbasian Chaleshtari, and Reza Foudazi
Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States

The aim of this work is to evaluate the colloidal gelation of silicone oil in aqueous solutions containing sodium dodecyl sulfate (SDS) and poly(ethylene glycol)-diacrylate (PEGDA). Therefore, we investigate the rheological response of the nanoemulsions with different volume fraction by using simple and oscillatory shear flows. It is observed that the liquid nanoemulsions transformed into viscoelastic gels at 25% of oil volume fraction, ?. The apparent viscosity, yield stress, and storage modulus of the nanogels increase with oil volume fraction up to 45% of oil volume fraction. The storage modulus rapidly increases at the onset of gelation, followed by a gradual increase at higher ?. Weakening in gelation due to oscillatory structural forces takes place at volume fraction higher than 45%. The structural forces are present due to the layered-structuring of excess micelles in the interdroplet regions resulting in loss of droplet aggregation. The nanoemulsion gels developed could be used in low-fat foods, pharmaceuticals, and cosmetics products.

Wednesday 6:30 Ballroom on 4th floor PO63

Rheology of nanofluids used in solar collectors

Ovais Gulzar[1], Adnan Qayoum[2], and Rajat Gupta[3]
[1]Department of Mechanical Engineering, Islamic University of Science & Technology, Awantipora Kashmir, Jammu and Kashmir 192122, India; [2]Mechanical Engineering Department, National Institute of Technology Srinagar, srinagar, Jammu and Kashmir 190006, India; [3]Mechanical Engineering Department, National Institute of Technology Mizoram, Aizwal, Mizoram 796012, India

Nanofluids are engineered suspensions of nano-sized particles with improved thermo-physical properties. These have been widely researched for various engineering applications. The use of nanofluids in solar collectors has been advantageous in terms of efficiency and cost. The addition of nanoparticles(NP's) to a base thermal fluid improves its thermophysical properties such as thermal conductivity, viscosity, etc. However, an increase in viscosity is not desirable as it increases the pumping power and pressure drop across the collector tubes. As nanofluid flows in a solar collector, its rheological behavior plays a vital role in overall performance of the solar collector. The current study investigates the rheological behaviour of therminol-55 doped with alumina and titania NP's, and their hybrid combinations for use in solar collectors. The rheological behavior is studied using parallel plate geometry for a range of temperature and frequency. The role of NP concentration on viscosity and flow behavior is investigated. These nanofluids show newtonian as well as non-newtonian behavior, depending upon frequency and temperature. It was found that viscosity of nanofluid decreases with the increase in temperature and it increases with increase in nanoparticle concentration. However, at higher temperatures the effect of concentration is minimal which is well accounted to weakening of cohesive forces between the NP's and base fluid leading to decrease in viscosity. Increase in temperature also leads to decrease in resistance and Van der waals force between different layers which causes a decrease in viscosity. The results show that nanoparticle concentration plays an important in rheological behavior of nanofluids, and its effect is governed by temperature and pumping rate of the solar collector. The study also proposes optimal combination of NP's to obtain desired rheology for efficient use of nanofluids in solar collectors. It is aimed to improve operating efficiency and cost-effectiveness of solar thermal plants

Wednesday 6:30 Ballroom on 4th floor PO65

Dynamics of a single-grain intruder driven through a granular medium

Ryan Kozlowski[1], C M. Carlevaro[2], Karen E. Daniels[3], Lou Kondic[4], Luis A. Pugnaloni[5], Joshua E. S. Socolar[1], Hu Zheng[6], and Robert P. Behringer[1]
[1]Physics Department, Duke University, Durham, NC 27710, United States; [2]Instituto de Fisica de Liquidos y Sistemas Biologicos, CONICET, La Plata, Argentina; [3]Physics, North Carolina State University, Raleigh, NC 27607, United States; [4]Mathematical Sciences, New Jersey Institute of Technology, Newark, NJ 07102, United States; [5]Departamento de Fisica, Universidad Nacional de La Pampa, Santa Rosa, La Pampa, Argentina; [6]Geotechnical Engineering, Tongji University, Shanghai, China

A key question in granular materials is how a granular medium responds to local perturbations from a driven single-grain intruder as opposed to large intruding rods, sliders, or moving boundaries. Here we experimentally investigate the dynamics of a grain-scale intruder driven by a spring through an annular channel of photoelastic disks. We vary the grain packing fraction, interparticle friction, and basal friction between grains and the table surface; we observe dynamical regimes of either stick-slip or intermittent flow. In the former, the intruder gets stuck when grains form a stable network, the force on the intruder increases due to the driving spring, and the granular structure yields when a certain force threshold is reached, allowing the intruder to slip through the grains until a stable network quickly forms again. In the latter, the intruder flows through the medium with only occasional stick events, reminiscent of clogging-flowing dynamics. For cases with basal friction we observe a smooth transition from intermittent flow to stick-slip as packing fraction increases, and increasing interparticle friction decreases the threshold packing fraction region. Without basal friction, we only observe intermittent flow. DEM simulations of the system exhibit the same dynamical behaviors and are used to further explore the effects of basal friction on the single-grain intruder dynamics.

Wednesday 6:30 Ballroom on 4th floor PO66

Characterizing the rheological properties for both polydisperse and monodisperse colloidal rod systems

Shiqin He[1], Seth Lindberg[2], and Kelly M. Schultz[1]
[1]Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; [2]Corporate Engineering, The Procter & Gamble Company, West Chester, OH 45069, United States

Colloidal rod systems are used as rheological modifiers to tune the rheology of products. These materials can have monodisperse or polydisperse size distributions, which can have significant impact on its rheological behavior. This work compares and quantifies the change in rheological properties during sol-gel transitions for polydisperse, hydrogenated castor oil (HCO), and monodisperse, polyamide (PA), colloidal rod systems. Non-adsorbing polyethylene oxide (PEO) induces depletion interactions to drive gelation. Multiple particle tracking microrheology (MPT) and bulk rheology are used to characterize gelation of PA and HCO. In MPT, fluorescent probe particles are embedded in the sample and their Brownian motion is measured and related to rheological properties. We measure these systems by changing the concentration of PEO, the colloid and the stabilizing surfactant, linear alkylbenzene sulfonate (LAS). We first increase the concentration of PEO from 0.14 to 0.75 c/c* (c is the PEO concentration and c* is the PEO overlap concentration) at a fixed colloid and LAS concentration for both PA and HCO. From microrheological measurements, both materials gel with increasing PEO concentration. The same samples measured with bulk rheology do not measure these phase transitions because they are below the measurable moduli limit. Conversely, the elastic moduli for both HCO and PA increase with increasing colloid concentration, but this is not measured with MPT. These measurements highlight that using MPT and bulk rheology together lead to increased information about a system. Finally, we measure for HCO as we increase LAS concentration (0.8-3.2 wt%) the colloids

become destabilized and gel. However, at high LAS concentration (6.4-12.8 wt%) the surfactant stabilizes the suspension and inhibits gelation. This work provides a road map for the design of products by providing the compositional-dependent rheology over a large parameter space, thereby eliminating trial-and-error steps to achieve desired material properties.

Wednesday 6:30 Ballroom on 4th floor PO67

Rheological properties of self-assembled networks of nanoclay and wormlike micelles

Vyacheslav S. Molchanov, Marina A. Efremova, Tatiana Y. Kiseleva, and Olga E. Philippova
Physics, Moscow State University, Moscow, Russia

Soft nanocomposite hydrogels can be based either on polymer network or on self-assembled network of wormlike surfactant micelles (WLMs). To provide additional functionality to the matrix the hydrogels can contain delivery vehicle components, for instance, nanoclay tactoids, which make them very promising for drug delivery and tissue engineering applications. Injectable systems represent an evergrowing class of nanomaterials possessing a unique combination of physical and chemical properties. Such hydrogels can be used as control delivery systems, since they can be delivered in a minimally invasive manner, because their final form and shape are defined by the space, into which they are injected. The influence of organoclay on the mechanical properties of mixed WLMs of surfactants was studied by rheometry. The present study is devoted to soft nanocomposite based on network of WLMs composed of biocompatible zwitterionic and anionic surfactants with embedded plate-like bentonite nanoclay particles. It is shown that nanoparticles enhance significantly the rheological properties of WLM hydrogel acting as physical cross-links between micellar chains. It was explained by the formation of micelle-nanoparticle junctions as a result of binding of the WLMs end-caps to the layer of surfactant adsorbed on the particle surface. The studied network possesses gel-like properties. In particular, its rheological properties demonstrated plateau modulus, low values of loss factor. At the same time, under high deformation, the micellar chains was disrupted, which induced a much more pronounced drop of viscosity than the disruption of physical cross-links in polymer gels. The disrupted micellar chains were completely recovered due to restoration of non-covalent bonds between surfactant molecules within the micelle. It was demonstrated that the prepared nanocomposite hydrogels possess promising properties for injection applications.

Wednesday 6:30 Ballroom on 4th floor PO68

Connecting frictional dissipation with the rheology of confined suspensions

Shravan Pradeep, Yunhu Peng, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Connecting rheology and tribology of shearing surfaces separated by a non-Newtonian fluid in between is an important problem in industrial processing applications. The relative contribution of frictional forces to normal forces due to hydrodynamic lubrication in suspensions between sheared surfaces can be characterized using the Sommerfeld number (S). In this study, we use colloidal suspensions of smooth polyhydroxystearic acid grafted poly(methyl methacrylate) particles (diameter, 2a = 1.01 µm ± 6.9%) at volume fractions above 40% to relate non-Newtonian rheology to tribological behavior. Rheological measurements are carried out in a stress-controlled rheometer with a parallel plate geometry and 10 µm - 500 µm in gap height, while tribological measurements are carried out with a ball-on-three plate geometry at lubrication heights on the order of 10 to 100 µm. Errors from zeroing gap due to air squeeze flow and secondary inertial forces are corrected for all experiments. We generate a set of S values that are used to connect the non-Newtonian rheology to the viscous dissipation in narrow confinement.

Wednesday 6:30 Ballroom on 4th floor PO70

Vibration-assisted powder patterning

Nikola Dudukovic
Lawrence Livermore National Laboratory, Livermore, CA, United States

We present a study on vibration-induced flow of granular media through microfluidic nozzles for patterning of dry powders. The powders consist of microparticles smaller than 50 µm, and the nozzle sizes are on the order of hundreds of microns. The granular flow is induced by acoustic vibration, and the powder is deposited onto a substrate moving relative to the nozzle. We show that the flow and deposition of the powder depends strongly on the amplitude and frequency of the vibration, nozzle position, and substrate speed, as well as particle properties (size, distribution, cohesion).

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Wednesday 6:30 Ballroom on 4th floor PO71

Constraint-based rheology of graphite particles

Anders L. Søbye[1], Wilson Poon[2], John R. Royer[2], Daniel Hodgson[2], Jesper D. Christiansen[1], and Søren J. Andreasen[3]
[1]Department of Materials and Production, Aalborg University, Aalborg, Denmark; [2]School of Physics and Astronomy, The University of Edinburgh, Edinburgh, United Kingdom; [3]Serenergy, Aalborg, Denmark

Most studies in suspension rheology focuses on ideal particles such as monodisperse hard spheres, while the industry often looks to cheaper alternatives, which are not so well-defined. Graphite particles acquired at a reduced cost are highly polydisperse, they can have a wide range of shapes, and characterising their physical interactions and rheology is no trivial task. This study investigated the rheology of polydisperse graphite flake particles suspended in a Newtonian heavy mineral oil at volume fractions from 0.1 to 0.29. Among others, a constraint-based model was applied. Experiments showed a clear shear thinning, which became more pronounced as the volume fraction increased. Based on the apparent yield stresses predicted by the Herschel-Bulkley model, jamming fractions was calculated and compared, first to each other, and secondly to the constraint-based model.

Wednesday 6:30 Ballroom on 4th floor PO72

Understanding thixotropic behavior of drilling fluids: A comparative study on impact of fluid type, temperature, and density

Ali Ettehadi
Petroleum and Natural Gas Engineering Department, Izmir Katip Çelebi University, Izmir, -- 35620, Turkey

Yield point and gel strength of circulated drilling fluid are more associated with the thixotropic response of fluid. Therefore, it is essential to consider more realistic thixotropy characterization of fluid sample. A series of steady shear flow and oscillatory dynamic shear tests were performed using Discovery Hybrid Rheometer to characterize the gel structure, yield stress and thixotropy for mud samples used in this study. Oscillatory amplitude and time sweep tests were carried out to find rheological properties. Thixotropic loop and dynamic time sweep tests were also performed to analysis gel strength and thixotropic properties of mud samples at different temperatures for an unweighted and three weighted drilling fluid systems. Thixotropic properties of sepiolite, bentonite/polymer, KCl and lignosulfonate based muds were evaluated based on three above-mentioned methods. The rate of structural change of sample represented as a degree of thixotropy. A hysteresis loop gives a measure of thixotropy at its most basic, the magnitude of the loop indicating the degree of time dependency. Shear loading experiment using dynamic time sweep test examines thixotropic response and the change in structure will be detected by a corresponding change in shear stress. Shear thinning and thixotropy indexes were also determined based on common practices for fluid evaluation using a Model 35A viscometer. The effects of fluid type, temperature and density were analyzed. Fluid type and its components have the significant influence in thixotropic behavior of mud samples. Thixotropic response in clay base fluids is dominant over breakdown effect of shear compare to KCl mud sample. Unlike bentonite, sepiolite clay provided remarkable rate of buildup after breakdown the structure. Thixotropy is temperature dependent and while bentonite and KCl muds failed at high temperatures, sepiolite based mud yielded notable thixotropic response even at 150°C. Temperature effect on thixotropy is more apparent than the effect of density.

Wednesday 6:30 Ballroom on 4th floor PO73

Micromechanical modeling of heterogeneous suspensions

Corinne G. Weeks, Dolata E. Benjamin, and Roseanna N. Zia
Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States

We present a study of the stress tensor in semi-dilute dispersions of colloidal hard spheres undergoing arbitrary heterogeneous flow. Heterogeneous flows distort the suspension microstructure from its equilibrium value; this distortion is statistically non-uniform. In contrast to homogeneous flows, where the pair distribution function depends only on the relative separation between particles pairs, the pair distribution function in a heterogeneous dispersion, and hence the ensemble averaged stress tensor, depends additionally on the location of their center of mass due to the statistical non-uniformity of the flow. We formulate a six-dimensional statistically heterogeneous Smoluchowski equation describing non-uniform distortions to the microstructure arising from arbitrary heterogeneous flows. To compute the stress arising from this distorted microstructure, we derive a heterogeneous, pointwise ensemble average of the interparticle stress in center of mass coordinates. We solve the heterogeneous Smoluchowski equation in the linear response regime; the resultant pair distribution function is used in conjunction with our expressions for the heterogeneously averaged interparticle stress to derive a nonlocal constitutive equation for heterogeneous dispersions, valid in the linear response regime up to second order in volume fraction.

Wednesday 6:30 Ballroom on 4th floor PO74

Pre-shear holds the key to understanding discontinuous shear thickening in dense suspensions

Tabish Khan and Prabhu Nott
Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

The phenomenon of discontinuous shear thickening (DST) in dense non Brownian suspensions has gained considerable attention in the last few years. The dominant opinion expressed in previous studies is that it is a stress controlled transition from lubricated to frictional state, controlled by short range repulsion between the particles. Typically, most of the experiments are done in such a way that the suspension is first pre-sheared, typically for an hour or so, before rheological measurements are made. However, little is known about what happens during the pre-shear, and why it needs to be done for such long times. We provide clear evidence that pre-shear holds the key to understanding the microstructural changes that change the response from continuous shear thickening (CST) to DST, and finally 'jamming', where the suspension shows Newtonian behaviour at low shear stresses but creeps at higher shear stress, like granular solids. We provide credible arguments as to why such large strains are required, and comment on the implication of our findings on slurry transportation in industries.

Wednesday 6:30 Ballroom on 4th floor PO75

Concentration profiles of particulate suspensions sheared in a Taylor–Couette cell with flat and bumpy rough walls

Mohammad Sarabian[1], Bloen Metzger[2], and Sarah Hormozi[3]
[1]Mechanical Engineering, Ohio University, Athens, OH 45701, United States; [2]2Aix-Marseille Université, CNRS, Marseille, France; [3]Ohio University, Athens, OH 45701, United States

We experimentally investigate particle migration in a non-Brownian suspension sheared in a Taylor-Couette configuration with flat and rough walls and in the limit of vanishing Reynolds number. Highly resolved index-matching techniques are used to measure the local particulate volume fraction. In this wide-gap Taylor-Couette configuration with flat walls, we find that for a large range of bulk volume fraction the fully developed concentration profiles are well predicted by the suspension balance model of Nott & Brady. Moreover, we provide systematic measurements of the migration strain scale and of the migration amplitude which highlight the limits of the suspension balance model predictions. To study the effect of particle layering on the kinetics and dynamics of migration, the Couette cell is covered by two bumpy rough walls to disrupt the particle clustering happening at larger volume fractions. We find that the migration occurs with a faster rate once the particles don't organize into layers. However, the fully-developed concentration profiles remain unaffected.

Wednesday 6:30 Ballroom on 4th floor PO76

Fiber-level simulation of nanofibrillated cellulose suspensions

Jing-Yao Chen and Daniel J. Klingenberg
Chemical and biological engineering, University of Wisconsin-Madison, Madison, WI 53706, United States

Fiber-level simulations are used to study the structure and rheology of nanofibrillated cellulose. Fibers are modeled as linked rigid spherocylinders connected by ball-and-socket joints that interact via short-range attractive and repulsive forces, as well as interfiber friction. Angular potentials in the joints allow fibers to bend and twist, and return to their equilibrium shape at rest. The dependence of structure and rheological properties of these suspensions on such variables as fiber interaction parameters, fiber aspect ratio, flexibility, equilibrium shape, shear rate, and concentration will be discussed. We show that drying suspensions of fibers can lead to irreversible changes in rheological behavior, which can be related to changes in the suspension microstructure that result from interfiber interactions. Some conditions that produce flocculation lead to roller structures aligned with the vorticity direction, consistent with previously reported experimental observations. The nature of the structures, the conditions that produce them, and their impact on rheological properties will be discussed.

Wednesday 6:30 Ballroom on 4th floor PO77

Visualization of particle migration in converging-diverging flows

Bruna C. Leopercio[1] and Marcio S. Carvalho[2]
[1]Mechanical Engineering Department, PUC-Rio, Rio de Janeiro, Brazil; [2]PUC-Rio, Rio de Janeiro 22451-900, Brazil

Although not fully understood, the effect of suspended particles distribution and orientation in a flow is of major importance for processes such as flow of suspensions through porous media, slot coating of batteries, reinforced polymers production and hybrid solar cells production. Different mechanisms of particle migration may lead to viscosity and surface tension gradients, which can change the flow pattern and particle structure. Progress has been made in numerical simulations focusing on the development of flow models that describe suspensions behavior in complex flows. However, the available models have not been experimentally validated. Experiments of particle suspensions flows can involve non-uniform particle distribution; rheological behavior dependent on particle size, concentration and distribution; visualization of particulate systems; fast flows and free surfaces. In this work, we report the experimental validation of particle migration in the flow through a constricted capillary, which has a complex flow kinematics with regions dominated by shear and regions dominated by uniaxial and biaxial extension deformations. We use confocal microscopy. Polystyrene particles of 6μm are suspended in a water-glycerin mixture that matches the density of the particles. The suspension flows - at varied flow rates - through constricted capillaries with different channel to constriction ratios. Results show that particles migrate from the wall, where the shear rate is maximum, to the centerline, where the shear rate approaches zero and that this migration is intensified by the constriction.

Wednesday 6:30 Ballroom on 4th floor PO78

Dynamics of anisotropic Brownian particles by simultaneous control of position and orientation

Dinesh Kumar[1], Anish Shenoy[2], Channing Richter[1], and Charles M Schroeder[1]
[1]Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [2]Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Champaign, IL 61820, United States

In this work, we demonstrate simultaneous control over the 2D center-of-mass position and orientation of anisotropic Brownian particles using only fluid flow. In particular, we use a 4-channel microfluidic device with a model-predictive control scheme to generate a flow pattern that translates and rotates rod-like particles from their initial state to a final desired position and orientation. By quantitative experiments and modeling, we show how the rotational Peclet number (Pe) affects the orientation distribution dynamics of anisotropic particles in a steady extensional flow. Next, we investigate the orientation dynamics of anisotropic particles in time-dependent oscillatory extensional flow over a wide range of Peclet number (Pe) and Deborah number (De). Specifically, we measure the orientation distribution function of rod-like particles as a function of time. In this way, we present the dynamic shapes of Lissajous curves for anisotropic particles as a function of Pe and De using precise microfluidic techniques and fluorescence microscopy. These results are compared with theory by solving the Fokker-Planck equation for orientation distribution

function in oscillatory extensional flow. We also describe the non-equilibrium phase diagram of rods, describing the transition from isotropic (disordered) state to the aligned (ordered) state as a function of ow strength and cycle period of oscillatory extensional flow. Overall, the technique of controlling the 2D center-of-mass and orientation of anisotropic particles allows for the direct observation of single rod-like particle dynamics in well-defined time-dependent flows.

Wednesday 6:30 Ballroom on 4th floor PO79

The effect of confinement on the observed rheology of complex fluid flow in microcapillaries

Javen Weston and Elio Trigo
Chemical Engineering, University of Tulsa, Tulsa, OK 74104, United States

Properly characterizing the rheology of non-Newtonian fluids is a key step when designing any process where the fluid will be flowing. Numerous well-designed rheometers and viscometers can perfectly characterize the bulk rheology of even the most complex non-Newtonian fluids. However, in various applications, complex fluids flow in small capillaries (<200 µm in diameter), where deviations from bulk rheology due to surface effects and confinement become much more important to understanding the behavior and path of the fluid flow. In order to properly model fluid flow in porous media where pore diameters are relatively small, it is necessary to characterize the dynamical flow behavior of the fluid under those conditions rather than simply extrapolating from bulk rheological measurements made using a rheometer. This research uses capillary rheometry and microscopy to study how surface charge, surface hydrophobicity, and confinement affects complex fluid rheology in micron-scale capillaries. The data generated from model systems is then used to develop models to describe the fluid flow.

Wednesday 6:30 Ballroom on 4th floor PO80

The rheology of spherically confined, patchy Brownian suspensions

Jennifer L. Hofmann and Roseanna N. Zia
Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States

Microscopic forces and physical phenomena at the colloidal scale are involved with fundamental processes inside living cells. Examples of such phenomena include confinement within the boundary of a cell membrane or wall, and electrostatic interactions between constituents of the cellular milieu (e.g. proteins). In the case of electrostatic interactions, in particular, isotropic inter-particle potentials are often inadequate to reproduce experimental results, due to anisotropic charge distributions on particle surfaces. To connect these microscopic forces to whole-cell functions, we examine the interplay between spherical confinement and anisotropic ("patchy") inter-particle attractions in systems of Brownian suspensions. Here we present our results studying the dynamics and structure of these systems, using unbounded Brownian dynamics and our Confined Brownian Dynamics algorithm.

Wednesday 6:30 Ballroom on 4th floor PO81

Predicting the lubricated friction of textured soft substrates

Yunhu Peng, Christopher Serfass, Catherine Hill, and Lilian C. Hsiao
Chemcial and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905, United States

Natural cartilage is durable and elastic, providing a low friction coefficient to moving joints under frequent applications of heavy loads. However, the physical mechanisms contributing to this low friction coefficient is not well understood. We hypothesize that the non-ideal surface geometry of cartilage gives rise to its low friction coefficient in certain directions of motion. We design microtextured soft poly(dimethyl siloxane) (PDMS) substrates with lithography to study the influence of surface geometry on their frictional and lubrication properties. The PDMS surfaces consist of stripes with controlled dimensions and spacings between each other. Tribological tests performed with a thin layer of aqueous glycerol solution at different concentrations between the PDMS substrates show that the friction coefficient is a function of the sliding velocity. However, this tribological behavior does not follow the type of Stribeck curve that is typically observed with flat surfaces. Two major differences are observed at different velocity ranges. First, a significant frictional reduction is observed in the boundary regime where the sliding speed is relatively low. Second, a velocity-dependent friction peak is observed in the elastohydrodynamic lubrication (EHL) regime. We hypothesize that this friction peak arises due to the competition between micro-EHL and EHL at the microtextured surfaces. To test this hypothesis, we develop scaling theories that show how the localized maximum friction is a function of the differential lubrication generated by the geometry of the microtextured surfaces.

Wednesday 6:30 Ballroom on 4th floor PO82

Effect of interface rheology on drop coalescence in water-oil emulsion

Talita C. Botti and Marcio S. Carvalho
PUC-Rio, Rio de Janeiro 22451-900, Brazil

Emulsion formation is common and represents a great challenge in heavy crude oil production. It may lead to extremely high viscosity fluids that need to be transported through the well and riser and to the need of complex phase separation units. In order to hinder these problems, it is important to develop and understand ways of destabilizing oil-water interfaces. This work investigates the correlation between the rheological properties of oil-water interfaces and the drainage time of a thin oil film between an aqueous drop and a planar interface. Different concentrations of a nonionic surfactant (Span 80) dissolved in mineral oil (Primol 352) phase were evaluated. The interfacial rheological measurements were performed using the pendant drop method in a Tracker-S tensiometer. The results indicate the relationship between the structure formed in the oil-water to the high drainage time. Shorter drainage time, and consequently drop coalescence, can be promoted by weakening the interface elastic modulus chemically or mechanically.

Wednesday 6:30 Ballroom on 4th floor PO83

Dilatational rheology of Lysolipid and its effects on acute respiratory distress syndrome (ARDS)

Sourav Barman and Joseph A. Zasadzinski
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

A second, but less appreciated role of lung surfactant is to ensure uniform lung inflation. The dependence of the Laplace pressure, dP = 2?/R, on the alveolar radius, R, means that interconnected bubbles or alveoli are at best metastable if ? is constant. The high pressure in the small alveoli cause them to dump their contents into the lower pressure, larger alveoli, and the small alveoli eventually deflate, which is known as the Laplace Instability. However, while not generally appreciated in the medical literature, but well known in the foam and emulsion stability literature, the dynamic resistance of an interfacial film to compression can reverse the Laplace instability. The dilatational modulus, e=A??/?A, relates the change in surface tension, ?, to the change in the molecular area, A, as the interface is compressed at a frequency, ? (ranging from 10-100 cycles/minute for normal breathing). If the dilatational modulus is large enough, the resistance to interfacial compression can overcome the Laplace pressure so that the gas pressure in the alveolus no longer increases with decreasing radius. For (2e-?) > 0, the Laplace pressure decreases with decreasing radius and increases with increasing radius, which reverses the Laplace instability, thereby stabilizing the alveoli against collapse. Using a newly designed capillary microtensiometer, we will show that lysolipids, a product of the inflammation-induced degradation of phospholipids, can cause the dilatational modulus to decrease at low breathing frequencies, and thereby induce the Laplace instability, and perhaps acute respiratory distress syndrome. Increasing the breathing frequency can increase the dilatational modulus of lysolipids and may restore proper lung function.

Wednesday 6:30 Ballroom on 4th floor PO84

Fluid dynamics and particle deposition in porous filters using lattice Boltzmann simulation

Gi Wook Lee, Byoungjin Chun, and Hyun Wook Jung
Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea

The filtration mechanism of particulate fluids in the porous media is widely applied in industries such as automotive post-treatment devices (e.g., DPF and GPF) and RO membranes. It is important to understand filtration dynamics of particulate fluid systems, considering pore size, permeability, and tortuosity of porous media, because particle deposition inside porous media occurring during the filtration process greatly affects the performance of porous media devices. In this study, the flow behaviors in porous media are analyzed using mesoscale lattice Boltzmann method (LBM), which is capable of easily implementing complex structures of porous media. Effect of tortuosity of porous media was mainly interpreted for correlating structural factors under the same solid volume fraction. Also, the structural change of porous media was further elucidated by considering the temporal particle deposition on porous surfaces.

Wednesday 6:30 Ballroom on 4th floor PO85

A study on the boundary of the linearity of simple shear flows: Model calculations

Taehoon Kim and Kwang Soo Cho
Department of Polymer Science and Engineering, Kyungpook National University, Daegu, Republic of Korea

Relaxation modulus, a linear viscoelastic function can be calculated from the ratio of Laplace transforms of arbitrary stress and strain, in principle, under the assumption of linear viscoelasticity. If strain is controlled and stress is measured, the input strain should belong to linear regime. We investigated boundary of linear viscoelasticity for simple shear flows with various time functions of shear strain. We adopted the Phan-Thien and Tanner model and the Giesekus model in order to extract the linearity criterion as well as the correction terms in determine linear viscoelastic function from nonlinear viscoelastic data.

Wednesday 6:30 Ballroom on 4th floor PO86

Shear thinning and thickening behaviors of hollow carbon nanoparticles in Newtonian fluids

Parvin Kiany[1], Fatemeh Goharpey[1], and Reza Foudazi[2]
[1]Polymer Engineering, Amirkabir University of Technology, Tehran, Iran; [2]Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States

We investigated the rheological properties of hollow carbon spheres (HCSs) suspended in polyethylene glycol (PEG-400) at different volume fractions. The viscosity increases and the shear thinning behavior intensifies with volume fraction. At 12 vol% of HCSs, with increasing the shear rate, shear thinning is followed by shear thickening and a secondary shear thinning. This behavior can be attributed to the aggregation of HCSs due to their attractive surface (their zeta potential is lower than 30 mV). Based on Krieger-Dougherty equation, the maximum packing volume fraction of HCSs is about 0.53. Under weak shear, negative normal stress differences are observed, which can be attributed to the alignment of aggregates. When hybrids of bowl-like and spherical particles are used, the shear thickening behavior is diminished in the studied experimental shear rate range.

Wednesday 6:30 Ballroom on 4th floor PO87

Electro-elastic flow instabilities in microflows of non-Newtonian fluids

Le Song[1], Di Li[1], Liandong Yu[2], and Xiangchun Xuan[1]

[1]Mechanical Engineering, Clemson University, CLEMSON, SC 29634-0921, United States; [2]Hefei University of Technology, Hefei, China

Elastic flow instabilities in non-Newtonian fluids have been extensively studied in pressure driven flow at microscale. However, few works have been done for electric field-driven flow. In this work, we present a parametric experimental study of the electro-elastic flow instabilities in non-Newtonian fluids using a T-shaped microchannel. Flow instabilities can be observed in polyacrylamide (PAA) solution at the T-junction when the applied DC voltage is beyond a threshold value. Compared with the electrokinetic instability induced in Newtonian fluids with conductivity gradients, the electro-elastic instability in this study has longer wavelengths, and it seems to have no significant improvement in the microfluidic mixing. The effects of several parameters on electro-elastic instabilities were investigated in this study, including the buffer concentration, channel depth and PAA concentration. We also tested other four types of viscoelastic fluids, and similar flow instabilities can only be observed in Xanthan Gum (XG) solution, which indicates that the shear-thinning effect may play an important role in the electro-elastic flow instability.

Wednesday 6:30 Ballroom on 4th floor PO88

Transient evolution of flow profiles in shear banding wormlike micellar fluids

Peter Rassolov and Hadi Mohammadigoushki

Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310, United States

We report experiments on spatiotemporal evolution of flow fields in model shear-banding wormlike micellar solutions based on hexadecyltrimethylammonium bromide and sodium salicylate in a Taylor-Couette cell. Our goal is to systematically study the effects of fluid elasticity on transient evolution of flow fields in wormlike micellar fluids. By varying surfactant concentration, salt concentration, and temperature, we vary the fluid elasticity number in the range 4.21×10^4 to 8.57×10^6 while keeping entanglement density fixed at 5.1 ± 0.7, viscosity ratio fixed at 40.3 ± 2.9 Pa·s, and curvature fixed at 0.085. Our experiments show that these entangled solutions initially deform uniformly upon imposition of step shear, similarly to an elastic solid. As shear strain increases, shear stress shows an overshoot followed by a decay towards steady state. Simultaneously with shear stress decay, fluid moves in the opposite direction to that of the imposed motion in a subset of the gap (*i.e.*, back flow). Consistently with theoretical predictions, the back flow strengthens as elasticity number increases. However, at very high elasticity numbers, the transient back flow disappears, contrary to the same theoretical predictions. In addition to the back flow, a multiple shear band structure forms in the transient flow at high elasticity numbers. These transient multiple bands persist to steady state. We surmise that at high elasticity numbers where back flow is not observed, the formation of transient multiple bands prevents formation of transient back flows. Furthermore, while such multiple banding has been reported for polymer solutions and in wormlike micellar fluids in the cone and plate geometry, and predicted by theory, it has not been reported in wormlike micellar fluids sheared in Taylor-Couette geometry.

Wednesday 6:30 Ballroom on 4th floor PO89

Pipe flow engineering and design computations for non-Newtonian fluids - going open source

William H. Hartt[1], Setareh Shahsavari[2], Emilio Tozzi[2], and Marco Caggioni[3]

[1]Corporate Engineering Technologies Lab, The Procter & Gamble Co, West Chester, OH 45069, United States; [2]The Procter & Gamble Co, West Chester, OH 45069, United States; [3]Complex Fluids Microctructures, Procter and Gamble, West Chester, OH 45069, United States

We present an open source library for non-Newtonian pipe flow calculations. The library is available to anyone and contributions are welcome. The library accepts any Generalized Newtonian Fluid viscosity model. Standard viscosity models such as Herschel-Bulkley, Carreau, and power-law are provided. Calculations of pressure drop, flow rate, shear rate, shear stress, and residence time for laminar flow and turbulent flow, with variations of Reed-Metzner, are provided. The library is written in python and available on github. Our objective is to create a platform for general use and contributions of useful calculations.

Wednesday 6:30 Ballroom on 4th floor PO90

Role of elastic turbulence on oil displacement in microfluidic porous networks

Clayton Miller, Indranil Sinha, and Gordon Christopher

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

Polymer flooding is an enhanced oil recovery technique that can often produce 30-60% of a wells output. Although, initially it was believed increased viscosity and excess pressure drop were the mechanism of enhancement, recent studies have indicated that displacement is improved by the changes to flow patterns caused by elastic instabilities.

In this work, we demonstrate oil displacement by polymer flooding is improved in comparison to Newtonian fluid due to elastic turbulence flow patterns that occur over critical Mach numbers. The existence of elastic instabilities in regular porous networks of microfluidic channels is first examined through spectral analysis of pressure fluctuation. Over critical flow rates, instabilities are observed for polymer solutions based on both flow visualization and analysis of power spectra. Similar behaviors are not observed for Newtonian flows. Above critical flow rates, enhanced displacement is observed for polymer solutions, even in comparison to Newtonian fluids at identical driving pressures. Enhancement appears to

occur due to turbulent flows ability to displace locally trapped oil bridges through increased normal velocities. Furthermore, we find that the nature of the type of porous network has a pronounced effect on the efficacy of this mechanism.

Wednesday 6:30 Ballroom on 4th floor PO91

Effect of cooling on steady dynamics and stability in 2-D viscoelastic film casting process

Changhoon Lee[1], Ilyoung Kwon[2], Joo Sung Lee[3], Hyun Wook Jung[1], and Jae Chun Hyun[1]
[1]Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea; [2]LG Hausys, Seoul, Republic of Korea; [3]LG Chem, Daejeon, Republic of Korea

Film casting is one of the most commonly used extensional polymer processes, continuously producing uniform polymer films. Through this process, the target film dimension is determined by cooling and extensional deformation behavior. Over a certain draw ratio, the periodic fluctuation of state variables, called draw resonance, inevitably occurs, deteriorating the film quality. The critical draw ratios at given processing conditions are also closely dependent on thermal and viscoelastic properties of polymer. In this study, FEM-based simulations were performed for the steady behavior and stability analysis of two-dimensional (2D) viscoelastic film casting processes, combining the tension boundary condition and frequency response method. Phan-Thien and Tanner (PTT) fluid model as well as Newtonian and upper convected Maxwell fluid models were incorporated. The critical onsets were determined with Nyquist plots of transfer function between take-up velocity output and tension input in the frequency domain and also transient responses in the time domain. The effect of cooling condition on the film dynamics was systematically scrutinized.

Wednesday 6:30 Ballroom on 4th floor PO92

The roles of elastic and inertial forces in the formation of vortices

Jason LaRuez[1], Larry Villasmil[2], and Michael Cromer[1]
[1]School Of Mathematical Sciences, Rochester Institute Of Technology, Rochester, NY, United States; [2]Mechanical Engineering Technology, Rochester Institute of Technology, Rochester, NY, United States

Flow around sharp corners can involve large stresses and is thus strongly affected by the elastic and inertial forces. In particular, flow around a 90-degree bend may lead to the formation of vortices downstream (inertial) or upstream (elastic) of the corner. The goal of this work is to understand how the formation of these recirculation regions in polymer solutions is controlled by various nondimensional groups, namely the Deborah number (De), Reynolds number (Re), and viscosity ratio. We conduct a systematic numerical study of Newtonian and viscoelastic fluid models. We ultimately show that, computationally, the onset and size of the vortex is strongly dependent upon the mesh. Upon this mesh refinement, we find the critical Reynolds number for the formation of downstream vortices in the flow of Newtonian fluids around the bend. Decreasing the viscosity ratio and/or increasing the Elasticity number (De/Re) reveals how increasing polymer concentration alters the conditions and location of the vortices. Ultimately, we construct phase diagrams that reveal operating windows within which different behavior is expected: elastic vortex, inertial vortex, or no vortex.

Wednesday 6:30 Ballroom on 4th floor PO93

A kinetic model for a sol-gel transition in a colloidal dispersion: Application of the modified Bailey criterion

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

The sol-gel transition in a colloidal dispersion of anisotropic particles of Laponite is investigated by a kinetic approach. While undergoing the sol-gel transition, the colloidal dispersion spans the critical gel state wherein the system forms a space spanning percolated network. Understanding of gelation kinetics is important as the rheological properties depend on the extent of aggregate formation. In this work, we develop a kinetic model of a gelation process and, by making use of the modified Bailey durability criterion, we predict the time to achieve the critical gel state. The model parameters are derived from the gelation experiments conducted under the isothermal conditions. A comparison between the experimental result and the developed kinetic model explores the possibility of application of the modified Bailey criterion for a system undergoing sol-gel transition in a colloidal dispersion.

Wednesday 6:30 Ballroom on 4th floor PO94

Microscopic origins of caging and equilibration of self-suspended hairy nanoparticles

Xiaotun Liu and Lynden A. Archer
Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Well-dispersed, solvent-free silica nanoparticles tethered with polymers exhibit soft glassy rheology and jamming behavior due to the cages induced by interpenetrated chains. In this study, we use small-angle X-ray scattering (SAXS) and rheology to investigate slow structural and mechanical evolution of a soft glassy material composed of silica nanoparticles densely grafted with poly(ethylene glycol) methyl ether (mPEG) chains. We observe a significant equilibration process that has not been reported previously and show that the process is thermally activated and associated with local rearrangements of tethered chains to their equilibrium conformations. At fixed temperature, the strength of the equilibrated cages increases significantly, relative to their unequilibrated values, but decreases in a predictable manner as temperature rises. A simple geometrical model is used to rationalize these observations in terms of corona interpenetration, cage dynamics, and yielding of self-suspended nanoparticles.

Wednesday 6:30 Ballroom on 4th floor PO95

Tunable rheology of mixed hydrogels with different interactions

Minaspi Bantawa[1], Emmanouil Vereroudakis[2], Daniele Parisi[2], René P. Lafleur[3], Emanuela Del Gado[1], E.W. Meijer[3], and Dimitris Vlassopoulos[2]
[1]Department of Physics, Georgetown University, Washington, DC 20007, United States; [2]Institute of Electronic Structure & Laser, FORTH, Heraklion 70013, Greece; [3]Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, The Netherlands

Hydrogels with tunable mechanical response and physiological properties have potential for biomedical, environmental and engineering applications. The challenge is to synthesize materials with high water uptake without sacrificing the strength and resilience of the network along with dynamic physical interactions that promote processability and self-healing. We have focused on the unusual rheological properties of a class of hydrogels made of fibrillar supramolecular assemblies based on hydrogen-bonding units, which form physical networks akin to entangled polymers, and gel-like structures made of telechelic moeties, which exhibit different mechanical response. We find that, by mixing these distinct moeties in different compositions, a non-monotonic, non-additive mechanical response is obtained, suggesting additional interactions between the two components that enable fine tuning of the performance of the composite material. We analyze the gel rheology using a combination of experiments (rheology and microscopy) and numerical simulations. The simulations comprise networks made of two building units with different interaction strengths and capture the non-monotonicity of the mechanical properties, providing new insight into the possible mechanisms underpinning the tunability of the hydrogel response.

Wednesday 6:30 Ballroom on 4th floor PO96

Rheology of glassy and jammed emulsions

Cong Cao and Eric R. Weeks
Physics, Emory University, Atlanta, GA 30322, United States

We study the rheology of monodisperse emulsions with various mean droplet sizes. Above a critical volume fraction, these systems will exhibit solid-like behaviors and possess a yield stress. Previous simulation work suggests that for small thermal particles, rheology will see a glass transition; for large athermal systems, rheology will see a jamming transition. However, at the crossover of thermal and athermal regimes, the glass and jamming transitions may be well separated and observed at different volume fractions for a fixed mean droplet size. We conduct an experiment by shearing different sizes of emulsion droplets (500 nm-5 µm diameter) with a rheometer. In this way, we measure rheological properties near the critical volume fraction. By varying the shear rate and particle size, our experiments cover a wide range of Péclet number (the ratio of shear and thermal motions), including the crossover regime.

Wednesday 6:30 Ballroom on 4th floor PO97

Human mesenchymal stem cell migration in hydrogels quantified by bi-disperse multiple particle tracking microrheology

John A. McGlynn, Kilian J. Druggan, Kiera J. Croland, and Kelly M. Schultz
Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Human mesenchymal stem cells (hMSCs) are integral to the wound healing process. They migrate out of their native niche to injury sites where they control the inflammatory response. hMSCs secrete proteolytic enzymes called matrix metalloproteinases (MMPs) which degrade components of the extracellular matrix allowing for migration to occur using cytoskeletal tension. We encapsulate hMSCs in a poly(ethylene glycol)-norbornene based hydrogel which is cross-linked by an MMP-degradable peptide sequence. We then use multiple particle tracking microrheology (MPT) to quantify the spatial and temporal changes in rheology around a migrating cell. MPT measures the Brownian motion of fluorescent particles embedded in a material. Typically, MPT uses a single particle size for characterization, measuring changes on one length scale. Cell migration impacts many length scales in the cellular microenvironment. MMPs break cross-links at the molecular scale, cells extend themselves on the micrometer scale by pulling on the surrounding matrix, and this degradation affects the bulk rheology of the material. Using bi-disperse MPT, two particle sizes, 0.5 and 2 µm, quantify length scale dependent changes during cellular remodeling. When our material is degraded by enzymes in the absence of cells, the degradation of the material is independent of length scale. During cell-mediated degradation, bi-disperse MPT measures more degradation on the 2.0 µm scale than the 0.5 µm scale. This difference is not present when myosin-II is inhibited identifying cytoskeletal tension as the source of this difference in degradation. We introduce 4.5 µm particles in separate experiments and relate the degradation on all three scales to cell migration speeds. These results quantitatively relate scaffold structure to cell migration and the effects of cytoskeletal tension, and can be used to design biomaterials which leverage length scale dependent differences to direct cell behavior in clinical applications such as tissue regeneration.

Wednesday 6:30 Ballroom on 4th floor PO98

A rheological constitutive model for human blood via population balance modeling

Soham Jariwala, Jeffrey S. Horner, Antony N. Beris, and Norman J. Wagner
Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Human blood has been a subject of rheological studies, both experimental and mathematical, that aim at describing the origin of its vexing properties like yield stress, thixotropy, viscoelasticity, and shear thinning. Although blood is a dense suspension consisting of platelets, fibrinogen,

plasma, and red blood cells (RBCs), much of its complex rheology at low deformation rates is a result of RBCs forming coin-stack like aggregates called rouleaux. While the thixotropic rheology of blood has been modeled using structure kinetics approaches [1], there is a need for a more predictive physically based description that could potentially be used for diagnostic purposes. Better insight into the microstructure-rheology relationship underlying rouleaux formation could enable us to probe diseases and develop new health diagnostic tools based on changes in the rheological properties of blood.

In this work, we adapt a population balance-based approach first proposed by Mwasame *et al.* [2] to model the rheological effects of rouleaux formation in blood in the context of rheometric flows. Population balances are a powerful alternative to the existing structure kinetics models as they use a statistical approach to describe the aggregate size distribution with well-defined processes for both shear-induced and Brownian aggregation and breakup under shear flow. The rouleaux are described using independently validated rate kernels in the literature based on Smoluchowski aggregation and breakage model proposed by Spicer & Pratsinis. The model is fit and validated against rheometric measurements, including steady shear, transient, and uni-directional large-amplitude oscillatory shear (UD-LAOS) experiments, of whole blood, and compared against existing structure kinetics models [1]. Prospects for improvements in the modeling method will also be discussed.

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Wednesday 6:30 Ballroom on 4th floor PO99

Investigating heat-induced gelation of whey protein using simultaneous rheology and FTIR spectroscopy

Nathan C. Crawford
Material Characterization, Thermo Fisher Scientific, Golden, CO 80401, United States

Rheology coupled with *in situ* Fourier transform infrared (FTIR) spectroscopy was used to examine the thermal denaturation of aqueous whey protein solutions (50% w/w). FTIR is a powerful tool for monitoring structural molecular interactions which are not observable through standalone rheological analysis. Three major amide bands were detected using FTIR: Amide I (1700-1600 cm^{-1}; stretching vibration in the C=O bond), Amide II (1570-1510 cm^{-1}; bending vibrations of the N-H bond), and Amide III (1350-1200 cm^{-1}). The Amide I band at 1627 cm^{-1} was considered the best indicator of secondary structural changes and was used as a spectral marker to track whey protein gelation during simultaneous rheo-FTIR measurements. As the protein samples were heat-treated from 60-90 °C, they transitioned from liquid solutions to solid-like gel systems, indicated by a crossover point as well as exponential increases in both G' and G". The observed rheological sol-gel transitions were directly correlated with increases in the peak intensity of the Amide I band at 1627 cm^{-1}, suggesting that bulk gelation of the solutions were driven by denaturation and unfolding of the proteins. Overall, coupling of these two independent analytical techniques, rheology and FTIR spectroscopy, enabled a more complete evaluation of the gelation process and provided unique insights into the denaturation and aggregation of whey proteins.

Wednesday 6:30 Ballroom on 4th floor PO100

Microrheological characterization of covalent adaptable hydrogel degradation in response to pH changes that mimic the gastrointestinal tract

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

Covalent adaptable hydrogels (CAHs) dynamically change their structure in response to external stimuli. These dynamic covalent bonds reversibly break and reform when they are pushed out of equilibrium. This dynamically evolving structure makes CAHs promising in biological applications, such as oral delivery of therapeutics and nutrients. To study the potential of using CAHs as a platform for oral delivery, we characterize scaffold degradation in response to changes in environmental pH which mimic the gastrointestinal (GI) tract. The CAH we are characterizing consists of 8-arm poly(ethylene glycol) (PEG)-hydrazine that covalently cross-links with 8-arm star PEG-aldehyde. μ^2rheology, multiple particle tracking microrheology (MPT) in a microfluidic device, is used to mimic pH-dependent degradation in the GI tract. In MPT, fluorescent probes particles are embedded into the sample and Brownian motion is measured. Our microfluidic device enables the fluid environment to be changed around a single sample with minimal sample loss. μ^2rheology is used to characterize degradation at a single pH (pH 4.3, 5.5 and 7.4), consecutive degradation with a single pH exchange (pH 4.3 to 7.4 and pH 7.4 to 4.3) and temporal pH changes that mimic the pH in the entire GI tract. We quantitatively determine the gel-sol transition during degradation by calculating the critical relaxation exponent, which is independent of degradation pH. In addition, we determine that degradation kinetics and material property evolution are not influenced by degradation history. However, the initial cross-link density of the scaffold at each pH exchange can be decreased by degradation history which reduces the time to the critical gel-sol transition. This result indicates degradation can be tuned by changing scaffold cross-link density which can be done by changing polymer concentration or the ratio of functional groups. This work will inform design of this scaffold for site-specific oral drug delivery.

Wednesday 6:30 Ballroom on 4th floor PO101

Effect of endogenous non-starch wheat lipids on gluten network non-linearity

Gamze Yazar[1], Jozef Kokini[2], and Brennan Smith[1]
[1]School of Food Science, University of Idaho, Moscow, ID 83844, United States; [2]Food Science, Purdue University, West Lafayette, IN 47907, United States

Commercial vital gluten (6.2% moisture) was used to study the impact of endogenous non-starch wheat lipids on the non-linear rheological properties of gluten network. For this purpose, endogenous lipids were extracted from vital gluten with 95% ethanol. Mixing behaviors of lipid-removed vital gluten (freeze-dried and ground into powder after extraction, 4.2% moisture) and vital gluten were measured using the Farinograph

(Brabender, Duisburg, Germany) with 50-g mixing bowl attachment. Farinograms revealed differences in network formation patterns, hydration times, and water absorption capacities due to endogenous wheat lipids having strong functionality at very low levels. The development time (reaching 500 BU consistency) was delayed for 6-8 minutes in the absence of lipids and the water absorption capacity increased from 127% to 132%. Non-linear rheological properties of vital gluten and lipid-removed vital gluten were determined with DHR3 Rheometer (TA Instruments, USA) using Large Amplitude Oscillatory Shear (LAOS) tests. Gluten samples were mixed in the Farinograph with the same level of added water (127%) for 25 minutes. LAOS tests were conducted at 25 °C, between 0.01 and 200% strain at 3 different frequencies (20, 10, and 1 rad/sec). Non-linearity started to be observed between the strain values of 0.15%- 0.25% for both vital gluten and lipid-removed vital gluten at all frequencies applied. Higher G' values were obtained for the lipid-removed gluten in the linear and non-linear region at all frequencies. As the frequency decreased, the difference in G" values started to decrease. G' and G" values represented an increase at the onset of non-linearity followed by a decrease indicating a type IV non-linear behavior expressed as "strong strain overshoot". Elastic Lissajous-Bowditch curves showed narrower elliptical trajectories at high strain amplitudes for the lipid-removed gluten, which points out more elastically dominated viscoelastic behavior in the non-linear region compared to vital gluten.

Wednesday 6:30 Ballroom on 4th floor PO103

Rheological investigation of TEMPO-treated cellulose nanofibril hydrogel

Geun-Seok Choi, Hye-Jin Ahn, and Ki-Won Song

Department of Organic Material Science and Engineering, Pusan National University, Busan 46241, Republic of Korea

Cellulose nanofibril (CNF) has been known as one of the most abundant and renewable biomaterials. It has highly crystalized structure consisting of cellulose, hemicellulose and lignin, which shows remarkable viscoelasticity and biocompatibility. Due to excessive hydrogen bonding of hydroxyl groups on cellulose chains, however, CNF appears relatively low dispersibility and requires high energy expense to be divided into more thin fibrils without chemical damage.

These problems can be improved by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation. This method converts C6 primary hydroxyls of cellulose into carboxylate groups, which provides moderate ionic repulsive force to polymer chain. TEMPO-treated CNF has superior dispersibility and much smaller diameter compared to the non-treated one. In addition, converted carboxylate groups induce pH-dependent rheological behavior of reaction product, by changing its chemical structure depending on pH value.

Based on these properties, it can be optimally used as additive material in hydrophilic polymer films, food, cosmetics and medical products. As the demands for biocompatible materials gradually increase in these fields, it is more important to analyze and understand the quantitated rheological behaviors of TEMPO-treated CNF under various conditions.

The main objective of this study is to systematically characterize the rheological properties of TEMPO-treated CNF and its pH-dependent behaviors in several well-defined shear flow fields using a strain-controlled rheometer [Advanced Rheometric Expansion System (ARES)].

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Wednesday 6:30 Ballroom on 4th floor PO104

Rheology and characterization of platelet-rich and platelet-poor plasma

Harsa Mitra[1], Prathap Jayaram[2], Andrew T. Bratsman[2], Trevor Gabel[3], and Kamran Alba[3]

[1]Mechanical Engineering, University of Houston, Houston, TX 77025, United States; [2]Department of Orthopedic Surgery, Baylor College of Medicine, Houston, TX, United States; [3]Mechanical Engineering Technology, University of Houston, Houston, TX, United States

The effectiveness of blood-derived products, especially platelet-rich plasma (PRP) has been largely investigated in the past several years, which has the potential of being used in the treatment of various injuries. PRP is a type of plasma with more platelets as compared to blood, which has proteins called growth factors which can be a remedy to arthritis, sprained knees, and/or other tendon injuries, especially in athletes. Because of the ability of PRP to amend inflammation, it is thought of to be a therapy that can be used as a treatment for Post- Traumatic Osteoarthritis (PTOA) but is supported by limited sources in the literature. Although it is hypothesized that PRP can modify the biological microenvironment in the joints related to a variety of Osteoarthritis (OA) disease, the microenvironment in the joints of OA is complex. The aim of this paper will be to address this and understand the rheological properties of PRP which can provide further insight into its mechanism of action. We utilize shear rheology to test the mechanical properties of the PRP and Platelet-Poor Plasma (PPP). Through flow sweep and frequency sweep tests, we characterize the apparent viscosity of the PRP and PPP mixtures, evaluating possible shear-thinning and viscoelasticity associated with the interaction of cells within blood products. All tests are performed at 25°C and 37°C to study the effect of room and core-body temperature respectively. The PRP samples exhibit shear-thinning which appears to be of the Carreau-model type. The frequency sweep tests are furthermore carried out in a triplicate manner at different strain rates to evaluate the viscoelastic behavior of samples. Over the acceptable range of angular velocity, in the majority of the samples, the loss modulus dominates the storage one. Calculated boundaries of low/high-shear rates in flow sweep tests as well as minimum-torque, sample inertia, and instrument inertia limits in frequency sweep experiments are correspondingly provided for accurate interpretation of results.

Wednesday 6:30 Ballroom on 4th floor PO105

Rheological and parametric analysis of the effects of aspirin on human blood

Wes Pulles[1], Katleyn Rook[1], Matthew J. Armstrong[1], and Jeffrey S. Horner[2]
[1]Chemistry and Life Science, United States Military Academy, west point, NY 10996, United States; [2]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

Recent work modeling the rheological behavior of human blood indicates that blood has all of the hallmark features of a complex material, including shear-thinning, viscoelastic behavior, a yield stress and thixotropy. After decades of modeling steady state blood data, and the development of steady state models, like the Casson, Carreau-Yasuda, Herschel-Bulkley, etc. the advancement and evolution of blood modeling to transient flow conditions now has a renewed interest. Using recently collected steady state, triangle ramp, and oscillatory shear rheological data om human blood before and after a low dose, two week aspirin protocol we examine effect of the aspirin. The effect of the aspirin on the rheological properties will be analyzed directly, with mechanical contour maps, and via parametric analysis using two contemporary rheological models. The models used for analysis will be the modified Horner-Armstrong-Wagner-Beris (mHAWB), and a version of the viscoelastic Modified Delaware Thixotropic Model (MDTM). We will then use the best fit rheological model parameters from the mHAWB and VE-MDTM fits to compare with physiological blood parameters such as hematocrit, glucose, triglycerides, LDL and HDL, and analyze the effect of the aspirin on the rheological model parameters. To meet this end we will incorporate the correlation matrix, looking for statistically significant correlations by interpretation of the correlation coefficients and associated p-values. Lastly we will graphically show the most meaningful correlations and compare to similar work from literature. To fit the rheological data to the models a stochastic, global optimization algorithm is used.

Wednesday 6:30 Ballroom on 4th floor PO106

Optimal rheology for bio-implantable crosslinked hyaluronic acid gel; filler rheology to avoid edema & erythema

Keyong Ho Lee, Bokryul Choi, E Sle Kim, Ju Hee Kang, and Eun Kyoung Kim
R&D, Across Co. Ltd., Chuncheon, Republic of Korea

The popularity of hyaluronate-dermal fillers has grown rapidly in recent years since they offer rejuvenating and enhancing aesthetic improvements, previously only achievable with surgery. Edema is some transient swelling. The erythema is skin redness after the implantation in soft tissue. These symptoms are normal and occur with all dermal fillers. We published the rheological property on the crosslinked and non-crosslinked hyaluronic acid gels. We carried out a further study in a rabbit model, which measured level of erythema and edema to find out the optimum rheological values of crosslinked hyaluronic acid gel, as well as how to avoid edema and erythema in human soft tissue. Four samples of crosslinked hyaluronic acid gels were prepared to have certain values within the complex viscosity(G*) - range of commercial dermal filler products. G* of four different crosslinked gel samples were about 119, 219, 328 and 431 Pa.s, respectively. Edema did not occur in all samples during the experiment period(12days). Increased G' on crosslinked gels showed stronger symptom of erythema than gels having low values. Erythema level was negatively correlated with viscosity of crosslinked hyaluronic acid gels. Increase of G" was related to reduction in erythema level, whereas higher G' value exhibited stronger symptoms of erythema. Our study will give a reference guide to the ideal range of viscosity, elasticity and viscoelasticity for crosslinked hyaluronic acid gels to avoid and mitigate erythema when implanting in human soft tissue as dermal filler.

Wednesday 6:30 Ballroom on 4th floor PO107

Flow behavior of woody biomass in a lab-scale compression twin-screw compounder

Ehsan Akbari Fakhrabadi[1], Matthew Liberatore[1], and Jonathan Stickel[2]
[1]Chemical Engineering, University of Toledo, Toledo, OH 43606-3390, United States; [2]Biosciences Center, National Renewable Energy Laboratory, Golden, CO 80401, United States

Global interest in using biomass as an energy source has been increasing due to potentially significant socio-economic and environmental benefits relative to fossil energy. Although much more attention has been devoted to biomass conversion technologies, feeding and transport of solid biomass is one of the most problematic components of many biomass conversion processes. The oversight may derive from the assumption that biomass feedstock handling is similar to coal feeding operations. However, biomass particles, whether derived from woody or agricultural feedstock, vary greatly in size, shape, density, and moisture content. High cohesiveness, low bulk density, and poor material flow characteristics often prevent continuous feeding due to bridging, rat-hole formation, blockage, and seal failures. In this work, transporting biomass solids in compression-screw feeders is a primary focus. In order to mimic the flow properties of compressed biomass inside a compression-screw feeder, rheological properties of three types of compressed lignocellulosic biomass were investigated using a co-rotating twin-screw microcompounder. Experiments were conducted to find the impact of moisture content, particle size and type, and screw speed on rheological properties of forest residual particles and sawdust. Force and screw-speed data from the microcompounder were correlated to rheology data using low-density polyethylene and a traditional rheometer as controls. For woody biomass, increasing moisture from 10 to 50% reduced the viscosity of the compressed biomass. Also, higher screw speeds (10 to 90 rpm) led to a lower viscosity. At elevated screw speeds, significant temperature differences were measured between the initial and final states, which should be accounted for in equipment design and operation. Power-law and Cross models fit viscosity data well with parameters comparable to those of other high-solids biomass slurries.

Wednesday 6:30 Ballroom on 4th floor PO108

Rheological evaluation of hyaluronic acid and proteoglycan in well-defined shear flow fields

Hye-Jin Ahn and Ki-Won Song

Department of Organic Material Science and Engineering, Pusan National University, Busan 46241, Republic of Korea

Hyaluronic acid (HA), also called Hyaluronan, is one of the filler materials satisfying the biocompatibility factors, which has glucosaminoglycan structure with linear polysaccharides consisting of repeating units of D-glucronic acid and N-acetylglucosamine. Due to the HA exists in the dermis, the skin is possible to retain moisture, prevent wrinkles, activate skin cell to recover injuries caused by pimple or burn. Haigh ratio of HA, especially, acts like a cushion to protect intercellular matrix and to give proper volume.

As another notable substance, proteoglycan (PG) is one of the glycosylated proteins, which has a core protein with covalently attached glycosaminoglycan (GAG) chains containing repeated disaccharide units. Diverse species of proteoglycan are existed in extracellular matrices. Based on their characteristic complex structures, these proteoglycans can generate hydration and swelling pressure enabling to withstand compressional forces.

Becoming an aging society, interests in health care and cosmetics are getting bigger in order to keep or regain youthfulness. The functions/abilities of HA and PG (such as holding/maintaining the water or viscoelasticity in the skin or cartilage) can be assessed as being optimized for filler substance in medical and cosmetic industries. Especially, it will be the most popular raw material used for the medical injection products.

Rheological approach of these materials is of great importance and their correct evaluation can provide valuable information that can be used in quality control of commercial production, storage stability, and sensory assessments of consistency and texture in actual use.

The main objective of present research is to systematically evaluate and compare the rheological behavior of proteoglycan as well as HA fillers according to the extent of crosslinking using a strain and stress-controlled rotational rheometry system in various well-defined shear flow fields including steady, oscillatory, and transient shear flow conditions.

Wednesday 6:30 Ballroom on 4th floor PO109

Rheology of starch gelation using a new pressurized pasting cell

Yash Adhia, Amit Ahuja, Reginald Lee, Alina Latshaw, and Peter Foster

TA Instruments, New Castle, DE 19720, United States

Characterizing processing behaviors are vital for the successful production of food products. In the food industry, many food products experience extreme processing conditions of high temperature and high stresses. The measurements of sample behavior for water-based formulations above 100 °C is extremely challenging due to changes in material composition from the boiling of volatile ingredients. We have developed a high-sensitivity, pressurized starch pasting configuration (up to 5 bar) which utilizes a design free of mechanical bearings and seals, resulting in an order-of-magnitude improvement in torque sensitivity (1 µN.m in oscillatory and 10 µN.m in shear flows) compared to traditional rheometer pressure cells. A pressurized atmosphere suppresses boiling of the volatile components, allowing us to characterize the structure-property relationships of the sample over a range of testing conditions (-5 to 150 °C). In this work, the in-situ gelatinization of starch dispersions of varying starch particle weight fractions was studied as they were subjected to elevated temperature (120 °C) at a fixed shear rate. We determined typical parameters associated during gelatinization such as onset and peak temperature along with peak viscosity to probe the impact of high temperature on the gelation process and the rheological properties of the final starch paste. Additionally, yield stresses of the final paste, measured at 120 °C, were examined for varying particle weight fractions through traditional flow and oscillatory methods. The yield stress and the viscosity rapidly increase with increasing particle concentrations above a critical fraction of 0.04. Yield stresses at 120 °C ranged from 0.25 - 6.5 Pa for weight fractions between 0.05 and 0.15 following a power-law dependence, with 0.05 being the minimum starch weight fraction for which there was any measurable yield stress. The starch pastes were found to exhibit shear-thinning and significant thixotropic behavior.

Wednesday 6:30 Ballroom on 4th floor PO110

Relating lung surfactant phases and its bulk rheology

Clara O. Ciutara and Joseph A. Zasadzinski

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

Lung surfactant is a lipid-protein mixture lining the alveolar air-water interface that forms lipid bilayer vesicles in water. Using cone-and-plate rheometry, we demonstrate that three clinical lung surfactants: Survanta, Curosurf, and Infasurf exhibit shear-thinning behavior. We hypothesize that the different composition of each clinical surfactant dictates the different phases of the bilayers as reflected in the measured viscosity values that differ greatly. We observe that increasing temperature causes both an increase and decrease in viscosity for different lung surfactant mixtures, and we hypothesize that this is because the phase transition occurring with the change of temperature leads to bilayer phases with different deformability, and thus also different bilayer volume fraction as well as rigidity. This observation suggests that by varying temperature of lipid bilayer with different composition, the phase of the lipid bilayer can be tuned, and therefore also its rheological properties. We also note that despite the surface-active interface, the contribution from the interface to the measured bulk rheology of lung surfactant is not significant as we observe consistency throughout different geometry: cone and plate, cup and bob rheometry, capillary viscometry [Lu et al., 2009], and magnetic wire microrheometry [Thai et al., 2019]. This observation suggests that interfacial film formation does not always impart an artifact in bulk rheometry of surface-active materials.

Wednesday 6:30 Ballroom on 4th floor PO111

Characterizing rheological behavior of a corn stover biomass slurry

Ryan Szeto[1], Jonathan C. Overton[2], Antonio Carlos Freitas dos Santos[2], Eduardo A. Ximenes[2], Nathan S. Mosier[2], Michael Ladisch[2], and Kendra Erk[1]
[1]School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States; [2]Department of Agricultural and Biological Engineering, Laboratory of Renewable Resources Engineering, West Lafayette, IN 47907, United States

Application of effective flow models for predicting behavior of biomass slurries currently does not exist. Rheological properties of biomass are poorly understood due to their large particle size distribution and heterogeneity in shape which restricts viable test measurements. To create an accurate flow model for biomass slurries, samples are characterized with a four-bladed vane and starch cell fixture to account for sedimentation and wall slip effects. Biomass slurries are produced at multiple solids loading (10-30% w/v) of pelleted corn stover and mixed at multiple time scales between 30 minutes and 8 hours at a temperature of 50^{o}C. The effect of an enzyme liquefaction process incorporating Celluclast 1.5L enzyme is also observed. Flow curve experiments between 0.1-1000s^{-1} are conducted in a wide gap cell to determine the yield stress and flow behavior. A decrease in the yield stress from 170 to 60 Pa with an enzyme treatment is consistent with trends found in existing data. The effect of a rest period (1-360 minutes) between repeated flow curves is measured and shown to decrease yield stress (30-70% reduction) of slurries for short rest times. Mathematical models are fit to the corn stover flow curve data and can be fitted to flow curve data and describe the viscosity and shear thinning behavior observed in the samples. An accurate model for biomass slurries can be used to predict material flow behavior in a biorefinery to optimize the production of ethanol for biofuels.

This work was supported by DOE grant EE0008256, Analytical Modeling of Biomass Transport and Feeding Systems.

Wednesday 6:30 Ballroom on 4th floor PO112

Rheology of graphene oxide embedded and carbamoylated chitosan hydrogels

Sai Geetha Marapureddy[1], Prachi Thareja[1], Sharad Gupta[2], and Siddhant Kumar[2]
[1]Chemical Engineering, Indian Institute of Technology Gandhinagar, Gandhinagar, Gujarat 382355, India; [2]Biological Engineering, IIT Gandhinagar, Palaj, Gandhinagar, gujarat 382355, India

Hydrogels are 3D crosslinked network structures comprising of hydrophilic polymers holding water in the interstitial spaces of the network which can be crosslinked either chemically or physically. Natural polymers such as chitosan (CH) are non-toxic, abundant, and cheap, but they lack mechanical strength. In this study, we investigated both the ways of crosslinking on chitosan to explore biomedical applications such as drug delivery and tissue engineering. The carbamoylation reaction performed on chitosan introduced the uriedo linkage on the free amino groups and thus resulted in the gel formation due to the hydrogen bonding. The oscillatory rheology studies of Carbamoylated Chitosan (CC) showed that the storage modulus is 104 times of the pristine. 1 w/v% chitosan is flowable and cannot hold cells, but the gel-like structure of CC can hold cells. It is proven from the spheroid formation of A549 cells on the CC gel and also observed that cells are dispersed at different heights of the gel. This study emphasizes that CC can be used as a scaffold for tissue engineering. Chitosan is also chemically crosslinked by Glutaraldehyde (GA) by Schiff base reaction, but in order to reduce the GA content, the polymeric matrix is reinforced by the addition of Graphene Oxide (GO) in various concentrations. GO, has a high surface area and density of oxy functional groups on its edges and basal planes increases the hydrophilicity and reactivity. The ionic interactions between GO and CH result in the multifold increment in the storage modulus, G' of GO-based gels. G' value of 0.5 wt% GO comprised gel 7.2 times greater than the pristine. These nanocomposite hydrogels are cast as films and characterized with DMA, which shows 20 times more Young's modulus than the pristine chitosan which is in line with the observed rheological signatures. Drug delivery studies carried on these films showed an increased drug loading with the addition of GO and a restricted delivery due to the presence of GA.

Wednesday 6:30 Ballroom on 4th floor PO113

Determination of statistically significant correlations between physiological and rheological model parameters of human blood

Matthew J. Armstrong[1], Michael Deegan[1], Jason Barnhill[1], Ken Wickiser[1], Nick Clark[2], and Jeff Baker[3]
[1]Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States; [2]Mathematical Sciences, United States Military Academy, west point, NY 10996, United States; [3]Lab, Keller Army Community Hospital, west point, NY 10996, United States

Recent work modeling the rheological behavior of human blood indicates that blood has all of the hallmark features of a complex material, including shear-thinning, viscoelastic behavior, a yield stress and thixotropy. After decades of modeling steady state blood data, and the development of steady state models, like the Casson, Carreau-Yasuda, Herschel-Bulkley, etc. the advancement and evolution of blood modeling to transient flow conditions now has a renewed interest [1,2,5,11]. Using recently collected steady state human blood rheological data we show and compare modeling efforts with several new models including the new modified Horner-Armstrong-Wagner-Beris (mHAWB), the viscoelastic enhanced Modified Delaware Thixotropic Model (MDTM), and Bautista-Monera-Puig, and Blackwell TEVP model. We will then use the best fit rheological model parameters to compare with physiological blood parameters such as hematocrit, glucose, triglycerides, LDL and HDL. To meet this end we will incorporate the correlation matrix, looking for statistically significant correlations by interpretation of the correlation coefficients and associated p-values. Lastly we will graphically show the most meaningful correlations and compare to similar work from literature. To fit the rheological data to the models a stochastic, global optimization algorithm is used.

Wednesday 6:30 Ballroom on 4th floor PO114

Rheological characterization of dynamic re-engineering of the pericellular region by human mesenchymal stem cell-secreted enzymes in well-defined synthetic hydrogel scaffolds

Maryam Daviran[1], Sarah M. Longwill[2], Jonah F. Casella[1], and Kelly M. Schultz[1]
[1]Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; [2]Bioengineering, Lehigh university, Bethlehem, PA 18015, United States

Human mesenchymal stem cells (hMSCs) are able to migrate from their niches toward wounded areas to regulate the healing process and tissue regeneration. To migrate, hMSCs secrete matrix metalloproteinases (MMPs) to degrade and remodel the extracellular matrix (ECM). The ECM is complex and presents unique physical and chemical cues to the cells that affect cellular migration. Understanding these cell-ECM interactions is important to improve the design of scaffolds that direct cells to enhance wound healing. To understand these interactions, we encapsulate hMSCs in a synthetic hydrogel that recapitulates aspects of the native ECM. Our hydrogel is composed of 4-arm poly(ethylene glycol) end-functionalized with norbornene chemically cross-linked with an MMP degradable peptide sequence. We use multiple particle tracking microrheology (MPT) to dynamically measure hMSC-mediated reengineering of the pericellular region. MPT measures the Brownian motion of fluorescent particles embedded in the hydrogel. MPT measurements around hMSCs characterize a reverse reaction-diffusion profile with the greatest degradation in the farthest region from the cell center. We hypothesize that cells are also secreting tissue inhibitor of metalloproteinases (TIMPs). TIMPs bind to MMPs and inhibit MMP scaffold degradation by creating MMP-TIMP complexes. Four TIMPs have been identified (TIMP 1 - 4) and hMSCs mostly secrete TIMP-1 and -2. We investigate the role of TIMPs in matrix remodeling by neutralizing them. After TIMP neutralization, the degradation profile changes to a reaction-diffusion profile. We also measure a significant increase in cellular speed when both TIMPs are inhibited. After TIMP inhibition, MMPs are actively degrading the scaffold and there is less physical barrier for cell migration resulting in increased scaffold degradation and motility. This study could help us to better understand cell-material interaction which could lead to the design of implantable biomaterials that effectively deliver hMSCs to wounded areas.

Wednesday 6:30 Ballroom on 4th floor PO115

Comparison of the non-linear rheological behaviour of the Ocium basilicum seed mucilage with pectin gels

Bhuvsmita Bhargava, Jacob John, and Susy Varughese
Department of Chemical Engineering, Indian Institute of Technology, Madras, Chennai 600036, India

Hydration of the seeds of the Ocimum basilicum (Basil) results in a transparent mucilage which plays a vital role in seed germination, adhesion and dispersal. The mucilage is made up of polysaccharides such as pectin, cellulose and hemicellulose. Pectin is known for its ability to crosslink in the presence of calcium to form hydrocolloidal gels. The interplay between the pectin and calcium concentrations, degree of esterification and the pH determines the nature and extent of crosslinking and the rheological behaviour of these gels. The rheology of commercial, plant derived pectin solutions and gels has been extensively studied in the past due to their relevance in various food applications. However, it is not clear how the calcium crosslinking, cellulose content, degree of esterification etc. contribute to the gel structure of the seed mucilage. The present work uses Large Amplitude Oscillatory Shear (LAOS) rheology to determine the degree of esterification and the extent of calcium crosslinking in the Basil seed mucilage. Experiments carried out on the mucilage along with calcium crosslinked pectin gels are used to compare the response of both. We observe that the mucilage behaviour is largely gel-like, with a plateau at lower strain amplitudes and shear thinning at higher strain amplitudes. The non-linear signatures, such as the loss modulus overshoot and strain stiffening observed in pectin-Ca gels is compared with that of mucilage to understand the extent of calcium crosslinking and the degree of esterification.

Wednesday 6:30 Ballroom on 4th floor PO116

Cross-sectional focusing and vortex dynamics of red blood cells in a constricted microfluidic channel

Steffen M. Recktenwald[1], Asena Abay[1], Thomas John[1], Lars Kaestner[2], and Christian Wagner[1]
[1]Department of Experimental Physics, Saarland University, Saarbruecken 66123, Germany; [2]Theoretical Medicine and Biosciences, Saarland University, Homburg 66424, Germany

The cardiovascular system is a complex network of branching vessels that transport and distribute blood through our bodies. Blood vessels can exhibit complex geometries and cross-sections, such as sudden constrictions and expansions in stenosed arteries, that dramatically change the spatial distribution of passing cells or particles. To mimicking pathophysiological geometric blockages and obstructed vessels in the circulation, constricted microfluidic channels are commonly used to study the flow of red blood cell (RBC) suspensions. However, knowledge about the distribution of cells in the channel cross-section in non-confined flows is still missing, which can help to understand the unique flow properties of blood in microvessels and can improve high-throughput microfluidic cell sorting and plasma extraction.

Here, we experimentally probe the distribution and velocities of RBCs across the channel width as well as the channel depth in a sudden contraction-expansion geometry and demonstrate how the constriction dramatically affects the spatial cell distribution. Upstream of the contraction, RBCs are homogeneously dispersed in the channel cross-section. However, tracking individual RBCs in multiple planes across the channel depth reveals a strong focusing near the four channel faces post-contraction. Additionally, we observe cell-depleted zones in the channel center and close to the four corners of the channel cross-section. We discuss how this non-uniform spatial distribution of cells results in an apparent double-peaked velocity profile in particle image velocimetry measurements, providing a better understanding of the influence of geometry-induced focusing effects on velocimetry techniques. Covering a broad range of pressure drops demonstrates that this phenomenon arises above a critical Reynolds number. Further, we show that cell deformability influences the trapping of cells in the recirculation zones downstream of the contraction, highly relevant for biomedical cell-sorting applications.

Wednesday 6:30 Ballroom on 4th floor PO117

Rheology of thermosetting multi-layer coating systems

Steven V. Barancyk, Hao Sun, and Raymond A. Quiroz
Coatings Innovation Center, PPG Industries, Inc., Allison Park, PA 15101, United States

Automotive coating systems are typically comprised of multiple layers (clearcoat, basecoat, primer), which are applied wet-on-wet to each other and cured together. It is well known that underlying layers can influence the appearance and physical properties of the overall coatings stack. Studying the rheological properties of the layers separately can be useful, but can sometimes be misleading due to intermixing and migration of components between layers. Rheological measurements on multi-layer stacks can provide insight into the behavior of these complex systems.

Wednesday 6:30 Ballroom on 4th floor PO118

Rheology of Swiss cheese fondue

Pascal Bertsch, Laura Savorani, and Peter Fischer
IFNH, ETH Zurich, Zurich 8092, Switzerland

Cheese fondue is a traditional Swiss dish prepared by melting cheese under the addition of wine, starch, and seasoning. Thus, fondue is a multi-phase system with complex colloidal interactions and rheology. The viscosity of fondue is of particular importance for mouthfeel, flavor perception, and making the cheese cling to the bread for consumption. We tackled the complex multi-phase system fondue from a material science perspective, providing a scientific framework for the influence of fondue ingredients and their interactions on the rheology of cheese fondue*. Fon-due can be considered a water continuous system whose viscosity is influenced by the interactions of its main colloidal ingredients: dispersed casein micelles, emulsified fat droplets, and swollen starch granules. A model moitié-moitié fondue was prepared with water and the influence of starch concentration, ethanol content, and pH, on fondue rheology were assessed. Further, alternative thickening agents (xanthan gum and iota-carrageenan) were employed to investigate their behavior in a complex food system like fondue.

*Ref) Bertsch, P.; Savorani, L.; Fischer, P. Rheology of Swiss Cheese Fondue. ACS Omega 2019, 4 (1), 1103-1109.

Wednesday 6:30 Ballroom on 4th floor PO119

Material selection design tools for nonlinear elastic solids in soft machines

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

Soft machine design is a new frontier for using rheologically complex materials, however we lack a systematic design toolbox for such efforts. We study existing design tools, identify limitations, and present new design tools for rheologically-complex soft solids. We identify material properties and features that may be vital for optimal soft machine performance, such as intrinsic nonlinearities, variable stiffness, and strain to break. Keeping these properties in mind, we explore new design-based organizations of knowledge: (i) design motivated constitutive modeling, (ii) Ashby-style material selection charts, and (iii) material formulation recipes. As a result, we develop new Ashby-style diagrams with properties not typically reported, include soft materials that tend to be missing from material databases, and organize knowledge in a way that streamlines material selection for soft machines. Soft robot actuators, grippers, and skins, as well as medical devices, are just a few of the many soft systems that may benefit from the proposed soft machine design tools.

Wednesday 6:30 Ballroom on 4th floor PO120

Viscosity of an industrial, engineered polysaccharide slurry

Caroline E. Giacomin[1], Kyle Kim[2], and Norman J. Wagner[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]Experimental Station, DuPont Biomaterials, Wilmington, DE 19806, United States

An industrial polysaccharide ((1?3)-α-D-glucan), produced from an enzymatic reaction of sucrose, is characterized in aqueous solution. This study focuses on the rheological behavior when dispersed in water with varied dispersion techniques, concentration, and polymer chain lengths. A rheological protocol is developed to yield accurate and reproducible rheological measurements. Concentrated slurries show a pronounced yielding behavior that is followed by a flowing sample that further shear thins at higher shear rates, while more dilute samples show gravitational settling. The slurry viscosity observed beyond the yield stress can be approximated with a Cross model and the required constants have been determined: An exponent value of 1.18 and a characteristic shear relaxation time of 0.077 s. These constants are found to vary systematically with degree of polymerization. High shear processing is shown to reduce the skeletal density of the polysaccharide and increase the yield stress at constant weight fraction. The high and low shear viscosities can be approximated by a modified Mooney equation and percolation-like scaling is observed for the yield stress. These model parameters are interpreted in terms of the structure of the polysaccharide in solution. The shear rheology of this engineered polysaccharide viscosity can therefore be fully modelled when processing technique and solids weight percentage are known.

Wednesday 6:30 Ballroom on 4th floor PO121

Application of powder rheometer to determine powder flow properties

Xinzhu Gu, Hao Sun, Sarah Sisley, and Scott Moravek
PPG Industries, Inc., Pittsburgh, PA, United States

Flowability of powders is important in powder manufacturing and application processes such as mixing operations, storage, transportation, and spraying. Powder clumping or caking can significantly impact processing efficiency and product yield in industrial operations. Numerous methods of characterization have been previously developed and are currently used to measure flow properties of powders, such as measurement of an angle of repose, minimum aperture for a powder flowing out of a hopper, or packing density. While these tests have practical value, they do not yield fundamental insights into the material properties of powder systems or the mechanisms driving observed behaviors. Recently, we studied cohesive strength between powder particles by employing powder rheometer. The effect of storage temperature, water content, flow additives, and manufacturing process on flow properties of different powder systems was investigated. Structure-property relationship was further studied by thermal analysis and microscopy. Our results revealed that material properties such as particle size and transition temperatures, and environmental conditions like temperature and humidity all play important roles in powder flow.

Wednesday 6:30 Ballroom on 4th floor PO122

3D printing liquid metal-silicone composites for wearable electronics applications

Taylor V. Neumann and Michael D. Dickey
Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Additive manufacturing has received significant public interest due to its ability to manufacture unique designs not possible with traditional manufacturing techniques. For the field to make steps away from highly niche use cases, novel material designs are required. Specifically, we have focused on soft and conductive materials, for use in soft electronics and wearable devices. Typically, printing metals either requires high temperature sintering processes to achieve high conductivity. Instead, we have focused on composite materials using low-melting point metal alloys. These alloys are liquids at room temperature and feature the high conductivity of a metal. By dispersing these alloys as particles within a polymer matrix, we are able to develop an effective conductive "ink" that is useful for 3D printing. After printing and curing, these materials exhibit mechanical behavior similar to the polymer, but can be mechanically sintered with an applied pressure to exhibit high conductivity. Understanding the rheological properties of a material is a key step in developing a printable ink. Shear-thinning behavior is crucial for an ink that can be easily extruded but maintain an intended geometry after extrusion. The rheological behavior of these materials can be tuned by varying the loading of particles, which also impacts the eventual conductive behavior. Using these materials we can rapidly print and iterate on a variety of conductive patterns.

Wednesday 6:30 Ballroom on 4th floor PO123

Using dynamic shear rheological analysis to generate in-situ injection molded multi-scale wholly thermoplastic composite materials

Jier Y. Han and Donald Baird
Chemical Engineering and Macromolecules Innovation Institute, Virginia Tech, BLACKSBURG, VA 24061, United States

Wholly thermoplastic composites are the materials of choice for effectively reducing the weight of automobiles and thereby reduce fuel consumption and environmental pollution. They are materials that are based on matrices reinforced with thermotropic liquid crystalline polymers (TLCPs). In this work, small amplitude oscillatory shear (SAOS) measurements in temperature sweep mode were used to determine appropriate processing conditions of a TLCP, Vectra B, to reinforce a nylon 6 (PA6) matrix. Vectra B and PA6 have miss-matching melting points, and PA6 can degrade quickly at high temperature. Dynamic shear rheology under the time sweep mode was used to identify the feasibility of in-situ injection molding Vectra B/PA6 composites. The viscosity of PA6 has less than 10% change in 20 minutes under the in-situ injection molding processing temperature of 290o C. In order to enhance the mechanical properties of the in-situ injection molded wholly thermoplastic composite Vectra B/PA6, 1wt% addition of multi-walled carbon nano-tubes (MWCNTs) was applied. While maintaining the modulus and enhancing the strength by 28% in the transverse to fluid flow direction of the wholly thermoplastic composites, the super cooling behavior of Vectra B and degradation condition of PA6 have minor effect as shown by the rheological test. Moreover, MWCNTs have the ability to increase the viscosity of the matrix, PA6, which will reduce the difficulty of blending Vectra B into the matrix.

Wednesday 6:30 Ballroom on 4th floor PO124

Nonlinear rheological behavior of asphalt binders

Saqib Gulzar and Shane Underwood
Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, NC 27695, United States

Asphalt concrete is a primary road building material and is therefore used extensively throughout the United States and the world. The cement used to bind the rock together in this concrete and create a cohesive and strong material is asphalt binder. The rheological behavior of asphalt binders greatly affects the pavement performance and as a result there has been tremendous study on the properties of asphalt binder and their relationship to pavement performance. The majority of these efforts in the United States over the past three decades have focused on only the linear rheological behaviors even though when in-service these materials experience conditions exceeding their linear limits. Nevertheless, this practice has been sufficient for many practical engineering purposes owing to the predominant use of so-called straight run asphalt binder, which have largely similar relationships between their behaviors in the linear and non-linear ranges. However, the increased use of polymer and chemically modified asphalt binder systems obviates the implied correlations between linear and non-linear behaviors of the asphalt binder. These modified systems include crumb rubber, polymers, polymer nanocomposites, sulfur, phosphoric acid, and many others. As a result there is a need to effectively characterize the nonlinear rheological behavior of asphalt binders and better correlate these with the performance of pavements. In this study, large amplitude oscillatory shear rheology is used to characterize nonlinear rheological behavior of unmodified and modified asphalt binders. The stress response is analyzed using Fourier Transform rheology and stress decomposition to an orthogonal set of Chebyshev polynomials to obtain elastic and viscous components. Further, the dependence of nonlinearity on strain amplitude, frequency, and temperature is studied. The idea of using LAOS in asphalt binder community is articulated and its pros and cons are discussed.

Wednesday 6:30 Ballroom on 4th floor PO125

Rheology-guided direct-write printing of carbon nanotube structures

Crystal E. Owens, Gareth H. McKinley, and Anastasios J. Hart
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

The bulk properties of components fabricated by direct-write 3D printing are governed by the key characteristics of the original ink in combination with structure imposed by the printing process. Nanomaterials can provide novel properties not exhibited in bulk materials, and provide a route to functional inks that, for instance, can enable 3D printing of electronic and sensing components. In particular, carbon nanotubes (CNTs) have been measured to have outstanding electrical conductivity and current carrying capacity. Here, we present the development and direct-write printing of aqueous CNT inks in the interest of establishing novel manufacturing methods for printed electronics.

CNTs at high concentrations (>0.5%wt) entangle and act rheologically as thixo-elasto-viscoplastic materials. As CNTs behave as rigid rods in solution, strong shear and extensional flow have been shown to create flow-induced alignment. Due to strong shape anisotropy, the axial alignment of component CNTs is known to systematically affect ultimate strength and electrical conductivity of macroscopic CNT objects.

We print by dispensing CNT ink from a needle onto a motorized substrate, optionally extruding beneath a coagulating liquid that precipitates the CNTs, rapidly locking flow-oriented CNT structures in place. By tailoring the flow kinematics during our printing process, we enforce external control over the development of the microstructure, thus directing the final properties. We describe the effect of solution concentration on the rheology of single-walled CNTs dispersed in water, and explore the impact of shear-driven and extension-driven alignment on morphology and final properties of printed structures. We report the influence of processing parameters such as the rate of elongation, nozzle height, and shear rates on the feature resolution and conductivity of extruded features, and suggest relationships that connect rheological properties of the ink to printability of controllable and fine features.

Wednesday 6:30 Ballroom on 4th floor PO126

Direct visualization of thermoplastic melt in material extrusion 3D printing using neutron imaging

Jonathan E. Seppala
Materials Science and Engineering Divison, National Institute of Standards and Technology, Gaithersburg, MD 20899-8542, United States

Although ubiquitous and inexpensive, materials development for material extrusion (MatEx) additive manufacturing (AM) remains challenging. A limited understanding of heat transfer dynamics in the "hot-end" of the extrusion system leads to time consuming trial and error approaches to ensure proper performance of a given material in the extrusion (or print) head. In MatEx AM a thermoplastic filament 1.75 mm or 3 mm in diameter is fed into a heatsinked extrusion head using a pinch wheel mechanism. The diameter of the opening for the filament is slightly (~0.1) mm wider than the filament limiting thermal contact on startup. Where and how the polymer begins flowing remains an area of debate especially during startup flows. Using neutron imaging the startup flow and steady state melt pool can be directly visualized under different temperatures and feed rates.

Wednesday 6:30 Ballroom on 4th floor PO127

Structure formation in alkali-activated binders for development of sustainable construction materials

Jennifer N. Mills[1], Norman J. Wagner[1], and Paramita Mondal[2]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, United States

Cement production and use is one of the leading contributors to anthropogenic CO_2 emissions. Alkali-activated binders present opportunities for significant reduction in CO_2 emissions as well as in-situ resource utilization for lunar and Martian construction in support of human space exploration. The chemical composition of these types of binders has been shown to impact macroscopic properties such as workability and strength, but there is a lack of connection to the microstructure responsible or to the reaction mechanism of the 'geopolymer' hydration reaction and subsequent binder formation. Understanding the rheology development in such systems is crucial for applications ranging from traditional pumping, pouring, and setting as well as with the growing interest in 3D printing. Consequently, a mechanistic and quantitative understanding of the chemical kinetics and dynamics of microstructure formation and associated rheology development in model geopolymer binders will facilitate the universal engineering of construction materials from a variety of raw materials here on Earth, as well as those found on the surface of the moon and Mars.

The current work focuses on structural characterization of aluminosilicate gel hydrates with the objective of relating chemical composition to phase behavior. Gel formation kinetics are simulated through the dosing of the aluminum concentration in solution, the species which acts as the limiting reactant in the geopolymer binder, dissolving from aluminosilicate grains. Small amplitude oscillatory shear (SAOS) experiments characterize the microstructure development during transitions from liquid to gel. Complementary scattering data shows the microstructure responsible for this rheological behavior. A percolation threshold is identified at a relative concentration of 0.25 moles aluminum to 2 moles of silica and 1 mole of sodium in solution. These model system studies provide insight into the more complex rheological behavior of geopolymer cements.

Wednesday 6:30 Ballroom on 4th floor PO128

Application of melt rheology in the development of novel hybrid composites

Tianran Chen[1] and Donald Baird[2]
[1]Macromolecules Innovation Institute, Virgina Tech, Blacksburg, VA 24060, United States; [2]Virginia Tech-Chemical Engineeering, Blacksburg, VA 24061-0211, United States

Polymer rheology plays a significant role in many polymer processing operations such as extrusion, injection molding and fiber spinning. Understanding the rheological properties of polymers can help to optimize the processing conditions. The purpose of this work is to optimize the processing conditions of compounding TLCP, GF and PP with dynamic shear rheology and develop recyclable and high-performance hybrid composites. In this work, small-amplitude oscillatory shear (SAOS) rheology was used to optimize processing conditions of reinforcing PP with TLCP and GF. Due to the high melting temperature of TLCP, it is essential to evaluate the thermal degradation behaviors of PP at elevated temperature. The thermal stability of PP at processing temperatures was examined by a SAOS test in the isothermal time sweep mode. Transient shear step strain tests were used to identify the temperature where all the residual crystallites were removed. The presence of the tail of the relaxation modulus was associated with the existence of solid structures. Different compositions of TLCP/GF/PP composites were prepared by the injection molding process. Then these composites were mechanically recycled through grinding and reinjection molding. Mechanical properties of the hybrid composites were investigated. A combination of GF and TLCP as the reinforcement could enhance the recyclability as compared to a composite reinforced with only GF. The processing condition was rigorously devised by utilizing rheological tests to determine the best combination of the recyclability and mechanical performance of hybrid composites

Wednesday 6:30 Ballroom on 4th floor PO129

Effect of block copolymer micelles on the rheology of 3D printable epoxy inks

Daniel V. Krogstad[1], Rishabh Ekbote[1], Gavin J. Donley[2], and Simon A. Rogers[2]
[1]Applied Research Institute, University of Illinois at Urbana-Champaign, Champaign, IL 61820, United States; [2]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Direct Ink Writing (DIW) is a particularly interesting 3D printing technique due to the versatility of the materials classes that can be printed including thermoplastics, thermosets, hydrogels, nanocomposites and ceramic slurries. Contrary to some other 3D printing techniques, the printability of the materials is directly linked to the rheological properties rather than any thermal properties. However, the required rheological behavior can be very complicated and it is poorly understood. This poster will describe our recent efforts to increase our understanding of the structure-property relationships of nanostructured inks using rheology, small angle x-ray scattering (SAXS) and DIW. Our materials system consists of a base epoxy ink, which uses nanoclay to provide shear thinning properties, and block copolymers, which form micelles in the inks. Our work has shown that flow curves, generated from transient creep testing performed at a variety of stresses, can be used as a strong analog to the flow behavior during the printing process. Using this method, we have identified that the flow of these materials has a strongly time-dependent behavior in which the effective yield stress increases over time. This behavior can lead to large decreases in the material flow during printing over time. Interestingly, when the block copolymer micelles are added to the system, the time-dependent increase in the yield stress is minimized relative to the base ink. These results provide new insights in how we can characterize nanostructured inks and the roles of the various components in our formulations.

Wednesday 6:30 Ballroom on 4th floor PO130

Rheology of bacterial suspensions under confinement

Zhengyang Liu and Xiang Cheng
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Bacterial suspensions, a premier example of active fluids, show intriguing rheology different from their counterpart colloidal suspensions. While the bulk rheology of bacterial suspensions has been excessively studied, the rheology under confined geometries has not been experimentally explored. Here, by using a microfluidic channel viscometer, we investigate the viscosity of E. coli suspensions under different degrees of confinement. Strong shear thickening is observed at low flow rates, in consistency with a number of previous studies. More importantly, a strong confinement effect is found when the confinement length is comparable to the running length of a single bacterium. The viscosity of bacterial suspensions decreases by a factor of 3, when the confinement decreases from 60 down to 25 microns. By using fast confocal microscopy to study the velocity profiles, we find that upstream swimming bacteria near the confining walls play a key role in the confinement effect. Based on this picture, we formulate a simple model which qualitatively captures this confinement effect. Our study reveals the interplay between the microscopic dynamics and rheology of bacterial suspensions under confinement. Our results provide a benchmark for testing different rheological models of active fluids and are useful for understanding the transport of microorganisms in confined geometries.

Wednesday 6:30 Ballroom on 4th floor PO132

Investigation of suspension mechanics for cell growth in rotating wall vessel (RWV)

Joshua Adeniran, Mingyang Tan, and Travis W. Walker
Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, SD 57701, United States

Growth of cells have been performed in stagnant broth for ages. This technique has been proven inefficient, as the cells tend to flocculate and settle, leading to deficiency and non-uniformity in nutrient supply to the cells. Rotating bioreactors were developed by NASA to solve these problems, as the environments exhibit "microgravity," and the cells remain suspended in the fluid. Using spherical particles as a surrogate, studies have been completed on rotating reactors, both by experiment and by numerical modeling, to investigate the forces on the cells that influence their movements under these conditions. Further, investigations have been completed into how nutrient transport to the cells are being influenced by the rotation speed of the reactors. However, these cells may exhibit shapes that are aspherical, in which studies are lacking. In this work, Stokesian dynamics was used to simulate and examine the behavior of cells under a wide range of gravitational forces and rotation speeds. To investigate aspherical shapes of cells, the shape is discretized into constitutive spheres that are constrained into rigid-body assemblies and then studied using Stokesian dynamics. Experiments are also being performed to compare with our deductions from simulations.

Wednesday 6:30 Ballroom on 4th floor PO133

Manipulating blood rheology with external magnetic field and application to lower blood pressure

Kazi M. Tawhid-Al-Islam[1], Rongjia Tao[1], Xiaojun Xu[1], Hong Tang[1], and Michael Autieri[2]
[1]Department of Physics, Temple University, Philadelphia, PA 19122, United States; [2]Department of Physiology, Cardiovascular Research Center, Temple University, Philadelphia, PA 19140, United States

Risk of cardiac diseases, such as heart attack, increase greatly with high blood viscosity. Also, turbulent blood flow allows the development of atherosclerotic plaque in vasculature. Presently available medicines, such as Aspirin, may reduce blood viscosity, however, only to worsen the turbulence because the Reynolds number goes up as the viscosity lowers. Here, I will report our Magneto-Rheology (MR) research that addresses both viscosity reduction and turbulence suppression simultaneously. Following the technique of manipulating the rheology of suspension with external influence, we applied a strong Magnetic Field along the blood flow direction. We have observed red blood cells become polarized and aggregate into short chains, which lowers the viscosity along the flow direction. Concurrently, motions deviated from the flow direction are slowed, thus suppresses the turbulence, as evidenced in a system of in-vitro blood flowing through a microfluidic channel placed inside field. Comparing before and after the MR treatment, we found viscosity reduces by 30%. For clinical application, an electromagnet device is designed such a way that only wrist area of right arm would expose to field. Then blood pressure is monitored from the left arm. This study indicates there is definite effect of Magnetic Field on Blood Pressure in human. Besides in-vivo experiment, a small magnet was surgically implanted adjacent to the jugular vein in mice to examine the atherosclerotic plaque formation. With FDA approval we are now proceeding with clinical trials. Upon successful completion, we expect to establish a standard operating procedure for this MR therapy.

Wednesday 6:30 Ballroom on 4th floor PO134

Controlling polymer rheology and self-assembly via low-strength magnetic fields

Karthika Suresh and Michelle A. Calabrese
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

Magneto-active polymer (MAP) materials undergo large deformations or changes in mechanical properties when subjected to a magnetic field. MAP materials consist of dispersed magnetic particles in a polymer matrix, and are promising candidates for next generation soft active materials. However, obtaining magnetically responsive "pure" polymer has traditionally been costly and complex as it required the use of very large fields (= 5T). We recently discovered anomalous rheological responses of concentrated block polymer (BCP) solutions exposed to low strength magnetic fields (=0.3T). These anomalous responses are seen at field strengths over an order of magnitude below previously observed responses and the predicted behavior based on the magnetic susceptibility of the BCP. These self-assembled solutions exhibit up to a 10 order-of-magnitude increase in the elastic modulus with field application, which is reversible upon field removal. The magnetic transition and relaxation dynamics are governed by the field strength, concentration, block chain length and ratio, and the self-assembled structure. No rheological response is observed when homopolymer solutions of the individual blocks are subjected to similar strength fields. This simple way of controlling the properties of concentrated BCP solutions will open an array of applications including sensors, smart vibration absorbers, and artificial muscles.

Wednesday 6:30 Ballroom on 4th floor PO135

Yielding behavior of active colloidal gels

Keara T. Saud[1] and Michael J. Solomon[2]
[1]Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States; [2]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

Colloidal gels are well studied systems which have a network of attractively bonded particles. This network is the origin of important rheological properties such as their linear elasticity and yield stress. Previous work has shown that when embedded with active particles, colloidal gels have enhanced dynamics and a reduction in elastic modulus. These trends are a direct function of the amount of active energy inputted. Here, we extend this research further by looking at the yielding behavior of such active colloidal gels. Activity is triggered by the addition of hydrogen peroxide which, through asymmetrically decomposition, results in self-diffusiophoretic motion. Apparent yield stress of the gels is characterized by three tests: startup of steady shear tests, creep tests, and oscillatory strain amplitude sweeps. Our results show a reduction in the apparent yield stress with increasing activity level. These suggest that embedded active particles switch the material into a mechanically weaker state. These findings further the characterization of gels with multi-state mechanical properties which can be useful for the coating industry, consumer products, and agricultural formulations.

Wednesday 6:30 Ballroom on 4th floor PO136

SoR member survey

Laura Merner
AIP Stat Research Center, College Park, MD 20740, United States

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Gallery of Rheology

Symposium GR
Gallery of Rheology Contest

Organizers: Sibani Lisa Biswal and Steve Hudson

Wednesday 6:30 Main Lobby on 3rd floor GR1

Kaleidoscopic mesophases: Colors of relaxation

Maria Marquez Garcia, Alireza Bandegi, and Reza Foudazi
Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States

Amphiphilic molecules can self-assemble into mesophase structures to minimize their free energy. The structures formed from this self-assembly are known as lyotropic liquid crystals (LLCs). Polarized optical microscopy reveals the characteristic optical textures of lamellar and hexagonal mesophases due to their birefringence. The aim of this work is to study the structural changes of surfactant/ionic liquid mesophases by using polarized optical microscopy. Applying high strains can change the alignment of LLCs, which evolves during relaxation process back to the unaligned state.

Wednesday 6:30 Main Lobby on 3rd floor GR2

The soapy terrace

Chrystian Ochoa and Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States

We visualize the stratified smectic films, and each colored tile represents a discretely distinct thickness.

Wednesday 6:30 Main Lobby on 3rd floor GR3

Schlieren imaging of transition to turbulence for submerged jets of dilute polymer solutions via elasto-inertial streaks

Sami Yamanidouzisorkhabi, Gareth H. McKinley, and Irmgard Bischofberger
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Dilute synthetic and biopolymer solutions have been shown to reduce turbulent drag in pipelines and around marine vehicles due to their viscoelasticity. The very low concentrations of polymer employed in drag reduction studies makes direct imaging of the mixing and turbulent flow structures an outstanding challenge and necessitates an experimental technique to track the evolution of material lines in the dilute polymer solution phase. In this poster, we use Schlieren imaging to visualize jets of dilute aqueous polymer solutions injected into quiescent water. The two phases, i.e., dilute polymer solution and water, have a very small density difference (<1%) making their detection with naked eyes impossible. However, this small density difference provides enough refractive index difference that is tractable with Schlieren imaging. Our visualization not only shows that the turbulence structure is fundamentally different for dilute polymer solutions, but it also reveals a new mode of transition to turbulence that we call it Elasto-Inertial Streaks (EIS). Unlike transition to turbulence for Newtonian fluids, where intermittent turbulent regions between laminar regions, i.e., turbulent puffs, are observed, here the intermittency is completely eliminated and transition to turbulence occurs through the growth and development of streaks of dilute polymer solution phase around the core of the jet.

Wednesday 6:30 Main Lobby on 3rd floor GR4

Baby's pacifier from saliva

Muchu Zhou[1], Zahra Abbasian Chaleshtari[1], Hadi Mohammadigoushki[2], and Reza Foudazi[1]
[1]Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States;
[2]Chemical and Biomedical Engineering, Florida State University, Tallahassee, FL 32310, United States

Saliva plays a vital role in the human mouth health, feeling, and chewing function. 95% of the saliva is water, while the other 5% includes inorganic molecules, lipids, various proteins, and enzymes. The properties of salivary flow have been studied through bulk rheological measurements to some extent. In the present poster, we display three properties of the human saliva, including extensional rheology, dripping, and hitting on the water surface. Unlike water, all of these studies prove the viscoelasticity of saliva and the presence of amphiphilic molecules in it.

Wednesday 6:30 Main Lobby on 3rd floor GR5

Mystic Smoke: The rheology of magic

Arif Z. Nelson[1] and Randy H. Ewoldt[2]
[1]Singapore-MIT Alliance for Research and Technology, Singapore 138602, Singapore; [2]Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Mystic Smoke is a material used in performance magic that is a highly-extensible yield-stress fluid. In this image, rapid extension of a thin film of Mystic Smoke between one's fingers creates numerous thin fibrils due to the material's high extensional viscosity. The fibrils persist due to the yield stress of the fluid and are then able to detach to create a "smoke" effect as shown. These rheological properties combine to allow a performer to produce smoke from their hands and can elevate a simple trick into something seemingly magical. Materials with properties like those of Mystic Smoke are relevant in adhesives as well as extrusion processes that include direct-write 3D printing.

Wednesday 6:30 Main Lobby on 3rd floor GR6

Nocturnal nanoemulsions

Kristine M. Smith, E. Daniel Cárdenas-Vásquez, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Attractive interactions within a colloidal nanoemulsion cause the formation of gel networks which can be spun into fibers. This image, produced using a confocal microscope, illustrates these networks within the cross section of a fiber. The internal fiber structure of the oil (fluorescent) and aqueous (black) phases can be varied by altering temperature and shear rate during fiber spinning. The bright image of the fiber microstructures fluorescing against a black background bears resemblance to the craters pocketing the surface of the moon. Occasionally, defects are created during sample preparation of fiber cross sections. These defects can resemble many forms, from a passing cloud to an NC State wolf calling for its brethren on a cold October night.

Wednesday 6:30 Main Lobby on 3rd floor GR7

Elastic effects in extension with yield-stress fluids

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

Elastic effects in yield-stress fluids manifest as thickening behavior under extensional flows when these fluids are modified to be "stretchy" in addition to being viscoplastic, in contrast to being shear-thinning. We visualize this unique behavior in a new model material in the class of extensible yield-stress fluids: an aqueous suspension of Carbopol microgel particles and high molecular weight poly(ethyleneoxide) (PEO). This demonstrates the unique ability of extensible yield-stress fluids to hold their shape under low stresses, but form continuous filaments under extensional deformations. Such properties are useful for extensive applications including sprays, jets, and 3D printing.

Wednesday 6:30 Main Lobby on 3rd floor GR8

Metamorphosis through viscous fingering

Thitiporn Kaewpetch[1] and James F. Gilchrist[2]
[1]Polymer Science and Engineering, Lehigh University, Bethlehem, PA 18015, United States; [2]Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States

Drying of a droplet of polymer solution in a colloidal crystal demonstrates an evolution of structural morphology from capillary Haines jumping to viscous fingering. These images, taken using confocal microscopy across the entire droplet, are reminiscent of M. C. Esher's *Metamorphosis* series of tessellation inspired artwork.

Wednesday 6:30 Main Lobby on 3rd floor GR9

Flow-structure diptych

Patrick T. Corona[1], Barbara Berke[2], Manuel Guizar-Sicairos[3], Marianne Liebi[2], L. Gary Leal[1], and Matthew E. Helgeson[1]
[1]Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States; [2]Department of Physics, Chalmers University of Technology, Gothenburg, Sweden; [3]Swiss Light Source, Paul Scherrer Institut, Villigen PSI, Switzerland

Material properties of complex fluids are greatly influenced by the flow histories under which they are processed. In this work, we present a Warhol-inspired view into the structure evolution of suspensions of rigid nanoparticles in complex variations of flow type and strength. We employ a fluidic four-roll mill (FFoRM) to generate tunable flows that, when combined with scanning-SAXS measurements, enables the measurement of fluid microstructure under complex flow histories. In one representation, optically-measured streaklines trace the trajectory of fluid elements through such deformation histories; whereas, in another, pixel color and intensity indicate of the orientation and pair alignment, respectively, of the rodlike nanoparticles measured with scanning-SAXS as they move along the flow. Each scanning-SAXS measurement represents more than 2500 discrete measurements of fluid nanostructure in a unique set of flow histories. Varying the flows into the device creates new flow histories for the fluid to navigate, resulting in changes to the evolving suspension nanostructure.

Wednesday 6:30 Main Lobby on 3rd floor GR10

The vane geometry

Crystal E. Owens, Anastasios J. Hart, and Gareth H. McKinley
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

The vane geometry is a tool of choice for rheological characterization of yield stress fluids and gels, due to well-defined circular kinematics of fluid deformation paired with prevention of wall slip. Here, we depict a family of novel 3D-printed vane tools that combines desirable features of the standard 4-arm vane and cylindrical bob into hybrid fractal structures. These vanes, produced by stereolithographic (SLA) 3D printing, create a more axisymmetric stress distribution than the 4-arm vane, less material damage/displacement upon sample loading than the bob, and eliminate wall slip. Desktop SLA machines permit creation of intricate structures with resolution < 200μm from photopolymer materials having good mechanical stability and solvent resistance.

Wednesday 6:30 Main Lobby on 3rd floor GR11

Non-affine displacements in soft gels

Minaspi Bantawa and Emanuela Del Gado
Department of Physics, Georgetown University, Washington, DC 20007, United States

The richness and diversity of the rheological response of gel networks could be understood in terms of the propensity to undergo, or not, non-affine motion built-in in specific microstructural features. In gels where connections are sparse, extended softer domains can undergo large non-affine displacements even in presence of a small applied deformation. Gel microstructures which are more tightly and homogeneously connected, instead, will tend to feature smaller and especially more localized non-affine displacements that can be, however, strongly correlated through the efficient propagation of elastic strains.

The two figures are spatial maps of the microscopic non-affine displacements obtained when model gel networks are subjected to small amplitude oscillatory deformations, showing the case of sparsely and heterogeneously connected gels (left) versus more homogeneously connected ones (right). What are the implications in terms of the linear viscoelastic spectrum of these materials?

Wednesday 6:30 Main Lobby on 3rd floor GR12

Mechanical contour maps of human blood

Matthew J. Armstrong[1], Simon A. Rogers[2], Gavin J. Donley[2], and Jeffrey S. Horner[3]
[1]United States Military Academy, West Point, NY 10996, United States; [2]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; [3]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States

The mechanical properties of human blood are an underdeveloped area of study, yet with proper analysis, the mechanical properties of blood could be used for clinical diagnoses. Using the unique transient rheological signature of a blood sample, there is a possibility that blood rheology measurements could be used as a method of diagnosis and/or differentiation. Rather than focusing solely on traditional transient experiments such as Large Amplitude Oscillatory Shear (LAOS) hysteresis curves are utilized to depict blood flow. The results of these tests are visualized by blood "mechanical contours" that have the advantage of depicting the evolving mechanical properties of the material over a wide range of flow conditions. Rather than solely using the traditional discrete Fourier transform to analyze the hysteresis curve data, a more recent method, Sequence of Physical Processes (SPP), is applied to these transient tests.

Wednesday 6:30 Main Lobby on 3rd floor GR13

When drops collide

Bavand Keshavarz, Michela Geri, and Gareth H. McKinley
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Using high-speed photography, we study the patterns of Newtonian and viscoelastic droplets when they collide into each other.

Wednesday 6:30 Main Lobby on 3rd floor GR14

A nano-puffer fish having lunch

E. Daniel Cárdenas-Vásquez, Alan R. Jacob, and Lilian C. Hsiao
Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States

Polymer coatings are widely used to protect metal substrates from failure and corrosion. However, when the coatings are subjected to different etching environments, they form blister-like structures. A Through the Lens Detector (TLD) is used to obtain an electron microscopy image which shows a partially burst blister on the surface of a polymer-coated aluminum panel. The blister resembles the structure of a puffer fish that is about to eat.

Author Index

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Plenary Lectures and Award Presentation

Monday, October 21 *8:30 AM* *Rom 306*	**Statistical physics of active biological matter** Christoph F. Schmidt *Physics, Duke University*
Tuesday, October 22 *Bingham Lecture, 8:30 AM* *Room 306*	**Molecular rheology and synthetic chemistry: A critical partnership for designing flow-responsive matter** Dimitris Vlassopoulos *Institute of Electronic Structure & Laser, FORTH*
Wednesday, October 23 *8:30 AM* *Room 306*	**Rheology of gel networks: Softness, rigidity and failure** Emanuela Del Gado *Department of Physics, Georgetown University*
Thursday, October 24 *Metzner Award Presentation* *8:00 AM, Room 304*	**Symmetric shear banding and collective swarming of bacterial suspensions** Xiang Cheng *Chemical Engineering & Materials Science, University of Minnesota*

Social Program and Special Events

Sunday, October 20	**Rheology Research Symposium**	(continued from Saturday, Oct 19)
	SoR Outreach Event 1:00 PM – 4:00 PM	North Carolina Museum of Natural Sciences
	Welcoming Reception 6:00 PM – 8:00 PM	Main Lobby on 3rd floor of RCC
Monday, October 21	**Student-Industry Forum** 12:00 PM – 1:15 PM *Sponsored by American Institute of Physics and The Dow Chemical Company*	Room 402 of RCC
	Gallery of Rheology Preview 1:30 PM – 4:00 PM	Main Lobby on 3rd floor of RCC
	Monday Evening Reception 6:30 PM – 9:30 PM *Sponsored by TA Instruments*	North Carolina Museum of Art
Tuesday, October 22	**Gallery of Rheology Preview** 8:30 AM – 4:00 PM	Main Lobby on 3rd floor of RCC
	Society Business Meeting 12:00 PM – 1:30 PM	Room 304 of RCC
	Awards Reception 7:00 PM – 8:00 PM	Ballroom Lobby on 4th floor of RCC
	Awards Banquet 8:00 PM	Ballroom C on 4th floor of RCC
Wednesday, October 23	**Gallery of Rheology Preview** 8:30 AM – 4:00 PM	Main Lobby on 3rd floor of RCC
	Poster Session and Reception 6:30 PM – 8:30 PM *Reception sponsored by Anton-Paar USA*	Ballroom C on 4th floor of RCC
	Gallery of Rheology Contest 6:30 PM – 8:30 PM Online voting 10 AM – 8 PM	Main Lobby on 3rd floor of RCC

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