THE SOCIETY OF RHEOLOGY

85^{TH} ANNUAL MEETING PROGRAM AND ABSTRACTS

Hilton Montréal Bonaventure
Montréal, Québec, Canada
October 13 - 17, 2013

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Meeting Schedule

Monday, October 14, 2013

	WS	*VL*	*OT*	*MH*	*CS*
8:30	T. van de Ven (PL1) - *WS*				
9:20	Coffee Break				
10:00	SC1	IP1	MB1	PS1	EM1
10:25	SC2	IP2	MB2	PS2	EM2
10:50	SC3	IP3	MB3	PS3	EM3
11:15	SC4	IP4	MB4	PS4	EM4
11:40	SC5	IP5	MB5	PS5	EM5
12:05	Lunch Break				
1:30	SC6	IP6	MB6	PS6	EM6
1:55	SC7	IP7	MB7	PS7	EM7
2:20	SC8	IP8	MB8	PS8	EM8
2:45	SC9	IP9	MB9	PS9	EM9
3:10	Coffee Break				
3:35	SC10	MS1	MB10	PS10	EM10
4:00	SC11	MS2	MB11	PS11	EM11
4:25	SC12	MS3	MB12	PS12	EM12
4:50	SC13	MS4	MB13	PS13	EM13
5:15	SC14	MS5	MB14	PS14	EM14
5:40	End				
6:00	Industry/Faculty/Student Forum and Mixer *Rheology in the Real World*				

Tuesday, October 15, 2013

	WS	*VL*	*OT*	*MH*	*CS*
8:30	G. H. McKinley (PL2) - *WS*				
9:20	Coffee Break				
10:00	SC15	MS6	MB15	PS15	BM1
10:25	SC16	MS7	MB16	PS16	BM2
10:50	SC17	MS8	MB17	PS17	BM3
11:15	SC18	MS9	MB18	PS18	BM4
11:40	SC19	MS10	MB19	PS19	BM5
12:05	Lunch Break / Society Business Meeting				
1:30	SC20	IP10	MB20	NF1	BM6
1:55	SC21	IP11	MB21	NF2	BM7
2:20	SC22	IP12	MB22	NF3	BM8
2:45	SC23	IP13	MB23	NF4	BM9
3:10	Coffee Break				
3:35	SC24	GS1	MB24	NF5	SG1
4:00	SC25	GS2	MB25	NF6	SG2
4:25	SC26	GS3	MB26	NF7	SG3
4:50	SC27	GS4	MB27	NF8	SG4
5:15	SC28	GS5	MB28	NF9	SG5
5:40	End				
7:00	Awards Reception				
8:00	Awards Banquet				

Wednesday, October 16, 2013

	WS	*VL*	*OT*	*MH*	*CS*
8:30	P. Carreau (PL3) - *WS*				
9:20	Coffee Break				
10:00	SC29	GS6	MB29	NF10	SG6
10:25	SC30	GS7	MB30	NF11	SG7
10:50	SC31	GS8	MB31	NF12	SG8
11:15	SC32	GS9	MB32	NF13	SG9
11:40	SC33	GS10	MB33	NF14	SG10
12:05	Lunch Break				
1:30	SC34	GS11	MB34	NF15	BM10
1:55	SC35	GS12	MB35	NF16	BM11
2:20	SC36	GS13	MB36	NF17	BM12
2:45	SC37	GS14	MB37	NF18	BM13
3:10	Coffee Break				
3:35	SC38	GS15	MB38	NF19	BM14
4:00	SC39	GS16	MB39	NF20	BM15
4:25	SC40	GS17	MB40	NF21	BM16
4:50	SC41	GS18	MB41	NF22	BM17
5:15	End				
5:30	Poster Session & Reception				

Thursday, October 17, 2013

	WS	*VL*	*OT*	*MH*	*CS*
8:00	P. T. Underhill (AP1) - *WS*				
8:40	SC42	GS19	MB42	NF23	BM18
9:05	SC43	GS20	MB43	NF24	BM19
9:30	SC44	GS21	MB44	NF25	BM20
9:55	Coffee Break				
10:25	SC45	GS22	MB45	NF26	BM21
10:50	SC46	GS23	MB46	NF27	BM22
11:15	SC47	GS24	MB47	NF28	BM23
11:40	SC48	GS25	MB48	NF29	BM24
12:05	SC49	GS26	MB49	NF30	BM25
12:30	End				

Session and Room Codes

AP = Award Presentations
BM = Rheology and Processing of Bio-based Materials
EM = Experimental Methods
GS = Gels and Self-assembled Systems
IP = Interfacial Phenomena
MB = Polymer Melts and Blends
MS = Rheology at the Microscopic Scale
NF = Non-Newtonian Flows

PL = Plenary Lectures
PS = Polymer Solutions
SC = Suspensions and Colloids
SG = Solids, Glasses and Composites

CS = Côte-St-Luc
FN = Salons Fontaine C-H
MH = Mont-Royal/ Hampstead
OT = Outremont
VL = Verdun/Lachine
WS = Westmount

Contents

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Monday Morning

Symposium PL

Plenary Lectures

Monday 8:30 Westmount PL1

Rheology of cellulose hydrogels

Theo van de Ven[1], Leila Jowkarderis[2], and Reghan Hill[2]
[1]Department of Chemistry, McGill University, Montreal, Canada; [2]Department of Chemical Engineering, McGill University, Montreal, Canada

Cellulose hydrogels are finding applications in medical applications, such as wound dressings, templates for growth of artificial tissue, in lab on chip applications such as actuators and in many other fields. Characterizing such gels is important for optimum performance. Cellulose gels can be made by crosslinking dissolved cellulose, crosslinking nanocellulose, or by physical entanglement of cellulose nanofibers (CNF). CNF can be made by TEMPO-mediated oxidation of cellulose pulp fibers, followed by mechanical disintegration in a homogenizer. CNF are typically a few micrometers long and have a diameter in the range 5-10 nm and contain carboxyl groups on their surface as a result of the oxidation process, typically in the range 1.5-2.0 meq/g. Above a critical concentration CNF form a gel, which as a result of these charges swells in water. The dynamics of these gels have been studied with a capillary rheometer, an oscillatory rheometer and by holographic microrheology. Besides the expected effects of salt and pH, the rheology shows a number of interesting hysteresis effects. Dilute suspensions below the gelation point allow measurements of the intrinsic viscosity of the cellulose nanofibers, as well as of the second viral coefficient in viscosity.

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Monday 10:00 Westmount SC1

Coarsening in colloidal gels: Micromechanics and rheology

Roseanna N. Zia[1], Benjamin J. Landrum[2], and William B. Russel[2]
[1]Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States; [2]Chemical and Biological Engineering, Princeton University, Princeton, NJ 08543, United States

We study the evolving structure and time-dependent rheological properties of an aging colloidal gel, with a focus on understanding the non-equilibrium forces that drive late-age coarsening. The gel is formed from a dispersion of Brownian spheres that interact via a hard-sphere repulsion and short-range attraction, as would occur in the presence of a polymer depletant, for example. The O(kT) strength of attractions leads to an arrested phase separation, and the resulting structure is a bi-continuous, space-spanning network that exhibits elastic and viscous behaviors: the gel may sustain its weight under gravity, or flow under shear. With O(kT) attractions the colloid-colloid bonds are reversible, giving rise to a continuous breakage/formation process as the gel ages. This balance favors coarsening over time, accompanied by an increase in feature size and heterogeneity in the gel. We show here that anisotropic surface migration leads to heterogeneous coarsening, and that this migration is driven by gradients in particle-phase stress.

Monday 10:25 Westmount SC2

Fluid flow through networks in the collapse of colloidal gels

Alexander M. Mertz[1], Alan L. Graham[2], Shihai Feng[2], Antonio Redondo[2], and Marc Ingber[3]
[1]Mechanical Engineering, University of Colorado Denver, Denver, CO, United States; [2]Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, United States; [3]University of Colorado Denver, Denver, CO, United States

In unstable colloidal gels, the viscous flow through the non-neutrally buoyant colloidal network determines the initial rate of collapse [1]. The resistance to this flow through the network is characterized by the permeability. The permeability is generally accepted to be a power-law function of volume fraction, where the power is dependent on the fractal dimension of the network. To test this with direct numerical simulations, randomly generated diffusion-limited-cluster-aggregated networks of spheres and other particle are generated along with ordered lattices that span the containing structure or periodic cells. These networks will be characterized using the fractal dimension by measuring the length of the network strands with different sized measurement scales [2]. The permeability is then determined using finite element solutions of

the Navier-Stokes equations of pressure-driven flow of Newtonian fluids through the networks. With this method, we calculate the permeability's dependence on volume fraction, particle size and shape, and fractal dimension. In addition, a comparison of periodic boundary conditions to networks in finite size containers is used to test the effect of particle pressure on the dynamics in these systems [3].

[1] S. Manley, J. M. Skotheim, L. Mahadevan, and D. A. Weitz, "Gravitational Collapse of Colloidal Gel," PRL 94, 218302 (2005). [2] B. Mandelbrot (1967). "How Long Is the Coast of Britain? Statistical Self-Similarity and Fractional Dimension", Science 156 3775, 636 (May 5, 1967). [3] Y. Yurkovetsky and J. F. Morris, "Particle Pressure in Sheared Brownian Suspensions," J. Rheol. 52, 141 (2008).

Monday 10:50 Westmount SC3

Anomalous large-scale dynamics of colloidal gels probed by dynamic microscopy

Yongxiang Gao and Matthew E. Helgeson

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

There has been considerable debate regarding the thermodynamic origin of gelation from suspension and its impact on the structure and rheology of colloidal gels. Some systems exhibit gelation that proceeds by dynamic percolation of particle aggregates, whereas others show gelation reminiscent of arrested phase separation of the colloid. We reveal in a recently discovered thermogelling nanoemulsion system that gelation proceeds as arrested spinodal decomposition. Specifically, at the gel point we find that the system develops a dynamically evolving bicontinuous structure of dense clusters and colloid-poor voids, whose characteristic length scale forms at the nanoscale and grows until it is visible by optical microscopy. We show that the characteristic scale grows linearly with time, demonstrative of the spinodal decomposition, before it slows down and becomes arrested at a scale inversely proportional to the degree of thermal quench into the gelled state. Applying newly developed dynamic microscopy techniques allows us to reveal and interrogate previously unreported large-scale dynamics of the dense cluster phase during approach to the arrested state. Namely, the fluid exhibits a convolution of short-time diffusion and slow hyperdiffusive modes. By tracking the motion of clusters in real space, we discover that these dynamics are a direct result of clusters coarsening via directed motion. These results suggest rules for controlling the large-scale structure and dynamics of colloidal gels arising from arrested phase separation, and provide critical links to understanding both their linear and nonlinear rheological behavior.

Monday 11:15 Westmount SC4

Effects of particle scale dynamics on the structural evolution of anisotropic colloid–polymer systems

Suhasini Kishore[1], Yingzhu Chen[2], Sunita Srivastava[3], and Surita R. Bhatia[3]

[1]Department of Chemical Engineering, University of Massachusetts, Amherst, Amherst, MA 01003, United States; [2]Department of Chemistry, Stony Brook University, Stony Brook, NY 11794, United States; [3]Centre for Functional Nanomaterials, Brookhaven National Lab, Upton, NY 11793, United States

The aim of this work is to understand re-entrant transitions in anisotropic colloid - polymer systems. Techniques like Rheology, Dynamic Light Scattering (DLS) and X-Ray Photon Correlation Spectroscopy (XPCS) were combined to investigate aqueous dispersions of Laponite RD with Poly-ethylene Oxide (PEO). Laponite solutions at high pH are known to form a colloidal glass. Adding low to intermediate molecular weight (M_w) PEO significantly slows down dynamics and decreases the elastic modulus. However with increasing polymer concentration (C_p), it was observed that the system regains elasticity to form a metastable disordered state whose particle interactions are primarily governed by weak attractive interactions. We compare linear rheology, DLS and XPCS to investigate particle scale relaxation processes that are observed during cooperative particle rearrangements. Finally, preliminary LAOS measurements were made to investigate microstructural changes at higher oscillation amplitudes. We observe that at amplitudes beyond a critical strain systems show a weak strain overshoot whose G" peaks depend on aging time, polymer M_w and C_p. We believe that this may be attributed to the competitive interactions resulting from the breakdown of the network of clay-polymer bridges and the elastic buildup due to the rearrangement of the Laponite particles at large deformation.

Monday 11:40 Westmount SC5

Flow behavior and dynamics of colloid-polymer depletion mixtures in confinement

Rahul Pandey[1] and Jacinta C. Conrad[2]

[1]Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States; [2]University of Houston, Houston, TX, United States

We used confocal microscopy, particle-tracking, and bulk rheology to study the effects of confinement on the flow behavior and dynamics of colloid-polymer mixtures, which serve as simple models of attractive particulate suspensions. We synthesized slightly charged poly(methylmethacrylate) spheres that were suspended in a refractive-index and density-matched solvent, and induced a controlled short-range interparticle depletion attraction between particles by adding non-absorbing linear polystyrene at two different concentrations, corresponding to a weak (~1 kBT) and strong (~10 kBT) interparticle attraction. First, we investigated the effect of interparticle attractions on the microchannel flow of these suspensions. In suspensions with weak interparticle attractions, the number density of particles increased downstream in the channel due to shear-induced migration and consolidation. Suspensions with stronger interparticle attractions contained an interconnected network of particles, which suppressed these mechanisms and prevented the increase in density downstream. Second, we investigated the effects of particle size dispersity on confinement-induced solidification of colloid-polymer mixtures. We formulated suspensions of polymers and bidispersed colloidal particles at particle size ratio aS / aL ˜ 0.49. We fixed the total volume fraction of particles and measured the dynamics of the large particles as a function of the volume fraction of small particles. The dynamics of the large particles became slower as the volume fraction of small particles was increased or the confinement thickness was decreased, indicating increasing solid-like behavior. The dynamics was slowest at minimum confinement thickness and maximum volume fraction of small particles, suggesting that solidification of attractive suspensions in confined geometries can be tuned by modulating the particle size dispersity.

Symposium IP

Interfacial Phenomena

Organizers: Suzanne Giasson and Lynn M. Walker

Monday 10:00 Verdun/Lachine IP1

Template induced directed self-assembly of an intrinsically disordered protein at model hydrophobic interfaces: Can studying interfacial phenomenon tell us more?

Prajna Dhar
University of Kansas, Lawrence, KS, United States

The self-assembly of intrinsically disordered proteins into highly organized fibrillar structures forms a defining hallmark of several protein aggregation diseases, including Alzheimer's disease. Microtubule associating protein, Tau, is one such intrinsically disordered protein that aggregates into paired helical filaments in several neurological disorders. It has been suggested that the aggregation of Tau may be influenced by the presence of hydrophobic templates or negatively charged inducer molecules. In this talk, we will discuss our recent results focusing on the adsorption and aggregation kinetics of Tau proteins at model hydrophobic interfaces. Surface tension measurements are correlated with surface rheology and quartz crystal microbalance measurements to record possible alterations due to point mutations in the longest isoform of Tau protein. We find that even though tau is a soluble protein, it is highly surface active even at nanomolar concentrations. Moreover, our surface rheology data show differences in the evolution of surface viscosity with time, suggesting interface induced aggregation, possibly leading to oligomer formation.

Monday 10:25 Verdun/Lachine IP2

Dynamic contact angles of Newtonian and viscoelastic fluids on hydrophobic and superhydrophobic surfaces

Jeong-Hyun Kim and Jonathan Rothstein
Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003, United States

The dynamic contact angles of Newtonian and non-Newtonian fluids were measured on both hydrophobic and superhydrophobic surfaces using a modified Wilhelmy plate experiment. For the Newtonian case, water and aqueous solutions of low molecular weight polyethylene oxide solutions were studied in order to vary the liquid's viscosity. For the viscoelastic case, a series of solutions of high molecular weight polyacrylamide solutions were studied with varying relaxation time and viscosities. The Wilhelmy plates consisted of hydrophilic acrylic, hydrophobic Teflon, and an acrylic surface sprayed with a commercially available paint to make it superhydrophobic. In all cases, the advancing and receding contact angle were measured as a function of plate velocity, fluid viscosity and fluid elasticity. For the Newtonian fluids, the advancing and receding contact angle on the hydrophobic Teflon surfaces were found to obey the expected scaling trends with capillary number. Specifically, $\cos\theta s - \cos\theta d \sim Ca^{2/3}$. The response of the dynamic contact angle on the superhydrophobic painted surfaces was quite different. The advancing contact angle was not found to change with velocity, but remain constant at $\theta a = 160^{o}$. More interesting, the receding contact angle on the superhydrophobic surface was found decay with increasing capillary number while obeying a new scaling relation, $\cos\theta s,r - \cos\theta d,r \sim Ca$. The origins of this new scaling will be discussed. In addition, a series of viscoelastic solutions were formulated to investigate the role of elasticity on the dynamic contact angle. Measurements were performed on both hydrophilic and hydrophobic plates. Our measurements show that the dynamic contact angle depends not only on capillary number, but Weissenberg number as well.

Monday 10:50 Verdun/Lachine IP3

Simultaneous interfacial rheology and mesostructure measurement of particle laden interfaces using a modified double wall ring interfacial rheometer

Sourav Barman and Gordon F. Christopher
Texas Tech University, Lubbock, TX 79409, United States

The study of particle laden interfaces has increased significantly due to the prevalent use of particle stabilized Pickering Emulsions in many industrial sectors. Pickering emulsions' bulk rheology and stability are highly dependent on particle laden interface's interfacial rheology, which is a function of interfacial mesostructure determined by particle properties and bulk conditions. However, there have been no attempts to correlate dynamic interfacial mesostructure to rheology, making it difficult to understand the physical mechanisms behind particle laden interfaces' deformation response.

To overcome this problem, a double wall ring interfacial rheometer has been modified to allow real time, simultaneous interfacial visualization and shear rheology measurements. The interfacial rheometer is capable of transmission, bright field microscopy of the interface at a single axial position over its entire radial width with magnifications up to 50x using long working distance objectives mounted below the interface. A high speed digital camera attached to the optical train captures videos of the dynamic mesostructure. The base also includes a Langmuir trough that provides symmetric interfacial compression and allows precise control of surface concentration.

To evaluate the rheometer's efficacy, model particle laden interfaces composed of 3 micron polystyrene particles at a decane/water interface have been characterized. We examine both aggregated and crystal morphologies, controlling interfacial mesostructure through bulk salt and surfactant concentration. We provide simultaneous measurements of mesostructure and rheology for both small amplitude oscillatory shear and steady deformations and correlate dynamic mesostructure to rheology to understand the physical mechanisms behind observed trends. Results are compared to known behaviors of this system. These unique measurements should have significant impact on the design and understanding of particle laden interfaces.

Monday 11:15 Verdun/Lachine IP4

Interfacial dilatational rheology

Gwynn J. Elfring, L G. Leal, and Todd Squires
Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106-5080, United States

Many methods for measuring the mechanical properties of fluid interfaces involve generating a flow at the interface with both dilatation and shear such as by translating a probe through a fluid interface. We examine here the force on a translating probe at an interface laden with a surfactant, that exhibits Newtonian interfacial rheology. If the surfactant is insoluble a common assumption is that the interface is incompressible, thus the motion of the interface is decoupled from surfactant concentration, and hence Marangoni and diffusive flows are no longer a factor. Conversely if the surfactant is soluble, it may be assumed instantly equilibrated, again decoupling the motion of the interface from surfactant conservation. In this study we assume that the interface is neither incompressible nor equilibrated. In particular we look at the effects on the force measured by a probe due to small deviations in the concentration field which result from the dilatational flows induced by the probe.

Monday 11:40 Verdun/Lachine IP5

Probing dilational interfacial stresses of complex interfaces using a microscale spherical bubble

Anthony P. Kotula[1] and Shelley L. Anna[2]
[1]Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15206, United States; [2]Depts of Chemical Engineering and Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15206, United States

The dilational properties of complex fluid-fluid interfaces are often correlated with the stability and bulk rheology of emulsions and foams. Probing the dilational response of an interface is challenging since it is often difficult to isolate dilational, shear, and other deformation modes. In this talk, we generate purely dilational deformation of a spherical bubble pinned at the tip of a capillary tens of micrometers in diameter. We oscillate the pressure jump across the interface at small amplitude while optically measuring the time-dependent radius of the spherical interface. The resulting dilational modulus can contain components arising from both interfacial rheological properties and transport to the interface from the bulk solution. Each of these phenomena can depend on radius of curvature of the bubble and applied frequency. Through careful analysis of the force balance on the interface in conjunction with several existing constitutive models, we show that radius of curvature and frequency can be used together to separate thermodynamic and dynamic effects. Various interfacial phenomena can be separated by examining the real and imaginary parts of the complex dilational modulus, as well as the radius-dependent crossover frequency at which the two moduli are equivalent. We validate these findings experimentally using two common nonionic surfactant systems: C12E8 and Tween 80 at air-water interfaces. In the case of C12E8, which adsorbs reversibly, the dilational modulus is solely a result of diffusion-limited transport to the interface. Tween 80, which is known to form an irreversibly adsorbed monolayer, exhibits a Kelvin-Voigt-type viscoelastic response. Finally, we apply this analysis to an interface stabilized by a mixture of colloidal silica and the cationic surfactant CTAB that is used in the generation of particle-stabilized emulsions and foams.

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Monday 10:00 Outremont MB1

Structure and rheological properties of a semiconducting polymer gel to manufacture a solar cell

Michael E. Mackay, Ngoc Nguyen, and Hao Shen
University of Delaware, Newark, DE, United States

The properties required for a gel (paint) of a semiconducting polymer to make a solar cell are: it must be capable of being applied to a vertical surface and when dry should have enhanced photovoltaic properties. Contemporary polymer-based solar cell fabrication is performed by taking a structureless solution of the semiconducting polymer and an electron acceptor (typically a C60 or C70 fullerene derivative), placing it on a substrate and controlling the drying conditions to generate a co-continuous network of the two components in a thin film (of order 250 nm thick). Our approach is to manufacture the structure prior to placing the solution (gel) on the substrate by pre-crystallizing the polymer and

assembling the electron acceptor into a coherent structure through shear. Small angle neutron and light scattering techniques, together with rheological characterization, are used to ascertain the effect of shear rate on manufacture such structures. Presently, the rheological properties have been found to promote easy coating onto any substrate and multiple devices with a power conversion efficiency approaching 3% have been made. After optimization of the shear conditions a higher efficiency is expected which will be discussed in the talk.

Monday 10:25 Outremont MB2

Does confinement promote coalescence in sheared immiscible blends?

Pieter De Bruyn, Ruth Cardinaels, and Paula Moldenaers
Chemical Engineering, KU Leuven, Leuven 3001, Belgium

Blending of immiscible polymers is often used as a route to produce materials with enhanced properties. These properties strongly depend on the morphology that is generated during processing and which is the result of the balance between droplet breakup and coalescence. There is also a continuous trend towards smaller length scales in processing equipment. When two-phase fluids such as immiscible polymer blends are processed in such devices, the characteristic length scale of the morphology can become comparable to the dimensions of the channels. Hence wall effects (confinement) can be expected to affect the morphology development. In the present work, the effect of geometrical confinement on the flow-induced coalescence of droplet pairs is studied systematically. A home-built counter rotating parallel plate device, equipped with a microscope, to visualize two interacting droplets in shear flow is used for this purpose. Both the viscosity ratio and the initial relative position of the droplets have been varied over a wide range. One of the interesting results is the occurrence of reversing droplets for confined droplets with a very small initial center to center distance in the velocity-gradient direction. Consequently and unlike in bulk conditions, there is a lower boundary for this distance in confinement, below which there is no coalescence. On the other hand, the vertical center-to-center distance up to which coalescence is possible, is larger in confinement as compared to bulk conditions. These differences in the dynamics of colliding droplets in unconfined and confined conditions can be explained on the basis of trajectory analysis, 2D numerical simulations and investigation of the rotation speed of the droplet doublets. Overall, confinement is seen to promote coalescence.

Monday 10:50 Outremont MB3

Entanglement and tube diameter in blends of stiff and flexible chains studied by primitive path analysis

Jun-ichi Takimoto, Sathish K. Sukumaran, and Yuta Suzuki
Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan

It has now been well established that, in homopolymer melts, stiff chains more easily entangle than flexible chains. Then what happens in a blend of stiff and flexible chains? To answer this question, we have studied blends of stiff and flexible chains by molecular dynamics simulation using Kremer-Grest type models. Stiffness of chains is controlled by changing the potential for bond angles. After equilibrating the blends (several blending ratio), the entanglemeant spacing N_e of each component chain is obtained by primitive path analysis (PPA). In homopolymers, flexible chain has $N_{eA} = 55$ and stiff chain has $N_{eB} = 11$. In blends, mean square end to end distance R^2 of each component chain has the same value as in the corresponding homopolymer. Entanglement spacing N_e, on the other hand, changes with blending ratio. What is interesting is that the tube diameters of flexible and stiff chains in a blend are almost identical; there is only one tube diameter a. Entanglement spacing in homopolymers has been well understood by the packing length hypothesis, which assumes that the number of entanglement strands n_e in a volume a^3 is independent of polymer species. This universality of n_e suggests that the entanglement strands of A and B chains in a blend are equivalent and only the total number of entanglement strands governs the entanglement. If we assume this, we can easily show that the tube diameters of A and B chains in a blend are identical, and derive the following blending rule for the (single) tube diameter a; $1/a = f_A/a_A + f_A/a_A$, where a_i (i = A, B) are the tube diameters in the homopolymers, and f_i is the fraction of component chain i. This blending rule agrees with our PPA results very well.

Monday 11:15 Outremont MB4

A thermo-rheological study on the structure property relationships in the reinforcement of nylon 6-POSS blends

Ricardo J. Andrade, Joao Maia, and Rongzhi Huang
Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, United States

In recent years POSS (polyhedral oligomeric silsesquioxanes) has been used in polymers as a copolymer, graft or as melt-blend filler. Due to its hybrid organic-inorganic nature, POSS has the advantage of providing molecular reinforcement, while its variety of functionalization schemes allows for reactions and/or other interactions with the matrix polymer. For example, various works in the literature have shown that strong POSS-polymer interactions exist that reduce shear viscosity and improve mechanical properties and thermal stability. Previous studies have shown the ability of POSS to reinforce polymers when incorporated through grafting or copolymerization, but there is a lack of work on the understanding of how POSS works as an additive. The main aim of the present work is to shed some light on this issue, using Nylon 6 as the matrix polymer. Nylon 6 is a semicrystaline thermoplastic polymer with an interesting morphology and hydrogen bonding ability that can be applied on a variety of applications. This ability is expected to lead to high levels of POSS-polymer interaction. In this work we focus on POSS AM0265, which has its primary amine in the aminopropyl group. Previous work showed significant increases in mechanical properties when nylon 6-POSS were melt-spun, while recently Jana and co-workers showed that the incorporation of POSS leads to a decrease in melt-viscosity. In this work we will focus on understanding the dynamics of POSS AM0265-nylon 6 interactions by performing a full spectrum of thermal,

chemical, viscoelastic and processability studies, with the focus on the thermo-rheological behavior of the blends. In particular we will explain the reason for the maximum reinforcement to happen at a 2.5% w/w incorporation content of POSS in the Nylon 6 matrix.

Monday 11:40 Outremont MB5

Dynamic dilution effect in binary blends of linear polymers

Evelyne van Ruymbeke[1] and Hiroshi Watanabe[2]
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We investigate and model, based on a tube theory, the viscoelastic properties of binary blends composed of linear chains in different concentrations. This allows us to discuss the validity of dilution processes such as constraint release or dynamic tube dilution, focusing on the role played by the fast motions of short chains on both the reptation and the early fluctuations process of the long chains. We also discuss the value of the dynamic dilution exponent. In particular, we point out possible extra relaxation processes, not taken into account in present tube models, which enhance the relaxation of the long chains, due to the blinking feature of the release/reformation of the long-short entanglements. In such a way, we show that the effective value of the dilution exponent, which is determined from the second -low frequency - plateau modulus, can range from 1 to 4/3, despite the fact that it has been fixed to 1 in the model.

Symposium PS

Polymer Solutions

Organizers: David F. James and Hagar Zohar

Monday 10:00 Mont-Royal/ Hampstead PS1

On the eigenfunctions for Hookean and FENE dumbbells

Michael Renardy
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We study the linear eigenvalue problem for the distribution function associated with Hookean and FENE dumbbell models. For Hookean dumbbells, the eigenfunctions can be expressed by generalized Laguerre polynomials. The eigenvalue problem for the FENE dumbbell leads to a confluent Heun equation. The first few eigenvalues are calculated numerically and by perturbation theory.

Monday 10:25 Mont-Royal/ Hampstead PS2

Quantifying chain deformation in Couette flow using FRET

Nikko Y. Chan[1], Ming Chen[2], Trevor A. Smith[3], and Dave E. Dunstan[1]
[1]Chemical & Biomolecular Engineering, University of Melbourne, Parkville, Victoria 3010, Australia; [2]Molecular Sciences, CSIRO, Highett, Australia; [3]School of Chemistry, University of Melbourne, Parkille, Victoria 3010, Australia

An optical quartz Couette cell has been used to measure time resolved FRET signals from end-tagged PMMA chains in flow. RAFT synthesis methods have enabled end-tagged PMMA with an alternate donor-acceptor FRET pair on the ends of the chains to be synthesized. Time resolved FRET measurements in flow have been performed at a range of shear rates in order to determine the end-to-end distances of the chains in real time under shear. Measurements on PMMA chains in solutions at concentrations above critical overlap show a decreasing end-to-end distance with increasing shear rate. These unexpected results may be predicted using a simple dumbbell model in which compression is assumed rather than extension. We postulate that the extension of the chains is prohibited by the presence of the surrounding chains.

Monday 10:50 Mont-Royal/ Hampstead PS3

Drag reduction induced by flexible and rigid molecules in a turbulent flow into a rotating cylindrical double gap device: Comparison between poly(ethylene oxide), polyacrylamide, and xanthan gum

Anselmo S. Pereira, Rafhael M. Andrade, and Edson J. Soares
Department of Mechanical Engineering, Universidade Federal do Espirito Santo, Vitoria, Espirito Santo, Brazil

Polymer-induced drag reducing flow has been investigated for over 60 years. One reason for this is that the drag reducers in flow systems have been successfully applied and represent a great potential benefit to many industrial processes. However, the phenomenon is not completely understood and many aspects of the problem remain unclear. Some important issues are related to the development of turbulent structures and to the breaking of the polymer molecules. These two phenomena impose a transient behavior on the polymer efficiency and the drag reduction, DR, can be clearly divided into three periods of time. Over time, at the very beginning of the test, the DR assumes a minimum value (sometimes negative) before reaching its maximum efficiency. When degradation becomes important, the DR starts to decrease until it achieves its asymptotic value, a time in which the polymer scission stops and the molecular weight distribution reaches a steady state. In the present paper, we study the drag reduction development from the very beginning of a turbulent flow into a rotating cylindrical double gap device. The DR is induced by three different polymers: Poly(ethylene oxide) (PEO), Polyacrylamide (PAM) and Xanthan Gum (XG). The first two are

known as flexible molecules while the last one is considered rigid. The goal here is to compare the effect of the different polymers on the DR over time, paying particular attention to the difference between the rigid and the flexible molecules. The tests are conducted for a range of Reynolds numbers, concentrations and temperatures, from the very start to the time when the drag reduction achieves its final level of efficiency. It is shown that the DR induced by XG is qualitatively different from that of the other agents, probably due to XG's being a rigid molecule and because this polymer, eventually, changes its molecular configuration during the test.

Monday 11:15 Mont-Royal/ Hampstead PS4

The role of normal stresses in shear, in flows with extension

David F. James

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Many flows of viscoelastic fluids are a mixture of shear and extension, and each type of deformation generates normal stresses. When extension is significant, the focus has generally been on extensional stresses because they can be so large, with little attention paid to the possible contribution of the normal stresses caused by accompanying shear. In a recent paper, we showed that the pressure drop due to elasticity in flows of Boger fluids through square arrays of rods was caused by N_1 and not by extensional viscosity, at least for widely separated rods. A subsequent analysis of strain shows that this result also applies to closely spaced rods. An analysis of normal stresses in flows of Boger-type elastic liquids through converging channels indicates that the pressure drop due to elasticity is caused primarily by N_1 and not by extensional stresses; as a consequence, such a flow cannot be used to measure extensional viscosity. Viscoelastic flow past a cylinder confined in a channel is investigated, and available experimental data reveal that the observed non-Newtonian effects are more likely related to normal stresses in shear, not extension. Also, flows of drag-reducing dilute solutions are examined for N_1 effects, based on measurements of N_1 for these fluids

Monday 11:40 Mont-Royal/ Hampstead PS5

Estimation of the first normal stress difference from the shear viscosity data

Vivek Sharma

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The relevant stress distribution for entangled polymer solutions and melts in response to a steady simple shear flow is expressed using three viscometric measures: the shear stress and two normal stress differences. The normal stress differences are associated with nonlinear viscoelastic effects, including rod climbing, and become vanishingly small in linear viscoelastic measurements. Normal stress measurements are relatively difficult to perform and require specialized equipment. By contrast, measurements of the complex viscosity/modulus (in oscillatory shear) or steady flow curves are relatively straightforward and far more accurate. The Cox-Merz rule and Laun's rule are two empirical relations that somewhat intriguingly allow the estimation of steady shear viscosity and first normal stress difference (nonlinear response), respectively, using small amplitude oscillatory shear measurements (linear viscoelastic response). Recently, by using a lesser known relationship also proposed by Cox and Merz, in conjunction with Laun's rule, Sharma and McKinley deduced an empirical relationship between the rate-dependent steady shear viscosity and the first normal stress difference. The new rule enables a priori estimation of the first normal stress difference using only the steady shear viscosity vs shear rate data of entangled polymeric solutions and melts. In this talk, we rigorously examine the dissipative and recoverable contributions to the measured nonlinear rate-dependent shear viscosity response, in pursuit of a self-consistent physical description of the correlation between the first normal stress difference and shear viscosity.

Symposium EM

Experimental Methods

Organizers: Nicole Demarquette and David C. Venerus

Monday 10:00 Côte-St-Luc EM1

Unambiguous determination of the yielding transition in elasto-visco-plastic materials undergoing large amplitude oscillatory shear

Simon A. Rogers[1] and Gareth H. McKinley[2]

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Elasto-visco-plastic materials are characterized by elastic deformation and creep below a critical stress, followed by a rapid transition to a flow regime at large imposed stresses. Unambiguously identifying the critical stress for yielding in such materials under oscillatory shear conditions is difficult because it depends on both the time-scale and amplitude of the imposed deformation history. We present a universal parameter, called the torsion, which indicates the instant of rheological yielding in large amplitude oscillatory shear (LAOS). Previous work [Rogers (2012)] has shown that linear viscoelastic deformations in small amplitude oscillatory shear (SAOS) constitute planar space curves with zero torsion everywhere, while nonlinear responses are twisted three-dimensional objects in the three-dimensional state space defined by the strain, rate, and stress vectors. Geometrically speaking, the torsion is a measure of the local 'twisting' of a material trajectory, and quantifies departures from a planar (linear viscoelastic) response. It is therefore also an instantaneous measure of material nonlinearity. Furthermore, it is well-defined at all instants of an imposed oscillatory deformation, not just those in the so-called time-periodic 'alternance' state. It can therefore be used to study thixotropic material responses. We calculate the torsion for the yield-stress-like limit of the Cross model, the Bingham model, and the Papanastisiou regularization of the Bingham model. In all cases, yielding is well described by a critical torsion of magnitude O(1). Finally, we show maps of the torsion for a frozen star micellar solution as it responds to imposed oscillatory shear of progressively larger strain amplitudes.

Monday 10:25 Côte-St-Luc EM2

Inline rheology measurement of foods, personal care products and oilfield fluids using a non-invasive rheometer

Emilio J. Tozzi[1] and Michael J. McCarthy[2]
[1]Aspect Imaging, Davis, CA 95616, United States; [2]Food Science and Technology, Univeristy of California,Davis, Davis, CA 95616, United States

The economical processing of non-Newtonian materials either in batch or continuous modes, requires tools for monitoring that state of system and perform corrective actions in a reasonably short time frame. Rheological measurements are often performed off-line, which introduces significant time delays, as well as challenges related to sample handling and storage. Some desirable qualities for an in-line rheology sensor include short response times, accuracy comparable to off-line rheometers, and reliable operation, even in the presence of complex materials such as suspensions containing large particles. We used the FlowScan™ system, to non-invasively measure rheograms of liquid foods, personal care products and oilfield fluids circulating in a pilot flow loop with 30 liter capacity. Comparison with off-line measurements and performance for systems with rapidly changing rheology are discussed.

Monday 10:50 Côte-St-Luc EM3

Effect of wall-slip phenomena on yield stress measurements in cyclopentane hydrate slurry

Amit Ahuja[1], Prasad U. Karanjkar[2], Genti Zylyftari[1], and Jeffrey F. Morris[1]
[1]Benjamin Levich Institute, City College of CUNY, New York, NY 10031, United States; [2]Benjamin Levich Institute, City College of CUNY, New York, NY 10031, United States

Hydrate slurry rheology is of major importance in the operation of petroleum pipelines. Liquid cyclopentane (CP) based hydrate slurry is prepared in-situ at atmospheric conditions from a neutrally buoyant water-in-oil emulsion by quenching it to a lower temperature at a fixed shear rate. A material transition, from an initial water-in-oil emulsion to a solid particle suspension, takes place during which the viscosity increases by several orders of magnitude and jamming may occur. This is indicative of hydrate formation on the dispersed water droplets and subsequent agglomeration. For cases in which a finite steady state viscosity is obtained, further rheological tests are done. In particular, effects of wall slip on the measurements of yield stress are examined for varying water volume fractions using a stress-controlled rheometer equipped with roughened and smooth-walled cylindrical cups with a vane rotor. The roughened cup with vane rotor, which mitigates wall slip, is utilized to make a comparison of various yield stress measurement methods. Decreasing shear stress ramp, oscillatory stress ramp, and nonlinear viscoelastic methods are used. In the last of these, the maximum in elastic stress, which is the product of elastic modulus (G') and strain (γ), gives a measure of yield stress. Good agreement for the yield stress is obtained by the various methods, and the yield stress is found to be increasing with increasing water volume fractions, with the minimum water fraction for which a yield stress was measured being 16%. Yield stresses for water fractions above 30% exceeded instrument limits. Results are reported in terms of time evolution of yield stress of hydrate slurries. The smooth cup with vane rotor exhibits significant wall slip effects on the inner wall of the cup, which is clear from large fluctuations in viscosity during the slurry preparation, and an underestimation of yield stress. The yield stress with smooth geometry can lead to 75% lower values than using roughened geometry.

Monday 11:15 Côte-St-Luc EM4

A Jeffreys rheology framework for gels under LAOS

Paulo R. de Souza Mendes[1], Alexandra A. Alicke[1], Ricardo T. Leite[1], and Roney L. Thompson[2]
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We show that a Jeffreys framework is suitable to interpret physically LAOS rheology data of structured materials like gels, that possess transition from solid-like to liquid-like behavior. All the possible mechanical responses, namely the ones of a (i) purely elastic solid, (ii) viscoelastic solid, (iii) viscoelastic liquid, and (iv) viscous liquid, can be captured as the structuring level of the material decreases. As the stress amplitude and frequency are independently varied, two classes of motion are observed, characterized by a non-sinusoidal and a sinusoidal response, respectively: structure-changing motions, when the stress amplitude is above the yield stress and the frequency is of the order of the reciprocal of the thixotropic characteristic time; and constant-structure motions, when either the stress amplitude is below the yield stress or the frequency is much larger than the reciprocal of the thixotropic characteristic time.

Monday 11:40 Côte-St-Luc EM5

Elements of the rheology of waxy oils

Rama Venkatesan

Chevron, Houston, TX 77002, United States

Waxes (paraffins) precipitate out of crude oil during production operations due to the temperature drop associated with heat loss to the production environment (such as sub-sea). This renders the oil non-Newtonian and leads to flow assurance problems such as deposition and gelation. In this presentation, several areas of research into the rheology of such waxy oils are discussed. During steady state flow of waxy oils in cold environment pipelines, the waxy oil behaves as a shear thinning fluid whose viscosity may be described by a combination of a Herschel-Bulkley type model superimposed with terms to include the amount of wax precipitated (which varies with axial distance due to varying temperature). However, during transient operations such as shut down and startup of pipelines, other phenomena such as stress overshoots and hysteresis are observed. Recent work (with a collaborating university) has helped develop a model that incorporates principles from plasticity and isotropic yielding to describe the complex rheology of these oils. The waxy oil also becomes a gel with a yield stress during a flow shutdown in a pipeline if the ambient temperature is below the "pour point" or gelation temperature of the oil. This yield stress is a function of several operating variables including the shear and thermal histories of the oil. Restarting the pipeline requires breaking the gel. Simple extrapolations from the yield stress over-predict the required restart pressure. Research on this subject (with another university) has yielded important insights into the pressure propagation and subsequent creeping of the gel prior to breakage. Finally, the rheology of "live" oils under high pressures is important in the energy industry for many applications. Under pressure, the light hydrocarbons (gases under normal pressure) are dissolved in the liquid oil phase. Rheometric experiments have been performed with a pressure cell (collaborating with a company) to determine the non-Newtonian behavior of a live waxy oil.

Monday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Monday 1:30 Westmount SC6

Effects of cell density and biopolymer addition of the flow behaviour of concentrated mammalian cell suspensions

Benoît G. Maisonneuve[1], Denis C. Roux[2], and Justin J. Cooper-White[1]

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Mammalian cells can be seen as active, deformable, 'sticky' microparticles that have the natural propensity to cluster or aggregate. This aggregation phenomenon, just as in many industrial processes dealing with flocculation, can be a serious issue when one wishes to culture and process cell suspensions within standard bioreactors formats or within newer generation encapsulation systems. With the rapidly growing interest in the development of bioprocess systems to culture and expand mesenchymal stem cells for a host of cell therapy and regenerative medicine applications, greater understanding of the structure-function-property characteristics of mesenchymal cell suspensions is required. We present in this paper the results of an experimental study into the flow behaviour of concentrated suspensions of living mesenchymal cells over a wide range of volume fractions, with and without the addition of associative and non-associative biopolymers of varying molecular weight. We show in this study that such cell suspensions exhibit complex but relatively consistent rheological signatures that include yield stress behaviour, shear thinning and even fracture. These signatures are significantly perturbed by the addition of a single type of biomacromolecule, the magnitude of which is dependent on the concentration, charge and molecular weight of the biomacromolecule. We present a simple analytical model that considers the structures resident within these suspensions of adhesive, deformable, dynamic 'particles' under varying shear regimes that, when coupled with two-photon microscopy, permits rapid estimation of the average adhesion force (nN) between individual cells in such suspensions. This insight highlights the mechanism by which biomolecule addition modulates the rheological footprint of these living suspensions and provides the pathway by which we may eventually customise the flow properties of many other cell suspensions at high volume fractions.

Monday 1:55 Westmount SC7

Margination and segregation of self-propelled particles in blood flow

Amit Kumar and Michael D. Graham

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

Self-propelled particles like swimming bacteria and microbots have been envisioned for various applications in the human body including drug delivery and minimally invasive surgery. The efficacy of these particles in their respective applications will depend critically on their distribution in the wall normal direction, i.e., whether the particles flow close to the walls (margination) or close to the vessel center (antimargination). In this work, we numerically examine the margination behavior of self-propelled particles in a suspension of deformable capsules subjected to simple shear flow in a slit geometry. The effect of a variety of parameters is characterized including the particle shape, aspect ratio, size, swimming speed and the mode of propulsion (pushers and pullers). Our studies indicate that dead swimmers accumulate in the near wall region at the edge of the capsule depleted layer, i.e., they marginate. At sufficiently high volume fractions of capsules, both the pushers and pullers demarginate, i.e. they escape to the channel interior, with increasing swimming speeds. In contrast, at low capsule volume fractions, the pushers are found to flow close to the wall irrespective of their swimming speed, while the pullers demarginate with increasing swimming speeds. The demargination of particles is found to occur due to their collision with capsules, which may instantaneously orient them in the wall normal direction, thereby leading to their escape to the interior due to their self-propulsion. The difference in demargination behavior of pushers and pullers at low volume fractions arise because the pushers tend to get attracted towards the wall, while pullers tend to get pushed away from the wall. This behavior, coupled with the fact that at low volume fractions the capsule depleted layer thickness can be larger than the particle size, leads to the aforementioned result. Additional insights on the effects of size and shape of the swimmers on their margination behavior will also be provided.

Monday 2:20 Westmount SC8

Numerical simulation study of the deterministic vector separation of rigid particles and deformable capsules over slanted open cavities

Jorge A. Bernate[1], Yang Mengfei[1], Hong Zhao[1], Sumedh Risbud[2], Colin Paul[2], Matthew Dallas[2], Konstantinos Konstantopoulos[2], German Drazer[3], and Eric Shaqfeh[1]

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Planar microfluidic platforms for vector separation, in which different species fan out in different directions and can be continuously sorted, are particularly promising for the high throughput separation of multicomponent mixtures. We carry out a computational study of the vector separation of dilute suspensions of rigid particles and deformable capsules transported by a pressure-driven flow over an array of slanted open cavities. The numerical scheme is based on a Stokes flow boundary integral equation method. The simulations are performed in a periodic system without lateral confinement, relevant to microfluidic devices with much larger width than the dimensions of the open cavities and the ridges that create them. We study the deflection of rigid spherical particles, of flexible capsules as a model of white and red blood cells, and of rigid discoidal particles as a model of platelets. We characterize the deflection of different particles as a function of their size, shape, shear elasticity, their release position, and the geometric parameters of the channel. The simulations provide insight into the separation mechanism and allow the optimization of specific devices depending on the application. Good agreement is observed with microfluidic experiments measuring the deflection of silica and polystyrene particles, white and red blood cells, and MCF-7 breast cancer cells. Promising applications of this platform include the fractionation of blood and the capture of circulating tumor cells. This platform also has the potential to yield samples with controlled polydispersity at high throughputs, which would allow the study of the rheological behavior of complex fluids with desired particle size distributions.

Monday 2:45 Westmount SC9

Self-propelled soft-core dumbbells for the simulation of living fluids

Denis F. Hinz[1], Alexander Panchenko[2], Tae-Yeon Kim[1], and Eliot Fried[1]

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In this talk we present a simple model for the simulation of self-propelled bacteria solutions based on the dissipative particle dynamics (DPD) framework. To mimic the rod-like geometry of an individual bacterium, two DPD particles are connected by a stiff harmonic spring to form a single DPD molecule. The bacterial motility is modeled through a constant self-propulsion force applied along the rod axis of each DPD molecule. We perform numerical simulations of this system using a customized version of the open-source LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software package. To investigate the influence of the particle volume fraction on the statistics of the system, we study statistical objects such as probability density functions of the velocity field, equal-time velocity correlation functions, velocity energy spectra, and structure functions of longitudinal velocity increments.

Monday 3:35 Westmount SC10

Shear-induced diffusion of cubic colloids

John R. Royer[1], Daniel L. Blair[2], and Steven D. Hudson[1]

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It is poorly understood how anisotropic interactions influence the rheology of a suspension, even though numerous industrially relevant suspensions, including protein solutions, are made up of anisotropic particles. A key challenge is to simultaneously study micro-scale particle motion and macro-scale rheology in a system with well-characterized, well-controlled and tunable anisotropic interactions. Here we use confocal-rheometry to study a colloidal suspension of mono-disperse, hollow, silica cubes. We induce an attractive interaction between the faces of the cubes through a depletion interaction and vary this interaction strength through the size and concentration of the depletant. Tracking the 3-D position and orientation of the cubes as they move under steady shear, we characterize the packing structure and shear-induced diffusion of the cubes varying the shear rate, packing density, and depletion induced attraction.

Monday 4:00 Westmount SC11

Suspension of cubic particles under shear

Rajesh K. Mallavajula, Lynden A. Archer, and Koch L. Donald

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Shape of the nanoparticles is one of the important factors that determine the suspension flow behavior. Cubes are the simplest polyhedral particles that has flat surfaces, corners, edges and yet no aspect ratio. We have studied the structural and rheological properties cubic particles in suspensions using both theory and experiments.

We have synthesized cubic particles of varying sizes (10 nm to 4 microns) and chemistries (PbTe, Fe3O4, MnCO3, SiO2) to study the suspension properties. Spherical particles of identical chemistries and similar sizes were also synthesized to understand the effect of cube shape on the flow behavior. Using confocal microscope connected to a shear cell, suspension of cubic particles with 1 micron in size is used to analyze

the structure experimentally. We have also developed Brownian dynamics simulations to gain insights into the dependence of shape on structure and flow properties of the suspension.

Suspension flow properties were measured over a wide range of volume fractions and shear rates to compare them with the theoretical findings. For dilute suspensions, irrespective of the cube size, size distribution and surface chemistry, we find that the value of intrinsic viscosity is 3.1, which is in excellent agreement with the theoretical calculations. For higher volume fractions, the measured results were correlated with the theory and simulations.

Monday 4:25 Westmount SC12

Modeling tube-tube interactions in carbon nanotube suspensions

Giovanniantonio Natale[1], Gilles Ausias[2], Marie-Claude Heuzey[1], Pierre Carreau[1], and Julien Ferec[2]
[1]Chemical Engineering, École Polytechnique de Montréal, Montreal, Canada; [2]LIMATB, Université de Bretagne-Sud, Lorient, France

Carbon nanotubes (CNTs) hold remarkable promises for the next generation of materials, with potential applications in organic electronics, reinforced and electrically conducting composites and even new types of biological sensors and devices. Despite these potentialities, CNT melts and suspensions are inherently difficult to process and in order to design efficient processing schemes, it is necessary to fully understand and predict their rheological behavior. In this work, a new model is developed in order to explain the shear thinning of untreated CNT suspensions, one of their rheological signature. The CNTs are described as rigid cylinders dispersed in a Newtonian matrix and the evolution of the system is controlled by hydrodynamic and rod-rod interactions. The force due to the interactions is modelled as a non-linear lubrication force which is a function of the relative velocity at the contact point, and is weighted according to the contact probability. The total stress tensor is evaluated calculating the well-known fourth order orientation tensor and a new fourth order interaction tensor. The Fokker-Planck equation is numerically solved for steady state simple shear flows using a finite volume method avoiding the need of closure approximations. The model predictions show a good agreement with the simple steady shear data of CNTs dispersed in a Newtonian epoxy matrix. In addition, we confronted the model predictions with the rheological data of a composite system made of glass fiber filled polybutene (data from the literature), demonstrating its ability to describe the behavior of micro and nano scale particle suspensions.

Monday 4:50 Westmount SC13

Rheological hysteresis of periodically functionalized multi-walled carbon nanotubes non-Brownian suspensions

Soheil Sadeghi and Uttandaraman Sundararaj
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In this study, periodic functionalization of multi-walled carbon nanotubes (MWNT) was achieved by controlled solution crystallization of linear low density polyethylene (LLDPE) in presence of carbon nanotubes dispersed in p-xylene. This procedure resulted in formation of a nano-hybrid shish-kebab superstructure. Transient and steady-state linear and non-linear rheological properties of periodically functionalized MWNT non-Brownian suspensions were captured over a wide range of frequency and shear rate. The hysteresis loop area measurement was done by sweeping down then up the shear rate as a function of sweep rate. Hysteresis loop area for both functionalized and unfunctionalized MWNT reaches a strong maximum with sweep rate. This can be considered as an indication of the existence of a characteristic time-scale for microstructural dynamics. The hysteresis loop area measured for functionalized MWNT is negligible compared to unfunctionalized MWNT. Moreover, the characteristic time-scale for functionalized MWNT is one order of magnitude smaller compared to unfunctionalized MWNT (tens of seconds versus hundreds of seconds). Interestingly, the flow-curve of functionalized MWNT exhibited a monotonous behavior. Whilst, unfunctionalized MWNT showed a clear non-monotonic behavior signaling a structural transition as a result of shear-induced aggregation. It is also worthy to note that functionalized MWNT suspension showed a weaker network in the linear region compared to unfunctionalized MWNT due to less friction and attractive interactions.

Monday 5:15 Westmount SC14

The use of interaction tensors to describe and predict rod interactions in rod suspensions

Julien Férec[1], Emmanuelle Abisset-Chavanne[2], Gilles Ausias[1], and Francisco Chinesta[2]
[1]Université de Bretagne-Sud, LIMATB, Lorient, France; [2]GeM-Ecole Centrale Nantes, Nantes 44300, France

Recently Ferec et al. [1] proposed a model for non-dilute suspensions of rods where particle interactions are taking into account via a micromechanical approach at the microscopic scale. They derived a macroscopic governing equation, where orientation tensors describe the statistical conformation of a rod population and interactions tensors modify the orientation kinetics due to the interactions. To completely close the model, the fourth order moments of the probability distribution function (i.e. orientation and interaction tensors) have to be expressed in term of the second order which involve the development of accurate closure approximations. Therefore new closure approximations are proposed based on the natural closure approach. Finally we derived a new closure relation to approximate the fourth-order interaction tensor in terms of the second-order interaction tensor to improve the simple linear or quadratic closures initially used. All these closures are tested against the particular method in a variety of flows fields. Results shown that the new closures are improved.

[1] Ferec J., G. Ausias, M. C. Heuzey and P. J. Carreau, "Modeling fiber interactions in semiconcentrated fiber suspensions," J. Rheol. 53, 49-72 (2009).

Symposium IP

Interfacial Phenomena

Organizers: Suzanne Giasson and Lynn M. Walker

Monday 1:30 Verdun/Lachine IP6

Quasi-linear rheological models and elastic contributions to pressure-area isotherm measurements

Jan Vermant, Tom Verwijlen, and Luna imperiali
Chemical Engineering, KU Leuven, Leuven b-3001, Belgium

Monolayers of surface active molecules or particles play an important role in biological systems or in consumer products, their behavior is controlled by thermodynamics as well as mechanical properties. For insoluble species forming Langmuir monolayers, surface pressure-area isotherms are typically used to characterize the thermodynamic state. A Langmuir trough equipped with a Wilhelmy plate is often used for such measurements. However, when Langmuir interfaces are compressed and become more structured, the elastic response of these interfaces interferes with the measurement of the surface pressure-area isotherm. Recent reports of compression data for highly elastic interfaces revealed a dependence of the apparent surface pressures on the geometry of the measurement trough. In the present work, this dependence is investigated by considering adequate constitutive models. Since deformations in compression experiments are large, linearized versions of the Kelvin-Voigt model do not suffice. We develop a framework for quasi-linear constitutive models by choosing suitable non-linear strain tensors, adequately separating the shear and dilatational effects in a frame invariant manner. The proposed constitutive models can be used as building blocks to describe viscoelastic behavior as well. The geometry dependence in isotherm measurements is then shown to be a consequence of varying contributions of the isotropic surface pressure and extra shear and dilatational elastic stresses. Using these insights, an approach is proposed to obtain the intrinsic surface pressure-area isotherms for elastic interfaces.

Monday 1:55 Verdun/Lachine IP7

Computational investigation of the effect of insoluble surfactant on drop formation in a microfluidic device

Park Jang Min[1], Martien A. Hulsen[2], and Patrick Anderson[2]
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Surfactants are commonly used in droplet-based microfluidics to stabilize the droplet interface. In this study, we investigate the effect of insoluble surfactant on drop formation in a capillary microfluidic device. We use a diffuse-interface method to describe the evolution of the interface covered with an insoluble surfactant. The Navier-Stokes/Cahn-Hilliard equations and the surfactant conservation equation are solved by a finite element method along with a grid de- formation method. As the surfactant has a non-uniform distribution during the drop formation in general, the surface tension has a gradient on the interface, which affects the flow field and interface evolution. The effect of surfactants is discussed for both the dripping and jetting regimes of the breakup process in a capillary microfluidic device.

Monday 2:20 Verdun/Lachine IP8

Interfacial shear rheology and drop-drop coalescence

David Harbottle, Krishna Moorthy, and Zhenghe Xu
Chemical and Materials Engineering, University of Alberta, Edmonton, Canada

With water and oil ubiquitous in the petroleum industry, the formation of unfavorable emulsions is inevitable. Stabilization of water drops by surface active species such as asphaltenes, resins and fine particles creates problems for fast and efficient dewatering. A novel integrated thin film drainage apparatus (ITFDA) was designed in-house to measure the true coalescence time of water drops immersed in dark/opaque asphaltene solutions of varying aromaticity. Equipped with a bimorph force sensor and a computer-interfaced video capture system, the apparatus uses the diaphragm of a high-frequency speaker as the drive mechanism for drop collisions/contacts over a wide range of physical properties such as approach velocity and applied force. Displacement of the upper drop towards the lower drop was initiated and the true coalescence time measured from the deflection in the bimorph. For a system of 0.1 and 0.4 g/L asphaltenes in toluene or heptol 1:1 (heptane : toluene) solutions, the coalescence time was measured to increase with increasing water drop aging, exhibiting a step-change transition in coalescence behavior from the order of seconds to no coalescence. At short aging time, the shear viscous component (G", N/m) dominated the film microstructure with little or no detectable shear elasticity (G', N/m). As the elastic contribution of the film developed with increased aging the film microstructure transitioned to a solid-like behavior , G' > G", with the transition time dependent on concentration and solvent aromaticity. It appears that the step-change behavior in drop coalescence coincides with the condition G' = G". The cohesive nature of the asphaltene film formed minimizes the shear mobility of the interfacial film, apparent yield stress ~103 to 104 N/m2, and could potentially dampen interaction instabilities when the opposing interfaces are in close proximity. Those characteristics elucidated by interfacial shear rheology provide physical understanding to the stability of problematic emulsions.

Monday 2:45 Verdun/Lachine IP9

Exploring the kinematics of extensional coalescence of drop pairs and chains

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The phenomena of hydrodynamically driven extensional coalescence, which can occur when closely neighbouring droplets are pulled apart, has been studied by a number of authors in recent years. In the current work we further develop this research and report on experiments conducted in a custom microfluidic device that, for the first time, allows an independent control of the kinematics of the droplet pair approach and separation. We observe an upper limit in separation velocity above which coalescence is suppressed and no apparent minimum velocity below which the drops separate without deformation. This behaviour is in apparent contradiction of both existing theory and physical intuition, so we reconsider the current interpretation of the theoretical models available. Subsequent to this analysis, we propose a simple dynamical coalescence criterion that suggests that the separation velocity alone is insufficient to describe the dynamical evolution tendency of the drop interfaces.

Symposium MS

Rheology at the Microscopic Scale

Organizers: John R. de Bruyn and Gordon Christopher

Monday 3:35 Verdun/Lachine MS1

Nonlinear signatures of entangled polymer solutions in active microbead rheology

Paula A. Vasquez[1], Jeremy A. Cribb[2], Gregory Forest[1], and Richard Superfine[2]
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We present an active nonlinear microbead rheology protocol applicable to volume-limited entangled polymer solutions. These dynamic experiments consists of pulling microspheres through different entangled biopolymer solutions. These experimental results, at modest magnetic forces, show a short-lived high viscosity plateau, followed by a bead acceleration event with a sharp drop in apparent viscosity that terminates on the shear-thinning slope from cone and plate data. Simulations with the Rolie-Poly model explain the full dynamics within a single polymer physics framework. The experimental conditions mimic movement of cilia tips, bacteria, and sperm in mucus, implying the physiological relevance of the phenomenon.

Monday 4:00 Verdun/Lachine MS2

Limitation in single-bead passive microrheology

Tsutomu Indei[1], Jay D. Schieber[1], Andres Cordoba[1], Mir Karim[2], and Rajesh Khare[2]
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Microrheology is a powerful alternative to measure viscoelastic properties of soft materials by tracking the motion of micrometer-sized tracer beads embedded in the materials. This technique is based on a fact that the tracer's diffusive motion is coupled with the host material's viscoelasticity. In this presentation, we elucidate in what frequencies and why the single-bead passive microrheology works. We provide a way to estimate the dynamic modulus G* at high frequencies beyond approximately MHz order where the conventional generalized Stokes-Einstein relation (GSER) fails. This can be attained by incorporating inertial effects of probe particles and host materials into the GSER. We performed molecular dynamics simulations to track the motion of a nanoparticle embedded in polymer melts. Simulation results reveal that corrections from material inertia are necessary in the conventional GSER at the high-frequency domain. On the other hand, in the ultra-high frequency where the particle inertia prevails the material inertia, the passive microrheology does not work in principle anymore because the particle diffusion is decoupled with the viscoelasticity of the host material in this frequency domain.

Monday 4:25 Verdun/Lachine MS3

Microviscosity measurements of protein solutions

Lilian Lam H. Josephson and Eric M. Furst
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Antibody-based drugs are the largest and fastest growing class of protein therapeutics with 35 approved drugs in the USA and over 350 more in the clinical pipeline. During the early development stage, a target molecular profile is used to guide the candidate selection process, specifying the key characteristics required for a protein molecule to assure stability, safety, and efficacy. For example, target properties for monoclonal antibodies include high affinity and potency, high physical and chemical stability, structural function, and low viscosity in high concentration formulations. A significant bottleneck lies between the discovery and pre-formulation stages, as only small amounts of protein molecules are available. Thus, it is critical for formulation screening methods to be accurate and precise with small samples. We focus on screening low viscosity formulations using microrheology, a powerful method to study scarce therapeutic materials [1]. We study the precision and accuracy

of multiple particle tracking (MPT) microrheology using the non-Gaussian parameter excess kurtosis and the van Hove self-correlation function at a range of lag times. In a typical MPT experiment, probes are only trackable when they diffuse in the observation volume. This limitation is most severe in the z-direction as probes move in and out of the field of observation, and leads to a peculiar statistical effect in MPT. Short trajectories are more prevalent than longer trajectories, but the probes may not have moved enough to allow for accurate assessment of the bulk solution viscosity. By examining the MPT statistics, we evaluate and optimize the precision and accuracy of the viscosity measurements. We also study probe stability in various buffer and excipient conditions. This work demonstrates that MPT microrheology is an accurate and precise method to characterize the viscosities of protein solutions over a large range of concentrations with microliter samples.

[1] K.M. Schultz & E.M. Furst. Soft Matter 8 (23) (2012) 6198-6205.

Monday 4:50 Verdun/Lachine MS4

Microrheology of polysaccharides found in the extracellular matrix of bacterial biofilms

Mahesh Ganesan[1], John G. Younger[2], and Michael J. Solomon[1]
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We use particle-tracking microrheology to characterize the effect of association and complexation on the dynamics of extracellular polysaccharides in bacterial biofilms. Microbial biofilms, a biological soft material, owe their viscoelasticity to the presence of a hydrogel like extracellular polymer matrix comprising of polysaccharides, proteins, and DNA. Recently, we showed that the polysaccharide intercellular adhesin (PIA) of *Staphylococcus epidermidis* biofilms exhibits self-association as well as intermolecular complex formation with proteins at concentrations and pH that are consistent with *in situ* conditions. Because of the small volumes of biofilms macroscopic rheological measurements cannot be used to characterize the role of the association and complexation on their mechanical properties. We therefore use diffusing wave spectroscopy to probe the thermal diffusion of submicron probes in solutions of self-associated PIA and PIA-bovine serum albumin complexes. The effect of pH and concentration of PIA is also quantified. Subsequently, using a generalized Maxwell's model, we extract the viscoelastic creep compliance response of the biofilm complexes. We discuss the results in light of recent reports on the bulk rheology of bacterial biofilms.

Monday 5:15 Verdun/Lachine MS5

High frequency dynamics of a liquid crystalline, cyanobacterial, sulfated polysaccharide studied by DLS/DWS microrheology

Tetsuharu Narita[1], Guylaine Ducouret[1], Mika Kawai[2], Tetsu Mitsumata[2], Maiko K. Okajima[3], and Tatsuo Kaneko[3]
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Certain bacteria can produce in abundance extracellular polysaccharides having different composition and properties, capable to self assemble in aqueous solutions. Their properties to jellify and absorb a large amount of water can be attractive for various applications. Recently we have extracted a novel polysaccharide "sacran" from a freshwater unicellular cyanobacterium, *Aphanothece sacrum*. This polysaccharide, containing calboxylate and sulfonate groups, has an extremely high molecular weight (more than 10^7 g/mol). Sacran has gelation properties binding efficiently with various heavy metal ions. Aqueous solutions of sacran form huge domains of liquid crystals at very low concentrations (> 0.5 %), suggesting high rigidity of this polysaccharide which self-orientates. In order to characterize the dynamics of the sacran chains in solution, we studied rheological properties of aqueous sacran solutions by microrheology by dynamic light scattering (DLS) and diffusing-wave spectroscopy (DWS) as well as classical rheometry. For microrheology polystyrene particles of 2 microns in diameter were used as probe particles. The mean square displacement of the probe particles were calculated from DLS and DWS autocorrelation functions. The complex modulus was calculated by using the generalized Stokes-Einstein relation with the inertial effect correction. Rheo-optical steady shear measurements showed strong shear thinning behavior of sacran solutions, showing flow birefringence. From the zero shear viscosity measurement we determined C* as 0.004 %. For the dynamic shear moduli, DWS microrheology and classical mechanical rheometry showed good agreement. We found that at high frequencies measured by microrheology the modulus scaled as $\omega^{3/4}$, indicating the dynamics of rigid rods. Effect of sacran concentration on the various characteristic length scales measured by microrheology and dielectric relaxation is discussed.

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Monday 1:30 Outremont MB6

Role of extensional viscosity in the formation and control of cocontinuous polymer blends

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Cocontinuous polymer blends are melt blended polymers containing two or more continuous and interpenetrated phases. Typically, the morphology and the characteristic size of these blends are predicted on shear rheology and interfacial properties of the blend components. However, since melt processing involves complex flow patterns, the extensional rheology properties of the polymer components can also influence the final blend morphology. Cocontinuous blends of polyethylene (PE) and polylactic acid (PLA) were prepared using different long-chain branching architectures to vary extensional rheological properties while keeping shear rheological properties largely constant. Shear rheological properties of the blend components were characterized by capillary and oscillatory rheometry. Extensional rheological properties were characterized by orifice entrance pressure drop and sheet wind-up. Blends from two branched polymers resulted in much larger characteristic sizes compared to blends containing linear polymers, since high extensional viscosity resisted stretching and breaking into smaller structures. However, blends containing at least one branched component showed cocontinuity over a wider range of composition compared to blends from linear polymers, as the branched polymers resisted breakup into droplets once a continuous network was formed. During annealing, all blends showed rates of coarsening which correlate with predictions based on their viscosities at low shear rate, consistent with the fact that coarsening is a slow process governed by shear flow.

Monday 1:55 Outremont MB7

Analysis of the phase structure of molten polymer blends using a modified Gramespacher-Meissner model

Matthias Mihalic and Alois Schausberger
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Oscillatory shear rheometry is a powerful tool for the detection of phase separation in molten polymers and thus for the investigation of the solubility of each component in a mixture. This is due to additional long-time relaxation processes, which are caused by the deformation of the interface between different phases.

A potential error source in such measurements is phase separation induced by crystallization during sample preparation, which might prevail througout the experiment. Therefore we designed an experimental set-up where the compounded melt is directly injected into the rheometer, thus avoiding any crystallization between mixing and the measurement.

In case of complete miscibility, the relaxation time spectrum obtained from the measured dynamic moduli will correspond with the spectrum calculated from the combined molar mass distributions of the components. Otherwise, the occurrence of phase separation will be reflected by a discrepancy between these spectra. Using the model of Gramespacher and Meissner, valuable information about the phase structure can be gained from this discrepancy. However, a modification to this model is introduced in order to describe the properties of the investigated blends more accurately.

Monday 2:20 Outremont MB8

Rheological and electrical determination of phase separation and localization phenomena in poly (methyl methacrylate) (PMMA) / poly (styrene-co-acrylonitrile) copolymer (SAN) / multi-walled carbon nanotube nanocomposites

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Department of Chemical and Petroleum Engineering, University of Calgary, CALGARY, Alberta T3A2H4, Canada

Nanocomposites of poly (methyl methacrylate) (PMMA) and poly (styrene-co-acrylonitrile) (SAN) blends containing multi-walled carbon nanotubes (MWCNT) were prepared at different compositions by melt mixing. The kinetics of phase separation, phase diagram and localization phenomena were investigated by using a combination of time-resolved volume resistivity measurement and rheological analysis. TEM and SEM imaging were also used in order to determine the ultimate morphology of the nanocomposites. It was observed that regardless of the blend composition multi-walled carbon nanotubes are preferably located in SAN-rich phase. In addition, it was shown that PMMA/SAN/MWCNT samples had lower electrical percolation threshold compared to SAN/MWCNT samples.

Monday 2:45 Outremont MB9

Rheology of PP/PPMA and PP/PPAA blends and its incidence on the crystalline structure of their cast films

Amir Saffar[1], Abdellah Ajji[1], Pierre Carreau[1], and Musa R. Kamal[2]
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The intrinsic hydrophobic character of polypropylene (PP) membranes limits their application in many areas such as biomedical and battery separators. This can be improved by hydrophilic modification of the membrane surface by blending with hydrophilic polymers. So, it is important to choose materials that will generate the desired lamellar morphology in order to achieve a good membrane. In fact, the crystalline orientation factor should be large enough to have a row-nucleated morphology suitable for porous membrane formation. Consequently, in this study, the effect of rheological properties on the alignment of the crystalline and amorphous phases of binary blends of polypropylene and commercial hydrophilic modifiers such as maleic anhydride and acrylic acid grafted polypropylenes (PP/PPMA and PP/PPAA) were studied. To this aim, polymer blends with different concentrations of modifiers were prepared and the orientation function of the crystalline phase determined for all the blends using FTIR and WAXD. Rheological characterization has been carried out to provide fundamental knowledge about the relation between orientation of the crystal blocks and molecular structure. The modifier addition effect on the melt relaxation spectrum of the blends was investigated using the NLREG (nonlinear regularization) software. Finally, good linear correlations between the relaxation time and crystalline orientation for the blends were observed. The results showed also that the modifiers decreased the orientation function of the crystalline phase and crystallinity of the blends compared to neat polypropylene films as a result of the reduction in chain regularity.

Monday 3:35 Outremont MB10

The rheological behavior of poly(lactic acid)/poly(butylene succinate) blends

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A series of blends based on biodegradable poly(lactic acid) (PLA) and poly[(butylene succinate)-co-adipate] (PBSA) were prepared using the twin screw extruder. The blends were prepared for PBSA contents ranging from 25 % wt to 75 % wt. Selected blends at 30% wt PBSA with 2% wt epoxy-based multi-functional chain extender were also prepared using a laboratory internal mixer. The chain extender and PBSA were used to enhance the melt strength of the blends. The morphology and structure of the blends were examined using field emission scanning electron microscopy and transmission electron microscopy. Rheological properties (dynamic oscillatory shear measurements and elongational viscosities) of the blends and pure components were studied in detail. Strain hardening behavior was observed for blends composed of 50 % wt and higher PBSA. The blends with chain extender exhibited strong strain hardening behavior at lower PBSA content, whereas the blends without chain extender exhibited only weak strain hardening behavior. Measurements of the linear viscoelastic properties of the melts suggested that the chain extender promoted the development of chain branching. The results showed that PBSA contributed to significant improvement of the ductility of PLA/PBSA blends, while the chain extender did not have a significant effect on the elastic modulus and strain at break of the blends. The combined blending of PLA with PBSA and the incorporation of the chain extender imparted both ductility and melt strength to the system, thus enhancing both performance and processability.

Monday 4:00 Outremont MB11

Effects of montmorillonite on the rheological properties of SBS/asphalt/sulfur blends

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The dynamic and transient material functions of soft conventional asphalt modified by linear SBS block copolymer, the natural or organically modified montmorillonite and a small amount of sulfur, were studied at high service temperature of 58°C. The role of modifiers and their concentrations on the modified asphalt (MA) were previously studied in three factors - five levels design of experiments. The optimum ratio of modifiers determined from these experiments, (3.5 wt% of SBS)/(3wt% of montmorillonite)/(0.06wt% of S), was used for the preparation and subsequent testing of MA samples. In the linear viscoelastic domain (T=58°C) the sample of MA with organoclay exhibited better engineering properties than the sample with no or 3wt% of natural clay (e.g. lower values of the shear creep compliance and the loss compliance). Stress overshoots were observed in start-up experiments performed on all MA samples. No overshoots have been observed in the base-conventional asphalt. The magnitudes of overshoots depended on the shear rate and on the presence and type of the clay additive. The stress overshoots preceded the overshoots of N1 . The magnitudes of N1 - overshoots were generally ten times larger than the shear stress overshoots. The strength and a gradual recovery of the internal structure of MA, disturbed in the interrupted star-up tests, were investigated for shear 2s-1. The full recovery was longest (1h) in the sample with 3wt% of organoclay. Based on the performed tests one can conclude that the presence of organoclay in MA improved the engineering properties of this asphalt.

Monday 4:25 Outremont MB12

Constitutive model for flow-induced orientation and disentanglement in extensional flows of entangled polymer melts and solutions

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We present a simple model that predicts the observed monotonic extension thinning in steady state viscosity η_E even at extension rates above the inverse Rouse time for entangled polystyrene melts (Bach et al. 2003), while preserving the extension thickening seen in entangled solutions for extension rates above inverse Rouse time(Bhattacharjee et al. 2002). Inspired by an analogy between aligned Kuhn segments of entangled flexible polymers and entangled rigid rod-like molecules, we have incorporated a Kuhn-segment alignment effect on the tube diameter into the terminal relaxation τ_d and plateau modulus G_N of a simplified version of the tube model, namely the Doi-Edwards-Marrucci-Grizzuti (DEMG) model. Our formula for τ_d is derived from an expression for the tube diameter that depends on orientational order parameter in rod-like polymers due to Sussman and Schweizer (2012). Using this model, with no adjustable parameters, we predict only extension thinning for entangled polystyrene melts, while for entangled polystyrene solutions, because of their higher molecular weight between entanglement points, there is more chain stretch before Kuhn-segment alignment becomes high enough for disentanglement to occur, and extension thickening is predicted at extension rates beyond the inverse Rouse time, consistent with experiments.

Monday 4:50 Outremont MB13

Rate-dependent strain hardening of commercial polyethylene resin observed with an entension rheometer

Tieqi Li, Wen Lin, and Joo W. Teh
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Strain-hardening of the polyethylene (PE) melt has been an important feature for many applications. Through extensive experiments with an SER fixture, we have observed three different type of strain hardening in uniaxial extensional flow with commercial polyethylene polymers: 1. Hardening appears at all strain rates; 2. Hardening appears only above a critical strain rate; 3. Hardening is only observed at lower strain rates. The increase of the stress growth function over time can also be different within each of these three categories. The hardening behavior as monitored by the stress growth function, therefore, proves to be an effective way to differentiate different polyethylene resins in certain cases that the routine analytical methods such as GPC and DMA would not provide conclusive characterizations.

Monday 5:15 Outremont MB14

Entangled comb polymers in uniaxial extension: Experiments and modeling

Helen Lentzakis[1], Dimitris Vlassopoulos[1], Daniel J. Read[2], and Chinmay Das[2]
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We investigate the uniaxial extensional rheology of well-characterized entangled comb polymers, one of the simplest model systems with multiple branch points. Our comb polystyrenes have been synthesized by Roovers and characterized by state-of-the-art temperature-gradient interaction chromatography by Chang. In order to quantify the extensional data on stress growth coefficient (recently published and new), three methods are compared, (a) the original pom-pom model of McLeish and Larson, (b) a modified version of the BOB software program, and (c) a modified pom-pom model which accounts for the regularity of comb architecture. Concerning the latter, the stretch evolution equation of the original pom-pom model is modified. The key assumptions made is that the tube is aligned in the direction of flow and that the comb backbone can be separated into equal segments corresponding to the distance between two branch points and the distance between the branch point and free ends. A characteristic time corresponding to the relaxation time of each backbone segment is introduced. This new parameter-free comb model which takes into account all relevant tube theory concepts such as hierarchical relaxation and dynamic tube dilution and predicts reasonably well the extensional rheology data of a variety of model comb polymer systems. Possible extensions to H-polymers are also discussed.

Symposium PS

Polymer Solutions

Organizers: David F. James and Hagar Zohar

Monday 1:30 Mont-Royal/ Hampstead PS6

Emulsification in viscoelastic solutions

Clémentine Locatelli-Champagne[1], Roger Bonnecaze[2], and Michel Cloitre[3]
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Emulsification of hydrophobic substances in the form of nanometer or micrometer-sized particles in aqueous solvents is central to the design of many advanced materials. One important issue in applications is the need to control the size distribution and the stability of the dispersion. The models of Taylor and Grace [Proc. Roy. Soc (London) A146, 501, 1934; Chem. Eng. Comm. 14, 225, 1982] apply to situations where both the dispersed and continuous phases are purely viscous liquids. However, modern technologies often use Non-Newtonian fluids, for which the prediction of the dispersion properties remains an important challenge.

We will study the emulsification of Newtonian substances in viscoelastic polymer solutions. Starting from a phenomenological description of the dynamics of a single drop immersed in an immiscible matrix [Maffetone & Greco, J. Rheol. 48, 83, 2004], we propose a model that connects the viscoelasticity of the continuous phase to the characteristics of the final dispersion. One key parameter is the first normal stress differences that tend to stabilize droplets against deformation and delay their rupture to large shear rates. The model provides a good description of emulsions made of hydrophobic oils in comb-like amphiphilic polymer solutions where both the surface and the rheological properties are tuned at will through the molecular composition and the architecture of the amphiphilic groups of the polymer.

Monday 1:55 Mont-Royal/ Hampstead PS7

Role of secondary protein content in the rheology of synovial fluid

Zhenhuan Zhang and Gordon F. Christopher
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A human diarthrodial joint, like the knee, is an encapsulated system, which uses synovial fluid to lubricate cartilage surfaces of articulating bones. Synovial fluid is a viscoelastic solution, which is chiefly composed of the biopolymer hyaluronic acid in addition to secondary proteins primarily consisting of albumin, ?-globulin and lubricin. Protein concentration varies depending on age, health, and pathological conditions which create secondary protein concentrations that are much higher than healthy synovial fluid. Furthermore, these conditions affect the concentration and molecular weight of hyaluronic acid, which varies from 0.8 MD up to 10 MD. Synovial fluid rheology is highly dependent on molecular weight and concentration of hyaluronic acid. However, the importance of interactions between secondary proteins and hyaluronic acid on synovial fluid rheology is still being debated.

We have characterized the rheology of two model synovial fluids representative of healthy and pathological patients composed of hyaluronic acid, bovine serum albumin and ? globulin as well as individual solutions of each protein, and their binary combinations with hyaluronic acid. In steady shear, there is a clear effect of secondary protein interaction in the low shear rate behavior of model synovial fluids, which is not an artifact of rheometer geometry as has previously been hypothesized. During oscillation, pronounced changes in frequency response and relaxation time between model systems are observed and are primarily caused by the concentration and molecular weight of hyaluronic acid and not affected by secondary protein concentration. Finally, a small yield stress is observed in the model synovial fluids, and the roles of protein interactions on this behavior are characterized. These results begin to clarify some of the confusion regarding the role of secondary proteins on both the linear and non-linear rheology of synovial fluid, and address the need to further characterize synovial fluid.

Monday 2:20 Mont-Royal/ Hampstead PS8

Is DNA a good model polymer?

Abhiram Muralidhar[1], Douglas R. Tree[1], Patrick S. Doyle[2], and Kevin D. Dorfman[1]
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Double-stranded DNA (dsDNA) has been widely used as a model polymer in single-molecule experiments. In particular, λ-DNA has been employed extensively to study polymer dynamics by fluorescence microscopy. Using scaling theory recent studies have questioned the appropriateness of dsDNA as a model polymer citing its semiflexible nature. In addition, the more flexible, and hence synthetic polymer-like single-stranded DNA (ssDNA) has been proposed as a substitute for dsDNA (F. Latinwo and C. M. Schroeder, Soft Matter, 2011). In this work, we test the predictions from scaling theory quantitatively through calculations of equilibrium and dynamic properties of long worm-like chains. We used a Monte Carlo chain growth algorithm called the Pruned-Enriched Rosenbluth Method (PERM) to grow long chains of dsDNA ($\sim 10^6$ base pairs) and ssDNA ($\sim 10^4$ bases). By evaluating metrics such as the end-to-end distance and comparing these results with renormalization-group theory predictions, we show that λ-DNA is neither an ideal chain nor a real chain. It in fact lies in the transition region between the two universal regimes. This fact is further reinforced by free energy calculations. Furthermore, computation of the Kirkwood diffusivity from equilibrium configurations shows that the dynamics of λ-DNA is neither Rouse-like nor Zimm-like. In other words, λ-DNA is partially draining.

From our simulations, we also find limits in the length of dsDNA and ssDNA for the onset of universal behavior with respect to both equilibrium and dynamic properties. We observe that the limit for the onset of real chain scaling depends on the metric under consideration and is not necessarily the same for all metrics. Our results are compared with available experimental data and the two are found to be in excellent agreement.

Monday 2:45 Mont-Royal/ Hampstead PS9

Single molecule studies of DNA collapse in slit-like confinement

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Single molecule experiments of DNA in the presence of condensing agents have informed scientists about the high density packing of DNA in biological systems. Such studies lead to a better understanding of the rheological properties of living systems. Typically, these experiments are performed in unconfined, in vitro environments with condensing agents such as multivalent cationic species (e.g. spermine 3+, Co(NH3)6 3+). However, relatively little attention has been given to single molecule DNA collapse in weaker condensing agents, such as ethanol. Moreover, studies on the effects of restricting DNA conformational space (e.g. via confinement) on kinetics of collapse are nearly non-existent. In this talk, we will discuss our experiments with single molecules of dsDNA in the presence of ethanol and confined to slit-like nanochannels. The compact states induced at our ethanol concentration (and in bulk) are shown to be much larger and amorphous than the highly condensed, orderly toroids seen in multivalent cation induced DNA collapse. We attribute this difference to the long lived, higher order intermediate racquet states that one sees when collapsing semiflexible chains in poor solvents. Furthermore, we study the kinetics of collapse of individual DNA molecules. We find that the collapse is a two step process much like a nucleation-propagation event. More strikingly, we observe that the time to collapse DNA is reduced by an order of magnitude, relative to bulk, when confining DNA to slit-like nanochannels. This behavior is further explained via scaling arguments. We believe these results will have future relevance in single molecule assays and biological physics.

Monday 3:35 Mont-Royal/ Hampstead PS10

Crooks fluctuation theorem for flowing polymer solutions

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In this work, we apply the Crooks fluctuation theorem to determine fundamental nonequilibrium steady state properties of polymer molecules driven by fluid flow. In general, nonequilibrium work relations provide a new framework to study the dynamics of complex fluids. Recently, by using the Jarzynski equality, we demonstrated the direct determination of equilibrium properties such as polymer chain elasticity from transient stretching trajectories of polymer molecules in flow. Here, we report the determination of steady state energies of polymers in flow using Brownian dynamics simulations of dsDNA molecules transitioned between strain rates in forward and reverse directions. Interestingly, the steady state energy allows for the determination of rheological quantities such as polymer relaxation time and single chain elasticity. In addition to free energies, we observe a polymer stretch hysteresis in flow that exists in the absence of intra-chain hydrodynamic interactions. We find that the ensemble-average stretching trajectories of polymer molecules strongly depend on the steady state history. Overall, analyzing complex fluids in the context of Crooks fluctuation theorem allows for the determination of fundamental flowing materials properties and the observation of history-dependent phenomena.

Monday 4:00 Mont-Royal/ Hampstead PS11

Coarse-grained model of polymer electrophoresis including conformation-dependent mobility

Harsh Pandey and Patrick T. Underhill
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Many applications of charged polymers involve applying external electric fields or field gradients to separate, stretch, and manipulate molecules. It is well-known that in free solution the mobility of DNA is approximately independent of length, which has led to other separation methods such as gel electrophoresis. It was believed that the independence on length was due to partial screening of the hydrodynamic interactions between polymer segments. Recently, it has been shown that the mechanism for this length independence is a cancelation of interactions that only occurs near equilibrium. If the molecule's conformation is deformed from equilibrium, the cancelation does not occur, which leads to interesting and important behaviors. Simulations and experiments using fluid flow to deform the molecule have shown that it can migrate across field lines due to variations in electrophoretic mobility. Experiments and theory have also shown that electric field gradients can stretch molecules, and that the mobility depends on the conformation.

We have developed a coarse-grained Brownian dynamics simulation model that incorporates the change in mobility with conformation. In this way, we are able to capture the effects seen in experiments and in more detailed simulations in a computationally efficient way. We will describe the development and advantages of the new model. We will also show that the new model can quantitatively capture both the cross-stream migration and the stretch dependent mobility seen experimentally.

Monday 4:25 Mont-Royal/ Hampstead PS12

Blob-theoretic predictions for coil-stretch hysteresis in extensional flows of self-concentrating polymer solutions

R. Prabhakar

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Recent experiments and molecular simulations of flexible polymers have challenged the conventional notion of diluteness in polymer solutions. It is observed that the boundary between the non-overlapping and overlapping regimes may be flow-dependent. This is particularly the case in extensional flows in the vicinity of the coil-stretch transition, where molecules can be highly stretched but the Weissenberg number is low enough to permit large conformational fluctuations in the direction transverse to the extensional axis. This causes molecular overlap and significant concentration dependence to emerge in nonlinear rheo-optical properties even in solutions that are very dilute under quiescent conditions.

A single-mode “dumbbell” model is proposed in which the molecular friction coefficient as well as the stiffness of the entropic resistance to stretching are functions of the relative sizes and numbers of three different kinds of blobs. The influence of solvent-quality on intramolecular self-avoidance is effectively accounted for through theta-blobs. Intermolecular screening of hydrodynamic and excluded volume interactions is taken into account through correlation blobs. Attenuation of the effect of self-avoidance as well as intramolecular anisotropy caused by molecular stretching are modeled with stretch- (or Pincus-) blobs. Competition between these phenomena is considered in detail while consistently calculating the fractional volume pervaded by partially stretched coils. The sole dimensionless parameters in the model are the solvent quality crossover parameter, the diluteness ratio and the number of Kuhn segments.

The conventional analysis of coil-stretch hysteresis by considering a balance between entropic resistance and frictional drag is extended to account for self-concentration effects. It is shown that for any given solvent quality, the width of the hysteresis window varies non-monotonically with concentration, going through a large peak around the critical overlap concentration.

Monday 4:50 Mont-Royal/ Hampstead PS13

Brownian dynamics simulations of semidilute polymer solutions undergoing planar mixed flow

Aashish Jain[1], Remco Hartkamp[2], C. Sasmal[1], A. S. Mehrotra[1], B. D. Todd[3], R. Prabhakar[4], and J. R. Prakash[1]

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The effect of flow-induced stretching of polymer molecules on the concentration-dependence of rheological properties of dilute and semi-dilute polymer solutions is studied with Brownian Dynamics (BD) simulations of steady, homogeneous, planar, mixed flows. Polymer molecules are modelled as bead-spring chains, and a fast Smooth-Particle-Mesh Ewald (SPME) algorithm is used to efficiently handle intra and inter-molecular hydrodynamic interactions in simulation boxes with periodic boundary conditions. A recently introduced technique for realizing periodic boundaries in planar mixed flows, in the context of non-equilibrium molecular dynamics simulations suggested by Hunt et al (J. Chem. Phys., 133, 154116, 2010), has been extended here to BD. The use of a narrow-Gaussian potential to model excluded-volume interactions between polymer segments enables a careful examination of the influence of solvent quality on rheological properties.

Monday 5:15 Mont-Royal/ Hampstead PS14

Stress relaxation of entangled polystyrene solution after constant-rate, uniaxial elongation

Yumi Matsumiya[1], Yuichi Masubuchi[1], Hiroshi Watanabe[1], Qian Huang[2], Henrik K. Rasmussen[3], Nicolas J. Alvarez[2], and Ole Hassager[2]

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For an entangled solution of linear polystyrene (PS 545k; M = 545k) in dibutyl phthalate (DBP), the stress relaxation after constant-rate uniaxial elongation was examined with an extensional viscosity fixture mounted on ARES (TA Instruments). The PS concentration, c = 52 wt%, was chosen in a way that the entanglement density M/Me of the solution coincided with that of PS 290k melt (M = 290k). After the elongation at the Rouse-based Weissenberg number Wi(R) ~ 3 up to the Hencky strain of 3, the short time stress relaxation of the solution was accelerated by a factor of ~4, which was less significant compared to the acceleration (by a factor of ~ 10) noted for PS melt under a similar condition. This result, being in harmony with the mild acceleration found for a 52 wt% blend of PS 545k with an oligomeric styrene (M = 1k), suggested that the segmental friction is reduced when the chain is highly stretched and oriented but this reduction weakens on an increase of the concentration of un-stretchable solvent molecules. This change of the stretch/orientation reduction of the friction with the solvent concentration appears to be consistent with the monotonic thinning of the steady-state elongational viscosity seen for melts and the lack of monotonic thinning observed for the semidilute solutions. Results for less concentrated solutions will be also presented on site.

Symposium EM

Experimental Methods

Organizers: Nicole Demarquette and David C. Venerus

Monday 1:30 Côte-St-Luc EM6

Linear oscillatory dynamics of flexoelectric membranes embedded in viscoelastic media with applications to outer hair cells

Milad Abou-Dakka, Edtson E. Herrera-Valencia, and Alejandro D. Rey
Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

In this paper we model the small amplitude oscillatory dynamics of a tethered circular flexoelectric membrane immersed in viscoelastic fluid media driven by a small amplitude harmonic electric field of arbitrary frequency. The objective of the device is to transform electric energy into fluid flow through the oscillation of the electric-field responsive flexoelectric membrane. A full characterization of the device is presented and the optimal materials properties of the fluid and membrane required to optimize performance are identified through thorough analysis and computation.

Monday 1:55 Côte-St-Luc EM7

Temperature-step rheology to probe unusual materials: From nanoscale materials to ancient fossil resins

Gregory B. McKenna, Wang Jinhua, Jing Zhao, and Astrid K. Torres Arellano
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It can be difficult to obtain reliable data on the dynamics of amorphous materials. For example, with nanomaterials, past methods of measurement of the properties of ultrathin polymer films have relied upon a new sample for every determination of, e.g., the glass transition temperature Tg as a function of thickness h, hence being tedious. In the case of fossil resins, once heated above the Tg, they become thermally rejuvenated and the unusually stable state that results from millions of years of aging is lost. Additional issues, such as small amounts of available material can exacerbate the problems. Here we show two novel temperature-step rheological methods that address these issues. First, we build upon the methods of Bodiguel and Fretigny [1] for determination of the viscoelastic response of ultrathin polymer films to develop a temperature-step dewetting procedure that gives the Tg-h relationship for multiple values of h from a single measurement. In principle, one can make a single measurement that provides the same information as do 10 to 15 measurements with current methods. Examples will be given for polymers dewetting from different liquids. In the case of fossil resins, temperature-step methods can be used to establish the relaxation times as a function of temperature with a single sample and before the glass is thermally rejuvenated. We have been able to determine upper bounds to the deep-glassy state relaxation times for a 20 million year old amber, and with this information challenge the classic paradigms of an ideal glass transition and finite temperature divergence of the relaxation times in glassy systems. Future challenges remain for the determination of the response of older fossil resins which are available in much smaller fragments. These will be discussed.

[1] H. Bodiguel and C. Fretigny, Phys. Rev. Lett., 97, 266105 (2006).

This work is supported by the J.R. Bradford Endowment at TTU and by the National Science Foundation under grants DMR-0804438 and DMR-1207070.

Monday 2:20 Côte-St-Luc EM8

Investigation of anisotropic thermal transport in polymers using infrared thermography

David Nieto Simavilla and David C. Venerus
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Polymers are characterized by large viscosity and low thermal conductivity. During processing, these give rise to a strong coupling between the induced stress and temperature gradients affecting final properties of the material. In our laboratory, we have investigated anisotropic thermal conductivity in polymers subjected to deformation using an optical technique based on Forced Rayleigh Scattering (FRS). A linear relationship between anisotropy in thermal diffusivity (conductivity) and stress, known as the Stress-Thermal Rule, has been found to be valid. We report recent measurements in a Polyisoprene network system, showing that the STR holds at stress levels where the well-known Stress-Optic Rule fails. This suggests that anisotropy in thermal conductivity is not dominated by chain orientation only, as is the case for birefringence. Results from a new technique based on infrared thermography are presented as a complementary method to the previously used FRS. With this new technique, a broader range of materials and additional properties, such as specific heat capacity and its dependence on deformation, can be examined.

Monday 2:45 Côte-St-Luc EM9

Extensional flow and small angle neutron scattering

Kathleen M. Weigandt[1] and Ronald L. Jones[2]
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Extensional flows are commonly observed in nature and industry, but still poorly understood when compared to shear flow. This is due to inherent experimental difficulties in making precise structural and mechanical measurements of fluids undergoing extensional strain. In recent years, there have been a number of groups using microfluidic devices to accurately measure the extensional rheology and birefringence of various viscoelastic fluids. At NIST we have recently redesigned a cross-slot flow cell so that we can now quantify nanostructural changes that occur in complex fluids that are undergoing extensional deformation near a stagnation point with small angle neutron scattering (SANS). In this talk we will describe recent improvements to the cross-slot flow cell used for SANS measurements. Additionally, we will present our most recent results from extensional flow SANS experiments studying various materials including worm-like micelle solutions, polymer solutions, protein solutions or other complex fluids.

Monday 3:35 Côte-St-Luc EM10

Precision rheometry: Surface tension effects on low-torque measurements in rotational rheometers

Michael T. Johnston and Randy H. Ewoldt
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For rotational rheometers, surface tension results in a torque that should not occur in an ideal, rotationally-symmetric geometry. For water we show that this phenomenon is easily measured above the low-torque limit of a commercial instrument. The effect appears as a constant torque independent of rate, which would appear inaccurately as apparent shear thinning. In oscillatory tests this may appear inaccurately as an elastic modulus. The effect is due to surface tension and contact line traction forces, and not surface rheology at the liquid-air interface. This surface tension torque is sensitive to wetting conditions and contact line asymmetries and cannot be deterministically corrected in experimental measurements. It therefore raises the lower bound of the instrument low-torque limit. The surface tension torque is reduced by maximizing rotational symmetry of the contact line, minimizing evaporation and the migration of the contact line, reducing the radial location of the contact line, and lowering the surface tension. Identifying and eliminating the surface tension torque phenomenon is critical for rheological measurement for low viscosities, intrinsic viscosities, soft materials, sub-dominant viscoelastic components, and any other circumstance where the low-torque limit is experimentally important.

Monday 4:00 Côte-St-Luc EM11

An enhanced rotational rheometer system with two motors

Joerg Laeuger
Anton Paar Germany, Ostfildern, Germany

A new rheometer concept based on two air bearing supported electronically commutated (EC) synchronous motors is introduced, which represents a large step in rheometer development and extends the capabilities of a rotational rheometer dramatically. The combination of two motors into one rheometer system offers increased sensitivity and many new testing capabilities not possible before. Three completely different testing modes such as combined motor transducer (CMT), separate motor transducer (SMT) and counter rotation are available in one single rheometer system. It combines two EC motor units in a modular setup: The upper motor is integrated in the rheometer head as in a standard rheometer motor, whereas the lower motor can be extracted for the CMT mode and integrated for SMT and counter rotation modes, respectively. The lower motor can be exchanged much like an accessory system of a standard rheometer. In the counter-rotation test mode the motors are set to rotate in opposite directions. The pre-set speed is divided and shared by the two motors, whereas the torque and normal force are measured at the upper motor unit. This mode is an invaluable option for microscopy applications by creating a stagnation plane allowing the observation of the structure elements of the sample during shear. Further typical applications of the counter rotation mode are extensional rheology and the investigation of flow instabilities under different shearing conditions. In the SMT mode the upper motor is kept at a fixed position and operated solely as a torque transducer, while the lower exclusively functions as a drive unit. In this way the new device is turned into an enhanced separate-motor-transducer rheometer for rotational and oscillatory tests at a wide measuring range down to extremely low torques and normal forces. The aim of the paper is to describe the new technologies involved and to present examples relevant for modern research on various rheological topics

Monday 4:25 Côte-St-Luc EM12

Orthogonal superposition (OSP) of small strain oscillation shear on steady or oscillation shear on a rotational rheometer

Aloyse J. Franck
R&D, TA Instruments, New Castle, DE 19720, United States

Many simultaneous techniques are being used to follow structural changes in materials as a result of an imposed shear deformation. Orthogonal superposition, first introduced by J. M. Simmons in 1966 is a mechanical technique and uses a small amplitude oscillation shear orthogonal to the applied shear deformation. In contrast to parallel superposition, the flow fields are not coupled and the orthogonal dynamic moduli only measure the effect of shear on the microstructure. OSP has been implemented in the ARES-G2 by modifying the transducer to apply a small

oscillatory displacement in normal direction, while the actuator of the rheometer performs the transient or oscillatory rotational shear deformation. The normal force transducer in this case applies the orthogonal deformation and records the force. The dynamic moduli, complex viscosity and phase are determined using the embedded instrument correlation technique. The flow cell used to apply rotational shear and linear axial shear is a modified double wall cylinder with an opening at the bottom to avoid annular pumping.

With the OSP option the rheometer is capable to perform the following additional test modes: 1. Small linear strain orthogonal oscillation superposed on rotational steady shear; 2. Small strain orthogonal oscillation superposed on rotational oscillation at the same frequency with varying amplitude ratio between axial and rotational oscillation shear; 3. Standalone small axial displacement oscillations.

Test results will be presented showing the variation of the viscoelastic properties as a function of the applied rotational shear and information on shear induced anisotropy in gels from 2D oscillation experiments.

Monday 4:50 Côte-St-Luc EM13

Effects of instrument inertia on the variation of experimental data in creep measurementssurements

Amirhossein Maani and Pierre Carreau
Chemical Engineering, École Polytechnique de Montréal, Montreal, Canada

Investigating the time evolution of strain under step stress loading can provide valuable information about viscoelasticity of polymers; however, the initial portion of experimental data obtained in a creep experiment is often discarded due to the lack of precision. The origin of this inaccuracy is mainly the instrument inertia and the steep variation of shear rate or in other words the fluid acceleration which becomes negligible with time as the shear rate tends to reach a steady state value. Although this effect is more pronounced in creep behavior of materials with high level of viscoelasticity, it can be shown that the deviation of experimental data from theoretical prediction of creep variables could be quite salient for the short initial portion of the test even in the case of Newtonian fluids. This study attempts to address this issue in creep measurements of various materials ranging from Newtonian fluids to highly elastic crosslinked rubbers and gels. Different kinds of viscoelastic models are used in order to couple the instrument inertia with fluid viscoelasticity and to evaluate the time evolution of the strain. The possibility of direct correction of experimental data using Boltzmann superposition theorem is also verified. The viscoelastic parameters obtained using the creep experiments were then used to extract the dynamic rheological properties and the results were compared with the viscoelastic properties measured using small amplitude oscillatory shear tests.

Monday 5:15 Côte-St-Luc EM14

Parallel-plate geometry correction for transient rheometric experiments

Paulo R. de Souza Mendes and Alexandra A. Alicke
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Although it is a well known fact that the shear rate is not uniform in the parallel plate geometry, stress corrections are available for steady state flow data only. The Weissenberg-Rabinowicz equation accounts for the shear-rate dependence of non-Newtonian fluids, correcting the stress by using the derivative of the logarithm of the torque with respect to the logarithm of the shear rate at the plate tip. It is clear, however, that data pertaining to transient rheometric tests performed with the same geometry also need correction. In this work, we analyze this source of error and propose stress corrections for the main rheometric experiments. To illustrate the methodology, we performed creep and oscillatory tests for a commercial hair gel. For oscillatory flows, a simple equation for the correction is obtained in terms of both the torque and the shear rate amplitudes, for the case of a sinusoidal input for the angular velocity. In addition, we discuss and point out the tests for which no correction is needed.

Tuesday Morning

Symposium PL

Plenary Lectures

Bingham Lecture

Tuesday 8:30 Westmount PL2

Power-law gels, Scott-Blair and the fractional calculus of soft networks

Gareth H. McKinley
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Many soft materials including foods, consumer products, biopolymer gels and associative polymer networks are characterized by multi-scale microstructures and exhibit power-law responses in canonical rheological experiments such as Small Amplitude Oscillatory Shear (SAOS) and creep. Even in the limit of small deformations it is difficult to describe the response of such systems quantitatively within the classical framework of springs and dashpots – which give rise universally to Maxwell-Debye exponential responses. Instead, empirical measures of quantities such as ‘firmness’, ‘tackiness’ etc. are often used to describe and compare material responses. G.W. Scott Blair, who was present with Bingham at the very beginnings of the Society, argued that such measures are best thought of as ‘quasi-properties’ that capture a snapshot of the underlying dynamical processes in these complex materials. The language of fractional calculus and the concept of a ‘spring-pot’ element provide a useful ontological framework that is especially well suited for quantifying the rheological response of power-law materials. We illustrate the general utility of this approach by describing fractional differential forms of the Maxwell and Kelvin-Voigt models to quantify the oscillatory & creep responses of a range of soft materials including gluten gels, skin and soft tissue, filled polymer melts, hydrogen-bonded biopolymer networks and the complex interfacial rheological properties of acacia gum and serum albumins. The fractional exponents that characterize the dynamic material response can also be connected directly with scaling parameters from microstructural models such as the SGR model. Having determined the quasi-properties that quantify the material response in a concise form, we show that it is also possible to couple these fractional differential equations with the equations of motion and/or lubrication analysis to predict *a priori* more complex non-Newtonian phenomena such as creep-ringing and tack/peel curves.

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Tuesday 10:00 Westmount SC15

Rheology and microstructure of concentrated, near hard-sphere colloidal dispersions under steady shear and LAOS in all three planes of shear

A. Kate Gurnon[1], Lionel Porcar[2], and Norman J. Wagner[1]
[1]Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; [2]ILL, Grenoble, France

We present the first experimental measurement of the complete 3-D microstructure of a shearing, near hard-sphere colloidal dispersion that is made possible by the development of novel instrumentation implemented on the small angle neutron scattering (SANS) beamlines of the ILL and the NIST Center for Neutron Research. This work is motivated by the intriguing rheology of Shear Thickening Fluids (STFs), which are concentrated colloidal suspensions that exhibit increases in viscosity under high shear rates of deformation. STFs have been critically studied for their steady shear properties [N.J. Wagner and J. F. Brady, Physics Today. 27-32: (2009)]. However, little is understood about the nonlinear dynamic properties of STFs. To address this, we utilize large amplitude oscillatory shear (LAOS) to investigate the dynamic rheological properties of a model STF suspension [Kalman, D.P. and N.J. Wagner, Rheol. Acta. 2009, 48:897-908]. We develop a new flow-SANS sample environment for time and spatially resolved measurements in the plane of flow (1-2 plane) and combine this with rheo-SANS in the radial direction (1-3 plane) and tangential direction (2-3 plane) to elucidate the connection between the microstructure and the measured shear rheology. For the first time, the microstructure of a colloidal suspension undergoing steady shear is measured in all three planes of shear. The flow-induced microstructure under steady and oscillatory shear flow is compared to the rheological behavior via stress-SANS laws that separate the thermodynamic and hydrodynamic components of the stress that drive shear thinning, shear thickening, and first normal stress differences. A new non-equilibrium microstructure is discovered during a LAOS experiment that proves to be important for understanding the rheology of

concentrated colloidal suspensions. This first, complete measurement of rheological and microstructural properties is invaluable for testing constitutive models for colloidal suspension rheology.

Tuesday 10:25 Westmount SC16

Examining the shear-induced thickening of fumed silica CMP slurries using high shear rheo-SALS

Matthew W. Liberatore[1], Nathan Crawford[1], Kim Williams[2], and David Boldridge[3]
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Chemical mechanical polishing (CMP) is a fundamental technology used in the semiconductor manufacturing industry for the fabrication of microelectronic devices (e.g., computer chips). During the high shear (=1,000,000 s^{-1}) polishing process, it is hypothesized that individual slurry particles (~0.1-0.2 µm) collide with one another to form large agglomerates (>0.5 µm) that cause the slurry to shear thicken. These CMP-induced agglomerates generate surface defects such as scratches or gouges during polishing, costing the semiconductor industry billions of dollars in lost production annually. We examined the shear thickening of a 25 wt% fumed silica slurry with 0.17 M added KCl using in situ small-angle light scattering during rheological characterization (rheo-SALS). The salt-adjusted slurry displayed a ~3-fold increase in viscosity at a critical shear rate of 20,000 s^{-1} during a stepped shear rate ramp from 100 to 25,000 s^{-1}. As the shear rate was reduced back to 100 s-1, the slurry thickened irreversibly displaying a final viscosity that was 100-times greater than the initial viscosity. Corresponding rheo-SALS images indicated the formation of micrometer scale structures (2-3 µm) that directly correlated with the discontinuous and irreversible shear thickening behavior of the fumed silica slurry. Scattering was only observable during and after thickening, no scattering was detected in the absence of thickening. Dynamic light scattering was employed to size the slurry particles after shearing and to corroborate the presence of micron sized structures indicated by the rheo-SALS patterns. A significant population of "large" particles from 0.3 to 0.7 µm were detected exclusively in the particle size distribution of the shear thickened sample.

Tuesday 10:50 Westmount SC17

Modeling the thixotropic behavior of concentrated suspensions in large amplitude oscillatory shear (LAOS) experiments

Matthew J. Armstrong, Antony N. Beris, Norman J. Wagner, and Jung Min Kim
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Applying large amplitude oscillatory shear (LAOS) to complex fluids induces nonlinear rheological responses, that, with proper modeling, can be used to sensitively probe the underlying microstructure dynamics. We attempt to perform that task here for model concentrated colloidal suspensions using a variety of semi-empirical thixotropic models developed around a scalar internal structural parameter. A thermo-reversibly gelling dispersion of octadecyl-coated 30 nm silica spheres in n-tetradecane at a volume fraction of 21% was subjected to steady shear and LAOS, the result of which was analyzed to quantify its level of structure. The experiments were performed on a strain-controlled TA Instruments ARES-G2 rheometer. The LAOS technique used for the microstructure probing is a versatile method that allows simultaneous probing of viscoelasticity and nonlinear rheology. Steady state and transient dynamic behavior were both analyzed.

In parallel to the experimental rheology, the microstructure and stress of the system were modeled with several different thixotropic models, all of them based on a scalar structural parameter that obeys a shear-rate dependent kinetic equation, all variants to the basic model discussed in [1]. The respective model parameters were found using a recently developed robust numerical method that stochastically and effectively searches for the global optimum of a least squares residual in the allowed parameter space. While all the models were found to be able to qualitatively fit the experimental data, quantitative differences remain. The LAOS experiments are shown to be rich enough to allow full fit of the model parameters. The advantages and disadvantages discovered for the different thixotropic structural models will be discussed.

Reference [1] Jan Mewis and Norman J. Wagner, Colloidal Suspension Rheology, Cambridge, 2012.

Tuesday 11:15 Westmount SC18

Discontinuous shear thickening as a dynamic jamming transition of frictional particles

Ryohei Seto, Romain J. Mari, Jeffrey F. Morris, and Morton M. Denn
Benjamin Levich Institute, City College of CUNY, New York, NY 10031, United States

The Discontinuous Shear Thickening observed in many dense athermal suspensions has proven difficult to understand and to reproduce numerically in the framework of pure hydrodynamics. The standard models, treating close interactions between particles as being dominated by lubrication, do not capture the abrupt shear rate dependence of the viscosity. Moreover, they miss the dependence on the nature of the suspended particles, in particular their surface friction. In this work, we propose a new simulation model including contact and hydrodynamic forces. Our model allows contacts between particles, assuming a breakdown of lubrication for a small interparticle gap. These contacts are treated with a model borrowed from granular physics. It exhibits an abrupt shear thickening and recovers the experimentally observed dependence on friction coefficient and volume fraction. Within this framework, we describe the discontinuous shear thickening as a dynamic jamming transition, showing a characteristic structural signature. We also discuss its relation to the static jamming transition of granular matter.

Tuesday 11:40 Westmount SC19

Shear-induced irreversible breakdown of shear thickening fluids

Jonathan E. Seppala[1], Ronald L. Jones[2], Kirk D. Rice[3], and Gale A. Holmes[1]
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Amorphous fumed silica/polypropylene glycol (PPG) suspensions were subjected to multiple steady shear and oscillatory shears above the critical strain rate and critical strain amplitude. After each strain sweep, the steady shear viscosity and oscillatory shear moduli decreased over the entire measured range, and the on-set of shear thickening occurred at increasingly higher critical strain rates or strain amplitudes. Analysis of the oscillatory intra-cycle stress-strain (Lissajous-Bowditch) curves indicated a single-cycle shear thickening occurred at strain amplitudes below the traditionally defined critical strain and only during the first pass. The changes in the material properties appear to be irreversible and are attributed to breakdown of fumed silica-PPG agglomerates. Simultaneous rheology and small angle neutron scattering (RheoSANS) was also used to test this hypothesis. Finally intra-cycle and non-linear responses for fumed silica-PPG on parallel plate and cone and plate were analyzed via the MITlaos package. Although qualitatively similar, differences between the geometries will be discussed.

Symposium MS

Rheology at the Microscopic Scale

Organizers: John R. de Bruyn and Gordon Christopher

Tuesday 10:00 Verdun/Lachine MS6

Carbon nanotubes as mechanical probes of equilibrium and non-equilibrium biopolymer networks

Nikta Fakhri[1], Matteo Pasquali[2], Frederick C. MacKintosh[3], and Christoph F. Schmidt[1]
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A biological cell is a soft material with complex mechanical properties arising from a composite and highly dynamic intracellular protein polymer network (consisting of actin, microtubules and intermediate filaments). Equilibrium soft materials show strain fluctuations due to random thermal stresses; living biological materials exhibit, in addition, non-equilibrium, internal stress fluctuations generated by active force generators (e.g. motor proteins). Understanding the dynamic properties of such heterogeneous and structurally complex networks requires probes that span length-scales from nanometers to micrometers. We use single-walled carbon nanotubes (SWNTs) as multi-scale micro-probes. SWNTs are nanometer-diameter hollow carbon filaments with micrometer lengths and a tunable bending stiffness. Their persistence length varies between 20 - 100 microns. Therefore they show significant thermal fluctuations on the micron scale. We study the motion of individual SWNTs in reconstituted actin (equilibrium) and actin-myosin (non-equilibrium) networks by near infrared fluorescence microscopy. At long times, SWNTs reptate in the networks. At short times SWNTs can sample the spectrum of local stresses in both equilibrium and non-equilibrium networks. We can calculate complex shear moduli from recorded fluctuations and observed power-law scaling in equilibrium actin networks. In the non-equilibrium networks we observed strong local shape fluctuations reflecting the activity of the molecular motors.

Tuesday 10:25 Verdun/Lachine MS7

Shear rheology of deformable microgel particles in direct confinement

Bruke D. Jofore, Paula Moldenaers, and Christian Clasen
Department of Chemical Engineering, KU Leuven, Heverlee 3001, Belgium

When the length scale of flow confinement for a complex fluid approaches the length scales of its internal microstructure, boundary effects such as wall slip, cohesive and adhesive failures can occur and will influence the flow behavior [1]. In this paper we present microgap dependent shear rheological measurements on suspensions of microgel particles of Carbopol 981 for three different concentrations covering the range from dilute to concentrated regimes [3]. The rheological measurements under confinement are done with the second generation of the flexure based microgap rheometer (N-FMR) [1]. We show that the general slip behavior of microgel suspensions based on an elasto-hydrodynamic lubrication [2] holds also for a direct confinement of single gel particles, as long as the particle response is Hertzian. A non-Hertzian response on strong confinement leads to a slip layer decrease and eventually to a breakdown of the lubrication layer depending on the length scale of the surface roughness of the shearing plates. At confinements beyond the hydrodynamic lubrication layer breakdown, the microgels exhibit a concentration independent boundary lubrication related to the shearing surface surface roughness. Both single particle confinement stresses and boundary lubrication friction coefficients are quantified for the first time by in situ measurements of the normal force arising from single particle confinement on the micrometer level.

[1] Baik, S. J., and Moldenaers, P., and Clasen, C. Review of Scientific Instruments 2011; 82(3), 035121. [2] S. P. Meeker, R. T. Bonnecaze, and M. Cloitre. Journal of Rheology 2004; 48(6):1295-1320. [3] J.M. Piau . Journal of Non-Newtonian Fluid Mechanics, 144(1):1-29, 2009.

Tuesday 10:50 Verdun/Lachine MS8

A vesicle instability at low reduced volume in extensional flow

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When deformable vesicles with an aspect ratio of at least 3.5 (reduced volumes of < 0.75) are placed into a planar or uniaxial extensional flow they undergo an elongation transition above a critical capillary number. For vesicles with aspect ratio below 5 this transition manifests itself as an asymmetric dumbbell separated by a long, thin cylindrical neck. Previous experiments in the literature with vesicles of aspect ratio > 8 have observed an elongation that does not show clear signs of asymmetry and also a subsequent pearling instability for high capillary numbers and high aspect ratios. In this research, we perform 3D boundary integral simulations of vesicles with aspect ratio of up to 10. We find that once the vesicle aspect ratio exceeds 5 (i.e. reduced volume ratio of 0.62), the vesicle's steady state shape in extensional flow at capillary numbers of order unity contains a short thin neck of bounded length. Adding an odd perturbation to these shapes leads to a growing instability primarily driven by odd modes, but the asymmetry between the dumbbells is visually more subtle than the drastic inequality simulated for the instability at more modest aspect ratio. Additionally, we present an analytic theory, valid in the limit of high capillary number, that allows the prediction of the critical aspect ratio at which the instability first occurs in agreement with simulations. The theory also predicts that this critical aspect ratio is independent of the viscosity ratio between the fluid inside and outside of the vesicle membrane, however, we further demonstrate that the growth rate of the instability does depend on viscosity ratio. The mechanism of the instability at all aspect ratios will be analyzed by examining the balance of energy in the interface deformation.

Tuesday 11:15 Verdun/Lachine MS9

Escape of a knot from a polymer under various states of tension

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Macroscale knots are an everyday occurrence when trying to unravel an unorganized flexible string (e.g. an iPhone cord taken out of your pocket). In nature, knots are found in proteins and viral capsid DNA, and the properties imbued by their topologies are thought to have biological significance. Linear polymers in flows and electric fields can also form self-entangled knotted states that dramatically affect their rheological response. Unlike their macroscale counterparts, thermal fluctuations are critically important in determining the dynamics of polymer knots. Here, we use Brownian Dynamics simulations to study the model problem of knot diffusion along a linear polymer chain. Our bead spring model incorporates chain flexibility via semiflexible bending energies and electrostatics via a screened Debye-Hückle potential. The model is parameterized to dsDNA, a model polymer used in previous simulation and experimental studies of knot dynamics. In our simulations, knot topologies are preserved by explicitly rejecting chain crossing steps. We have studied the process of knot diffusion and escape from linear chains extended by external tension in three canonical regimes: constant tension (e.g. dsDNA held by optical tweezers), linearly increasing tension (e.g. tethered dsDNA in uniform flow), and quadratically increasing tension (e.g. dsDNA in elongational flow). We systematically vary knot topology, ionic strength, and the magnitude of applied tension. Furthermore, we study the process of chain unraveling and extension in these tension regimes from initially knotted configurations, exploring a similar parameter space. We interpret these results via scaling arguments and kinetic theory. We anticipate these results will build on the growing body of fundamental studies of knotted polymers and inform future experimental study.

Tuesday 11:40 Verdun/Lachine MS10

Conformational dynamic behavior of single polyelectrolyte chains confined in micro and nanochannels

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Polyelectrolytes in the confined spaces exhibit distinguished structure and rheology compared to their behavior in the bulk, due to the interactions with bounding surfaces originated in the charged polymer chains and mobile counterions. We investigated the confinement-induced conformational dynamics of the polyelectrolyte chain by employing the coarse-grained Brownian dynamics simulations [1] as well as by considering the blob theory [2]. Submicron-sized biopolymer xanthan was chosen as a model polyelectrolyte taking into account both flexible and semiflexible chains for comparison. It is available to identify three primary regimes (i.e., weakly confined, de Gennes, and Odijk regimes) according to a competition between length scales with the three dimensional radius of gyration in bulk, the persistence length, and the channel width. Confined flexible and semiflexible chains exhibit a nonmonotonic variation in size in the weak confinements, where the relative radius of gyration interestingly shows a dip and then increases with decreasing the channel width. The rigid chain, realized at low Debye screening with a low ionic concentration, exhibits a sigmoidal transition without minima in size. Major attention should be on the dependence of scaling law exponents on the screening effect of the aqueous solution in the moderate confinement of the de Gennes regime. For experimental verifications, we also present the single xanthan visualization using a fluorescence microscope and the displacing motion of an individual molecule in slitlike channels. Our findings are expected to provide useful information and design platform aiming to develop the micro total analysis system, inter alia, DNA sequencing, genome analysis, and manipulations of soft-matters [3].

[1] J. Jeon, M.-S. Chun, J. Chem. Phys. 126, 154904 (2007). [2] M. Daoud, P.-G. de Gennes, J. Phys. (France) 38, 85 (1977). [3] J. Tang, S.L. Levy, D.W. Trahan, J.J. Jones, H.G. Craighead, P.S. Doyle, Macromolecules 43, 7368 (2010).

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Tuesday 10:00 Outremont MB15

Structural response of a pre-aligned cylindrical block copolymer to uniaxial extensional flow

Erica McCready and Wesley Burghardt

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In situ small angle x-ray scattering (SAXS) is used to probe structural changes in a cylindrically ordered triblock copolymer melt during uniaxial extensional flow. The sample is a styrene-ethylene butylene-styrene triblock copolymer melt. Sheets of macroscopically oriented polymer were produced using a lubricated planar squeezing flow die, from which sample strips were cut. Uniaxial extensional flow was imposed in the melt state using an SER extensional flow fixture housed in a custom built convection oven that allows x-ray access, to facilitate SAXS measurements of microdomain re-orientation and deformation during stretching and subsequent relaxation. Individual sample strips were cut from the molded sheet to facilitate measurements in which the stretching was imposed either parallel or perpendicular to the pre-alignment axis. Offline measurements of transient extensional rheology were also conducted using the SER fixture in a conventional rotational rheometer, using similar samples in order to explore connections between, and impact of initial orientation state on structural and mechanical responses. Samples with cylindrical PS microdomains initially parallel to the stretching direction showed significantly larger stresses during mechanical testing than samples with initially perpendicular alignment. Anisotropy in the mechanical response is also manifested in the flow kinematics produced by the SER fixture. While samples initially oriented parallel to stretching deformed in a nearly uniaxial manner, perpendicularly aligned samples deformed much more along the initial microdomain orientation direction, with the resulting flow kinematics being nearly planar rather than uniaxial.

Tuesday 10:25 Outremont MB16

Thermo-rheological behavior of TPUs under high-strain extensional flow and its relation with morphology development and rupture dynamics

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Thermoplastic polyurethanes (TPUs) are multi-block copolymers usually consisting of hard and soft segments. The hard segments (HSs), which are composed of diisocyanate and short-chain diols as chain extenders, are most often thermodynamically incompatible with soft segments (SSs) that are made of polyethers or polyesters. Therefore, phase separation occurs with HSs forming domains that consist in either glassy or semicrystalline regions, which act as physical cross-links and provide stiffness and reinforcement. The reversibility of these regions enables melt processing of these materials at temperatures above the highest melting or glass transition temperature of the domains. The nanostructure of TPUs, and consequently their mechanical properties, depends on the chemical structure and processing conditions, namely temperature and flow histories. Moreover, at low temperatures, i.e., below the lower glass transition or melt temperature associated with the HSs, strain also originates significant changes in the nanostructure of the material. In order to gain some insight into this complex relationship between thermo-mechanical history, especially extensional flows, and TPU structure, we study the thermo-rheological behavior of different multi-block copolymers TPUs in uniaxial extension using a recently developed high-strain controlled strain extensional rheometer (HS-CSER) and establish how this impacts morphology development under flow in the materials. In particular, we show how extensional flow induces a crystallization-like behavior and the development of a hierarchical structure, and how it alters the ultimate rupture behavior of the materials. This new rheometer is based on the Meissner principle but is small enough to fit in the oven of a standard rotational rheometer. It is limited in strain only by sample rupture (we recently achieved true strains of up to 8.1). True strain rate is monitored/imposed by filming the sample during deformation with a digital camera and a feedback control loop.

Tuesday 10:50 Outremont MB17

Mechanical characterization tools for thin polymer membranes at fuel cell operating conditions

Benjamin R. Caire[1], Melissa A. Vandiver[1], Yifan Li[2], Daniel M. Knauss[2], Andrew M. Herring[1], and Matthew W. Liberatore[1]

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While proton exchange membrane (PEM) fuel cells have been the focus of development in the past, anion exchange membranes (AEM) have the potential to dramatically lower the cost of fuel cells by utilizing non-noble catalysts and a variety of fuel sources. As part of a broader effort to develop novel, thin and robust anion exchange membranes, creating a test fixture for mechanical characterization at relevant fuel cell operating conditions is being explored. New polymers are synthesized in small quantities and are typically on the order of 10-100 microns thick to increase ion transport. Standard tensile tests or dynamic mechanical analysis does not allow for adequate testing of these small sample sizes. Hence, a modification of the Sentmanat Extensional Rheometer (SER) to perform tensile and dynamic modulus testing on thin membranes is presented. Since the as-designed L-shaped pins do not secure thin polymer films at lower temperatures, a screw down clamp replaces the pins, allowing for mechanical characterization of small amounts of polymer. In a parallel effort, a humidity delivery system is being developed for the TA Instruments ARES-G2 rheometer to allow for testing at a range of temperatures (20-100°C) and relative humidity conditions (0-100% RH) relevant to an operating fuel cell. The novel testing apparatus is benchmarked with low density polyethylene and Nafion. New anion exchange membranes, including a diblock copolymer of polyethylene-b-poly(vinylbenzyl trimethylammonium), are also compared.

Tuesday 11:15 Outremont MB18

Crystallization of polypropylene: The effect of different parameters and testing suspension models to describe shear effects

Maziar Derakhshandeh[1], Savvas G. Hatzikiriakos[1], and Antonios K. Doufas[2]
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The final mechanical properties of a plastic product which is made of semi-crystalline polymers depend significantly on the molecular properties and the applied processing conditions. Particularly, the formation of flow induced structures via polymer crystallization plays a major role in defining the final attributes of the product. In this study, the effects of shearing and temperature on the flow induced crystallization of several polypropylenes are examined using rheometry. Generally, strain and strain rate found to enhance crystallization in simple shear at temperatures between the melting and crystallization points. The effects of molecular weight and its distribution are also examined and observed to have a strong influence on flow induced crystallization structures.

Tuesday 11:40 Outremont MB19

Shear-induced crystallization of polypropylene: A rheological study with in-situ DSC and WAXD

Peter C. Roozemond[1] and Gerrit Peters[2]
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In this work we study the rheology of crystallizing polypropylene after strong shear flows which induce highly oriented crystal structures. We present two experimental methods. First, we used the novel RheoDSC device to perform simultaneously plate-plate rheometry and DSC for constant shear rate and varying shear time. If the shear time exceeds a certain critical value, material near the edge of the plates, evidently experiencing higher shear rates than material near the center, forms oriented crystal structures. This emerges in the DSC signal as two peaks; one from the oriented crystallization near the outer edge and one from the isotropic crystallization near the center of the geometry. From RheoDSC experiments we obtain a relation between crystalline space filling and viscosity for these oriented crystal structures. Next, we subjected the iPP melt to a poiseuille flow in a modified multi-pass rheometer (MPR). By combining in-situ wide angle synchrotron x-ray diffraction (with an unprecedented sample rate of 30 Hz) and the pressure signal in the MPR we are able to simultaneously probe crystalline structure and viscosity. The depth sectioning technique is applied to quantify structure formation for different positions along the flow gradient direction. It is shown that even during very short flows (0.20s with an apparent wall shear rate of 900 1/sec) the viscosity strongly increases due to the formation of crystalline structures. We used a phenomenological model to predict crystalline structure from chain stretch on a continuum level. By combining this model with the relation between space filling and viscosity from the previous experiment we are able to obtain a prediction of the pressure drop over the channel. It is shown that due to pressure gradients, the crystalline morphology is strongly dependent on position along the slit.

Symposium PS

Polymer Solutions

Organizers: David F. James and Hagar Zohar

Tuesday 10:00 Mont-Royal/ Hampstead PS15

Instability mechanisms in the viscoelastic flow past bluff bodies

Vincenzo Citro[1], Luca Brandt[2], and Flavio Giannetti[1]
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We study the linear stability of the non-Newtonian flow past a circular cylinder placed perpendicularly at the centerline of a channel by means of numerical simulations. We focus on dilute polymer suspensions where viscoelastic effects are modeled by the FENE-P closure and consider the role of the polymer extensibility and concentration on the onset of the oscillatory flow. We show that the polymer additives have a stabilizing effect on the first bifurcation of the cylinder flow, in agreement with previous numerical and experimental investigations [D. Richter, G. Iaccarino, E. Shaqfeh, Simulations of three-dimensional viscoelastic flows past a circular cylinder at moderate Reynolds numbers, J. Fluid Mech. 651, 2010, pp. 415 - 442.,P.M. Coelho, F.T. Pinho, Vortex shedding in cylinder flow of shear- thinning fluids I. Identification and demarcation of flow regimes, J. Non-Newtonian Fluid Mech. 110, 2003, pp. 143 - 176.]. The spatial structure of the unstable global modes is discussed at a relatively high Weissenberg numbers and a receptivity analysis is presented. We identify the core of the instability, the region in space where the flow is more sensitive to a feedback forcing, by building a spatial map of the product between the direct and the adjoint modes (the so called structural sensitivity [F. Giannetti, P. Luchini, Structural sensitivity of the first instability of the cylinder wake. J. Fluid Mech. 581, 2007, pp. 167 - 197.]). The modifications of the steady base flow are discussed to understand the role of the polymers in the stabilization. These modifications are strongly localized in the regions where the structural sensitivity is largest and the length of the recirculation region behind the cylinder is only slightly changing at the bifurcation onset. In addition to the inertial instabilities we will consider in the final contribution also the same flow configuration at low Reynolds numbers where three-dimensional elastic instabilities have been previously reported.

Tuesday 10:25 Mont-Royal/ Hampstead PS16

Why the true strain hardening in extension and shear indicates the limitation of the tube model?

Shi-Qing Wang[1], Gengxin Liu[2], and Hao Sun[2]
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The extensional "strain hardening" phenomenon has been extensively studied for entangled polymeric liquids. Our recent analyses [J. Rheol. 55, 1247 (2011), J. Rheol. 57, 89 (2013)] show that the behavior of polymers with LCB such as LDPE often do not reflect true hardening associated with non-Gaussian stretching in the finite extensibility limit and is merely a consequence of geometric condensation. In this talk we show two examples of real strain hardening due to non-Gaussian stretching of the chain backbone, involving (a) fast startup uniaxial extension of linear polymer melts and (b) fast startup simple shear of a comb-like PS solution. We will discuss why such phenomena cannot be accounted for by the theoretical oversimplification inherent in the smoothed-out mean-field single-chain treatment of the tube theory.

Tuesday 10:50 Mont-Royal/ Hampstead PS17

A rheological approach to determine the phase behavior and critical solution temperatures of polymer solutions

Mehdi Pakravan, Marie-Claude Heuzey, and Abdellah Ajji
Chemical Engineering, École Polytechnique de Montréal, Montreal, Canada

Several methods have been used to study the onset of phase separation in polymer solutions such as turbidimetry, thermo-optical analysis (TOA), light scattering and small angle neutron scattering (SANS). However, only improved scattering techniques yield more detailed information leading to both binodal and spinodal points. These costly techniques are complicated and require high tech instruments. In this work, for the first time we demonstrate the usefulness of a rheological approach to investigate the phase behaviour of polymer solutions. Using the combination of experimental and theoretical studies, we managed to satisfactorily predict the phase behavior of polymer solutions. The results revealed that rheological measurements are powerful and sensitive to detect even the early stage of phase separation of a well-known polyethylene oxide (PEO)/water solution as a model solution. In this approach binodal decomposition (BD) temperatures were estimated from isochronal dynamic temperature sweep experiments and spinodal decomposition (SD) points were quantitatively calculated on the basis of a mean field theory. This successful approach was then employed on our solutions of interest: chitosan/PEO at different ratios in aqueous acetic acid that have already showed anomalous behaviour in a forming process. Lower critical solution temperature (LCST) phase behaviour was observed for chitosan/PEO solution blends. Phase separation temperature, miscibility range and correlation length of the solutions were also determined. By using very fundamental theories in this method, key macromolecular and thermodynamic parameters such as the correlation length and Flory-Huggins interaction parameter (X) of the PEO/chitosan solutions are also estimated.

Tuesday 11:15 Mont-Royal/ Hampstead PS18

Thermal stability and rheological properties of viscoelastic surfactant in high-temperature high-salinity environment

Muhammad Shahzad Kamal[1], Ibnelwaleed A. Hussein[1], Abdullah S. Sultan[2], and Han Ming[3]
[1]Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia; [2]Petroleum Department, KFUPM, Dhahran, Eastern Province 31261, Saudi Arabia; [3]Saudi Aramco, Dhahran, Saudi Arabia

With increasing industrialization, crude oil demand is increasing while new oil filed discoveries are decreasing worldwide. To meet this growing demand of oil, it is extremely important to recover maximum oil from existing oil reservoirs using enhanced oil recovery (EOR) technique. Chemical EOR (cEOR) is a promising EOR technique which is most suitable for light oil reservoirs. The two important properties required for cEOR are ultra-low interfacial tension and high viscosity of displacing fluid. Surfactants are used to achieve low interfacial tension while water soluble polymers are used for maintaining high viscosity. One of the major disadvantages of these water soluble polymers is the hydrolysis of amide group at elevated temperatures. Viscoelastic surfactants (VES) are class of surfactants that have additional desirable property of improving mobility ratio in addition to lowering the interfacial tension. VES have excellent thermal and shear stability compared to water soluble polymers used for EOR. The objective of this paper is to study the rheological properties of the VES and their interactions with different salts and polymers. Discovery hybrid rheometer (DHR-3) was used for measuring rheological properties. Thermal stability of VES was evaluated using 1H NMR, 13C NMR, FTIR and TGA. Investigated VES showed excellent thermal stability and salt tolerance. No structural changes were observed after aging at 100oC in presence of salts. Rheological properties of VES and VES-polymer systems will be discussed

Tuesday 11:40 Mont-Royal/ Hampstead PS19

Rheological characterization and mass spectrum analysis of guar gum solution after mannanase treatment

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Guar is a naturally occurring polysaccharide with remarkable rheological properties. Guar gum is a major viscosifier used in hydraulic fracturing for proppant transport and placement. However, once the proppant is placed, guar gum needs to be broken down to facilitate the flowback of residual polymers. Enzymatic hydrolysis has a significant impact on the rheological kinetics of long-chain guar polymers, thinning and breaking the gum to allow low viscosity flow. In order to further understand structure-rheology relationships of guar gum, we performed a detailed characterization of guar polymers during mannanase treatment, with a focus on the rheological behavior and kinetics of the digested guar fragments. A novel, hyperthermostable mannanase was chosen that specifically breaks beta-1, 4 backbone linkages of guar polymers while keeping alpha-1, 6-glycosidic side chain bonds intact. Quantitative mass spectrum analysis was used to identify and characterize enzyme-treated guar fragments in a high throughput fashion. The changes in molecular weight and size distribution over time were recorded to paint a dynamic picture of the process, which is influenced by variables such as temperature, enzyme concentration, pH and time. Our results shed light on the mechanisms at the molecular level of guar degradation by a hyperthermostable mannanase enzyme. Correlation of rheological dynamics with molecular weight distribution patterns will be discussed in details.

Symposium BM

Rheology and Processing of Bio-based Materials

Organizers: Michel Huneault and James J. Feng

Tuesday 10:00 Côte-St-Luc BM1

Quantifying structural protein contributions to cell mechanics with a live cell monolayer rheometer

Claire M. Elkins[1], Wen-Jun Shen[2], Victor Khor[2], Fredric Kraemer[2], and Gerald G. Fuller[1]
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A number of biological fields would benefit greatly from a device capable of rapidly measuring cell mechanical properties. However, most existing technologies for analyzing cell mechanics are either low throughput single-cell measurements or complicated by the presence of a three-dimensional cell culture gel. Our research addresses this need through the construction of a device capable of rapidly measuring the average mechanical properties of an entire cell monolayer. In this device, a confluent monolayer of cells cultured on collagen-coated glass is gently compressed by a coverslip lowered down to contact the monolayer. After a wait period to allow attachment of the cells to the top coverslip, this top plate is sheared while a sensitive force transducer measures the applied stress, thereby allowing rapid measurement of average mechanical properties across the cell monolayer. The entire apparatus is mounted on a DIC microscope, allowing visualization of the cell deformation during these mechanical measurements. We have applied this cell monolayer rheometer to study the relative impact of several cytoskeletal structural proteins on undifferentiated and differentiated adipocyte cell mechanics. Step-strain experiments using this device show differences in relaxation modulus in cells with disrupted microtubules and actin filaments, as well as cells knocked out for the intermediate filament vimentin. These results indicate that the cell monolayer rheometer may be used to quantify the contribution of various cytoskeletal structural proteins to cell mechanical properties in a way that is relatively high throughput and allows for cells to maintain cell-cell contacts and their adherent morphology throughout the experiment.

Tuesday 10:25 Côte-St-Luc BM2

Attractive interactions among intermediate filaments control networks mechanics

Norbert Willenbacher
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Intermediate filaments (IF) serve as mechanical stress absorbers in eukaryotic cells. There are more than 70 different cell specific IF proteins which are divided in six different types according to similarities in their protein structure. Here we investigate intermediate filament networks of keratin 8 and 18 (K8/18) formed from the basic type I keratin 8 and the acidic type II keratin 18 in vitro that are typically found in abundance in simple (internal) epithelia. These networks show an unusually high plateau modulus (1 - 10 Pa at 1 g/l), which depends only weakly on concentration ($G_0 \sim c^{0.5}$ decreases by more than two orders of magnitude and follows a power law of $G_0 \sim c^2$. The addition of the surfactant not only alters the linear viscoelastic shear modulus, but also has a strong effect on the non-linear mechanical network response. Strain stiffening can be completely suppressed adding a sufficient amount of surfactant. In contrast, the network mesh size determined from microrheology and the bending stiffness of the individual filaments obtained from high frequency oscillatory squeeze flow experiments are not affected by the added surfactant. This is also true for the network structure revealed from electron microscopy. From these findings we conclude that attractive interactions among filaments govern the macroscopic properties of K8/18 networks and are pivotal for their linear and non-linear rheology. Networks of the type III IF-protein vimentin show the same decrease in the plateau modulus and in strain stiffening after addition of Triton X-100. This suggests that these attractive interactions are controlling the mechanical response of cytoplasmic intermediate filament networks. This at least seems to hold for the major representatives and this hypothesis is further supported by the strong effect of ionic strength on strain-stiffening of vimentin reported in the literature.

Tuesday 10:50 Côte-St-Luc BM3

Single particle tracking for understanding E. coli biofilm structure and dynamics

Alona Birjiniuk[1], Elizabeth Nance[2], Justin Hanes[2], Katharina Ribbeck[3], and Patrick S. Doyle[1]
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Biofilms are communities of bacteria that have adhered to a surface and enveloped themselves in extracellular polymeric substance (EPS), composed primarily of polysaccharides dissolved in water with smaller amounts of proteins, lipids, and DNA. By surrounding themselves with this gel, the bacteria gain mechanical stability against external forces and decreased susceptibility to antibiotics. As a result, they are problematic in healthcare and other industries, as they form on the surfaces of multiple types of devices, and are difficult to remove. Little is known about the internal structure of biofilms within the EPS, and most prior work on understanding its properties has produced averaged values which do not provide information on spatially variant structural details. By adding micron-scale beads to the biofilm in two ways - premixed with the cells and media before growth or to the media on top of an already grown biofilm - we have examined the motion of beads embedded in the EPS, as well as those that are in the biofilm but are not trapped within the gel matrix. Using beads of different surface charges and chemistries embedded within the biofilm, we have determined that E. coli biofilm has spatially variant charge density that is highest near the surface on which the biofilm is grown, and that matrix may grow around beads with which it does not interact, creating localized, size-dependent behavior. Observing beads added onto an already formed biofilm has provided evidence for the existence of pores through which micron-scale objects can travel and for the ability to form probe-matrix interactions on the order of hours. Further investigation of other clinically relevant biofilm-formers will help us better understand and characterize these structures. An improved understanding of biofilm structure may help us determine how they function and how to best disrupt and eliminate them from surfaces that are difficult to access or replace.

Tuesday 11:15 Côte-St-Luc BM4

Effect of viscoelasticity on the collective behavior of the suspension of motile cells

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The suspensions in which the motile microorganisms swim generally exhibit viscoelastic behavior due to secretion of the extracellular polymeric substances. Hydrodynamic interactions of large-scale flows induced by swimming microorganisms with polymers dissolved in the surrounding fluid produce complex chaotic dynamics. To elucidate this process, we used a kinetic model developed to study the behavior of self-propelled particles in conjunction with Oldroyd-B constitutive equation and the Stokes equations. We performed multiple numerical simulations of the system in order to analyze the effect of the viscoelasticity on the large-scale coordinated behavior of the microorganisms. In addition, we explored different regimes of the flow by varying the corresponding parameters of the problem, such as Weissenberg number and viscosity ratio, to gain insights regarding the characteristics of the flow patterns generated by the collective motion of microscopic swimmers.

Tuesday 11:40 Côte-St-Luc BM5

Upstream migration of endothelial cells in response to impinging fluid flows

Maggie A. Ostrowski[1], Eva Yi-Hsuan Huang[1], Ngan F. Huang[2], Travis W. Walker[1], John P. Cooke[3], Alexander R. Dunn[1], and Gerald G. Fuller[1]
[1]Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States; [2]Center for Tissue Regeneration, Repair and Restoration, Veterans Affairs Palo Alto Health Care System, Palo Alto, CA, United States; [3]Cardiovascular Institute, Stanford University, Stanford, CA, United States

Endothelial cell migration and polarization are fundamental to many physiological processes in development and disease and are critically reliant upon shear stress sensing. Shear stress gradients arising from complex fluid flows present in vivo drive cardiovascular development, exist at valve leaflets, and correlate with atherosclerotic lesion formation. We built an impinging flow cell that exposes endothelial cells to a gradient of shear stress. We investigated the response of endothelial cells to shear stress gradients that ranged from 0 to a peak shear stress of between 9-220 dynes/cm^2. At high confluency, endothelial cells migrate against the direction of fluid flow and concentrate in the region of maximum wall shear stress, while sub-confluent endothelial cells migrate in the flow direction. In addition, endothelial cells align parallel to the flow at low wall shear stresses but orient perpendicular to the flow direction and in a densely packed arrangement above a critical threshold in local wall shear stress. Our observations suggest that endothelial cells are exquisitely sensitive to both the magnitude and spatial gradients in wall shear stress. Their resulting migration and polarization may play presently unrecognized roles both during cardiovascular development and disease, particularly in regions of complex flow.

Tuesday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Tuesday 1:30 Westmount SC20

Concentrated hard sphere crystals under oscillatory shear: Stresses and dynamics

Nick Koumakis[1], John F. Brady[2], and George Petekidis[1]

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The mechanical properties and the underlying particle dynamics of hard sphere colloidal crystals created by the application of oscillatory shear on hard sphere glasses are studied by experiments (LS-Echo technique coupled with rheometry) and Brownian Dynamics simulations. Experimental comparison of the linear viscoelasticity reveals that upon shear induced crystallization of a hard sphere glass, the moduli become smaller, as the free volume and entropy per particle increase. Additionally, during nonlinear oscillatory shear, BD simulations show anisotropic particle rearrangements in the crystal, in contrast to the isotropic motions in the glass. Since, crystal displacements arise from cooperative motion of particle layers sliding over each other in the velocity-vorticity plane, they additionally exhibit a yield strain less than that of the glass. Past the yield point, the longtime shear induced displacements of the glass are found to be larger, while the stresses become smaller. Although at low strains the crystal exhibits higher particle displacements than the glass, due to relative larger local free volume (in-cage motion), at higher strains the crystal shows reduced particle rearrangements due to the anisotropic sliding layer motion. We conclude that during oscillatory shear of a monodisperse hard sphere particle glass, large out of cage displacements allow the system to explore the energy landscape and find the minima in energy, stresses and displacements by configuring particles into a crystal oriented parallel to shear.

Tuesday 1:55 Westmount SC21

Shear thickening behavior of colloidal suspensions under bi-axial shear

Neil Lin and Itai Cohen

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The anomalous flow behavior observed in shear thickening fluids has made them an important and ubiquitous material for various industrial applications including traction control, and the manufacture of body armor. Previous scattering and direct imaging experiments have shown that shear thickening behavior is accompanied by the emergence of hydroclusters – collections of particles that are immobilized by lubrication stresses. However, the structure and dynamical evolution of hydroclusters and their direct relations to the suspension rheological properties are still poorly explored. Here, by using a newly developed bi-axial confocal rheoscope, we investigate the anisotropic viscosity and microstructure of a shear thickened colloidal suspension. We impose a high frequency flow to shear thicken the suspension and simultaneously probe its response using a low frequency shear flow. We find that the viscosity in shear thickened suspensions is highly anisotropic. In particular, we find that the viscosity associated with the vorticity-gradient plane is three times higher than the viscosity associated with the flow-gradient plane. These findings suggest that the orientation of hydroclusters may be anisotropic and crucial in determining the suspension viscosity tensor.

Tuesday 2:20 Westmount SC22

The viscometric functions of concentrated shear-thickening colloidal suspensions

Colin D. Cwalina[1] and Norman J. Wagner[2]

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Concentrated colloidal suspensions display nonlinear behavior under shear, including shear thinning and shear thickening as well as normal stress differences that can vary, and even change sign, with shear rate. In contrast to the literature on non-colloidal suspensions, the experimental study of all three viscometric functions-the first and second normal stress differences, and the shear viscosity-for colloidal hard-sphere suspensions is limited. Simulation results for hard-sphere colloidal suspensions have shown that N_2 is always negative while the sign of N_1 changes from positive to negative through the shear thickening transition [Foss and Brady, 2000]. Other than the measurements of Lee et al. (2006), which qualitatively support this trend, there is a paucity of experimental data on model near hard-sphere colloidal suspensions. In this work, we report measurements of the three viscometric functions for near hard-sphere suspensions of varying concentrations and applied shear rates. The model colloidal suspensions consist of silica nanoparticles in a polyethylene glycol carrier fluid. N_1 was measured directly with a

cone and plate while N_1-N_2 was obtained from parallel plate measurements. In the shear-thickened state, we find N_1 and N_2 to be negative with $|N_2| > |N_1|$. Both N_1 and N_2 are shown to scale linearly with the Péclet number at high shear rates as expected for a system where hydrodynamic forces are dominant. Further, in the shear-thickened state we find the ratios N_1/t and N_2/t to be largely independent of the shear rate and a function of only the volume fraction. Surprisingly, our results for N_1/ t and N_2/t follow an extrapolation of a semi-empirical prediction of a square law dependence on volume fraction as determined from the simulation results of Sierou and Brady (2002) for non-colloidal suspensions. This universality in the ratio of the normal stress differences to the shear stress further supports the dominating role of hydrodynamic interactions in the colloidal shear-thickened state.

Tuesday 2:45 Westmount SC23

Constant pressure simulation of dense colloidal suspensions

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Rheology, particularly yielding phenomena, of dense colloidal suspensions near the glass transition (volume fraction 0.58) can provide insight into the dynamics of glassy systems. Many earlier simulation studies used molecular dynamics, but their appropriateness for investigating the rheology of overdamped, stochastic colloidal systems is open to question. In the colloidal regime parameter space accessible to traditional constant volume and constant strain rate simulations has been limited. Here we present a framework for simulating suspension rheology at constant pressure and shear stress where both the suspension volume fraction and the strain rate are allowed to fluctuate. Using this approach, we study the rheology of dense suspensions near the glass transition using Brownian dynamics (no hydrodynamic interactions). The new framework allows access to a much wider strain rate range and to probe the yielding phenomena. By scaling the strain rate from the imposed stress to the structural rearrangement rate from the suspension long-time self-diffusivity, the suspension friction coefficient – the ratio of shear stress to the osmotic pressure – collapses onto a universal curve for all volume fractions below the glass transition. Above the glass transition, we determine the dynamic yield stress by observing the accumulated strain in the suspension, and show that the friction coefficients of the yielded suspensions collapse onto a different curve. For a colloidal glass at rest, we find that the suspension dynamics strongly depends on the sample preparation protocol and waiting time, and particle diffusion persists. We compare our Brownian dynamics glassy system to earlier molecular dynamics studies, and discuss the implications for incorporating hydrodynamic interactions.

Tuesday 3:35 Westmount SC24

Rheology of a concentrated bimodal suspension

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In this work, the steady shear rheology of a bimodal suspension of neutrally buoyant, noncolloidal spheres in a viscous, Newtonian liquid is investigated. The smaller particles are alginate gel microbeads, which are deformable and porous, and the larger particles are rigid PMMA spheres with a diameter approximately three times as large. Potential applications of such a system include composites processing and separation column packing.

Measurements were acquired in a parallel plate rheometer under shear rates ranging from 5 to 200 s^{-1}. Monomodal suspensions of each particle type up to 0.5 particle volume fraction exhibit nearly constant viscosity or slight shear thinning over the range of shear rates. Average viscosity values for the small, gel particle suspensions were significantly lower than those of large, rigid particle suspensions at the same particle volume fraction. For bimodal suspensions with a total particle volume fraction of 0.5, the viscosity increases as the relative fraction of large, rigid particles increases. For suspensions with a majority of large, rigid particles, two qualitatively distinct types of non-Newtonian viscosity curves are observed over certain ranges of the total and relative particle volume fractions: strong shear thinning or non-monotonic curves with maximum values at intermediate shear rates. Mapping the regions of contrasting rheology will provide further insight into the flow of bimodal suspensions containing both rigid and soft particles.

Tuesday 4:00 Westmount SC25

Colloidal microstructure in sheared Boger fluids

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Microstructures of high volume fraction colloidal suspensions in Boger Fluids are measured using high speed confocal microscopy. Unlike pure hydrodynamic interactions, wall effects have a large effect on the kinematics of the flow and the microstructure. What is unclear is why low weight fraction high molecular weight polymers have a significant effect on structure even when the polymer is localized. Through fluorescence imaging, the polymer phase is seen to remain coiled and isotropic in low shear regions of the flow and extended in the flow direction in high shear. Results demonstrating the effect of weight fraction, molecular weight, and relaxation time of the polymer phase will be shown.

Tuesday 4:25 Westmount SC26

Diffusion and transport of nanoparticles in arrays of nanoposts

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We study the diffusive dynamics and convective transport of nanoparticles of diameter 200-400 nm in microfabricated arrays of cylindrical nanoposts using differential dynamic microscopy and single particle tracking. Posts of diameter 500 nm and height 10 µm were spaced by 1.2-10 µm on a square lattice. First, we measured dynamics of nanoparticles in quiescent dilute dispersions. As the spacing between posts was decreased, the diffusive dynamics slowed and on all length scales were best represented by a stretched exponential function. Both the relative diffusivity and the stretching exponent decreased linearly with increased confinement and, equivalently, with decreased void volume. Second, we measured the dispersion of nanoparticles as they flowed through the nanopost arrays. The distributions of particle velocity in the longitudinal and transverse directions exhibited distinct scaling behaviors with increasing confinement. Moreover, with increasing confinement the transverse dispersion became progressively non-Gaussian and increasingly important relative to the longitudinal dispersion. The appearance of non-Gaussian and stretched dynamics suggests that the transport properties of nanoparticles become increasingly cooperative when strongly confined

Tuesday 4:50 Westmount SC27

Capillary thinning dynamics of suspensions near pinch-off

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Within this paper we are presenting new findings on how the presence of particles alters the pinch-off dynamics of a liquid bridge. For moderate concentrations, suspensions initially behave as a viscous liquid with dynamics determined by the effective viscosity of the suspension. Close to breakup, however, the filament loses its homogeneous shape and localized accelerated breakup is observed. This paper focuses on quantifying these final thinning dynamics of different sized particles ranging from 6 µm to 40 µm dispersed in a Newtonian matrix with volume fractions ranging from 2 to 40 %. Capillary thinning experiments are visualized with a high-speed camera equipped with high-resolution optics that allows tracking the position of single particles within the thinning filament. For all samples, the accelerated dynamics are initiated by self-dilution of the suspension, due to local rearrangements of the particles. The radial velocity continues to increase and reaches a maximum when the interstitial fluid is thinning between two individual particles. This maximum velocity is higher than that of the pure matrix fluid [1] and we quantify its relation to the concentration and particle size. Contrary to Bonnoit et al. [1], we observe that the final thinning dynamics are dominated by a deceleration, where the interstitial fluid appears not to be disturbed by the presence of the particles and the pinching dynamics return to the self-similar scaling of a Newtonian liquid bridge between single particles in the final moments preceding breakup.

[1] Bonnoit, Bertrand, Clément and Lindner, Phys. Fluids 24: 043304 (2012), Accelerated drop detachment in granular suspensions.

Tuesday 5:15 Westmount SC28

Holistic modeling to predict stability of oil well cement slurries

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Technology advances in oil and gas exploration continue to be made in drilling and fracturing, particularly for long horizontal wells in medium and high temperature formations. These include the development of novel cementing systems that can be pumped long distances, through narrow annuli that are eccentric and have high temperatures, while maintaining stable suspension properties. After the stable cement slurry suspension is in place, it quickly transitions from a fluid to a semi-solid material that is capable of preventing channeling defects in the annular sheath. There is thus a need to be able to predict the suspension stability of cement slurries while being subjected to thermal and shear histories in the well bore. There is considerable knowledge in the literature regarding modeling of stable suspensions for simple Newtonian and Power Law fluid systems. However, there is a knowledge gap for complex suspensions that have multiple particle systems, with multiple densities and size distributions that ultimately result in shear thinning fluids that have finite yield points. This work uniquely combines various mathematical models that predict the effects of: base fluid rheology; multiple particle types, sizes, densities and concentrations; thermal history; shear history; and suspension additive concentrations on the final rheology and stability of the slurry. Being able to predict the down-hole stability of complex oil well cement slurries, after making early bench top measurements of prototype slurries, provides many benefits: saving time and expense of testing; serving as a direct slurry design tool; facilitating the optimization of slurry stability while minimizing cost.

Symposium IP

Interfacial Phenomena

Organizers: Suzanne Giasson and Lynn M. Walker

Tuesday 1:30 Verdun/Lachine IP10

Droplets break-up in high internal phase emulsion under flow

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Emulsions are widely used in industry (cosmetic, food, drugs...). The most common process to prepare emulsions involves shearing the two phases to create a mechanical disrupt of the droplets of the dispersed phase into the continuous phase. However this method leads to poor control of the droplets' size, resulting in a large polydispersity. A predictive model to design emulsions remains an important industrial challenge.

We study an emulsion of silicone oil in water, glycerol and surfactant. The emulsion is made transparent by matching the index of the two phases and only a small fraction of the droplets are dyed. We are able to visualize the deformation of a few dyed droplets interspersed in transparent droplets. The emulsion is injected in a crossflow micro channel, the geometry of which enables the creation of a pure elongational flow. Using a feedback system on the pressure we are able to keep one droplet in the center of the channel and visualize its geometry. We will explore the impact of the different experimental parameters (concentration, viscosity...) in order to get a predictive model to design emulsion.

Tuesday 1:55 Verdun/Lachine IP11

Liquid foams: Fracture dynamics and film instability

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A layer of foam bubbles between parallel plates (a quasi-two-dimensional liquid foam) has been shown to fail upon introduction of pressurized air in two different ways, resembling ductile and brittle fracture. The microscopic processes of deformation, plasticity, and loss of cohesion on the bubble scale are accessible in detail to experiment and modeling, using elements of fluid dynamics, stability theory, and surface chemistry. A simplified network model of liquid nodes captures both fracture modes and allows for quantitative assessment of microscopic effects. For the brittle crack propagation, which involves breakage of successive films, we show that viscosity and Marangoni stresses can play significant roles in determining film instability and thus foam failure, with important consequences for practical applications such as metal foam manufacture or oil recovery.

Tuesday 2:20 Verdun/Lachine IP12

Micro and macrorheological methods at fluid-fluid interfaces

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Microrheological methods have been developed to probe the rheological properties of fluid-fluid interfaces, but orders-of-magnitude differences in interfacial viscosities measured with micro and macrorheological techniques have been reported in the literature. In bulk fluids, microrheological techniques have successfully been developed around the generalized Stokes-Einstein relation (GSER) and can be expected to agree with macroscopic measurements under conditions where the GSER is valid. For microrheological measurements at interfaces, the assumptions of GSER are not generally met due to the multi-component, multi-length scale environment of fluid-fluid interfaces. Instead, hydrodynamic models that relate the motion of a particle at an interface to the viscosity of the interface and the surrounding bulk fluids have been used to extract interfacial shear viscosities from particle-tracking experiments. Models currently account for particle intrusion into the bulk phase, the effects of particle shape and the influence of Marangoni stresses. Notable omissions from these models are the effects of interface heterogeneity and electrocapillarity. We have investigated the orders-of-magnitude discrepancy between microrheological and macrorheological results at fluid-fluid interfaces and will discuss experimental results using both techniques on various interfaces.

Tuesday 2:45 Verdun/Lachine IP13

Free impinging jet microreactors: Controlling reactive flows via fluid viscoelasticity and capillarity

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Impinging free liquid jets can be used as wall-free continuous microreactors. Collision of two reacting jets forming a free-standing thin liquid sheet allows to perform rapid precipitation reactions to form colloidal particles, enhance micromixing, and to master challenging reactions with very fast kinetics. To control the shape, size and hydrodynamics of the impingement zone between the two liquid streams, it is crucial to

understand the interplay between capillary forces, fluid rheology and reaction kinetics [1]. Here, these aspects are studied using model fluids, each illustrating a different physical effect of surface and bulk fluid properties. First, solutions of an anionic surfactant below, near and above the critical micelle concentration are used to assess the roles of static and dynamic surface tension and dilatational surface rheology [2]. Secondly, solutions of different high molecular weight polymers with different extensional viscosities are introduced to control the morphology and flow patterns of the rapid free surface flow. If properly controlled, these effects can dramatically enhance control over the micromixing time scales to the extent that very rapid reactions can be performed with outstanding selectivity. The interplay between free surface flow and reaction kinetics is quantified using parallel-competitive reactions. Finally, the contribution also demonstrates how these results can be used to control the particle size in precipitation processes [3] via the effects of fluid viscoelasticity and capillarity.

References: [1] Erni P et al., Langmuir, article la-2013-01017, in press (2013). [2] Erni P, Soft Matter, 7, 7586 (2011). [3] Elabbadi A, Jeckelmann N, Ouali L and Erni P, ACS Appl Mater Interfaces, 3, 2764 (2011).

Symposium GS

Gels and Self-assembled Systems

Organizers: Jai Pathak and Matthew E. Helgeson

Tuesday 3:35 Verdun/Lachine GS1

Stress diffusion in shear-banding wormlike micelles

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Many complex fluids exhibit shear localization. In particular, solutions of wormlike micelles are well-known to develop steady shear-banding. Above a critical shear rate, the flow separates in domains of low and high shear rate corresponding to the boundaries of the so-called stress plateau delimiting the shear-banding regime on the flow curve. In the last fifteen years, diffusive terms on the stress and/or on the shear rate have been added to constitutive models in order to select an history-independent value of the stress plateau and a finite thickness of the interfaces between domains of different shear rates. Such terms are obviously necessary from a macroscopic viewpoint, but their microscopic origin is still debated. We will summarize recent experiments we have performed in order to measure the diffusion coefficient for shear-banding wormlike micelles systems. We will discuss the effects of the global shear rate and of the type and concentration of surfactant.

Tuesday 4:00 Verdun/Lachine GS2

Structure formation in extensional flow of wormlike micellar solutions as revealed by capillary breakup extensional rheometry experiments

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We have used the CaBER method to study the elongational behavior of wormlike micellar solutions. Experiments include horizontal filament stretching (tilted CaBER method) to determine the true axial force during capillary thinning.

Cetylpyridinium chloride / sodium salicylate (CPyCl/NaSal) and Hexadecyltrimethyl-ammonium bromide (CTAB) / NaSal solutions have been investigated. Both form cylindrical threads, which exhibit an exponential diameter decay characterized by the elongational relaxation time λ_e. More stable filaments are observed for CTAB/NaSal than for CPyCl/NaSal resulting in about two to three orders of magnitude higher filament lifetime and λ_e values for CTAB/NaSal even at substantially lower molar concentration.

For CPyCl/NaSal, the ratio λ_e/λ_s, where λ_s is the longest shear relaxation time, starts around 0.01 at R=0.5, increases with increasing R and levels off to a constant value of 0.5 at R=0.8 when the first viscosity maximum (R=0.6) is slightly exceeded. For CTAB/NaSal solutions, λ_e/λ_s starts at 100 and decreases with increasing R to a final value of about 1 slightly above the first viscosity maximum.

The high relaxation time ratios for CTAB/NaSal especially at low R are supposed to be due to the formation of a flow induced structures similar to what is observed in shear flow. The relaxation time ratio even increases with decreasing CTAB concentration. The increase in extensional relaxation time corresponds to a substantial increase of the apparent average micellar length by about a factor of 10.

The low relaxation time ratios for the CPyCl/NaSal are presumably due to micellar breakup in the strong elongational flow.

The factor of two difference in the relaxation time ratio between both systems at high R may be attributed to the higher flexibility of CPyCl/NaSal (l_p = 28 nm) compared to CTAB/NaSal (l_p = 55 nm).

Tuesday 4:25 Verdun/Lachine GS3

Flow pattern change through a formation of flow-induced structure in wormlike micelle solutions past arrays of microposts

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A surfactant, cetyltrimethylammonium bromide (CTAB) forms wormlike micelles in aqueous solutions with additive of sodium salicylate (NaSal). Wormlike micelles can self-organize under flow to form higher-order flow-induced structures (FISs), which are generally considered reversible. Recently, stable and irreversible FIS formation was reported first by Vasudevan et al. (Nature Materials, 2010). They reported that irreversible FISs were formed in the flow in a microchannel with high strain rates and high strains. In this study, flow patterns and a FIS formation are investigated experimentally in the microchannel flow past arrays of microposts. Test fluids used were entangled wormlike micelle solutions of CTAB and NaSal. At relatively low flow rates, we observed steady laminar flow patterns. The flow visualization results for the wormlike micelle solution and those obtained for DI water show a good agreement over the whole flow field. There, the flow can be considered as the Hele-Shaw flow. With increase of flow rate, the flow pattern was altered drastically, where the flow was no longer steady. The flow pattern change was accompanied by a formation of FIS in the wormlike micelle solution, which we observed directly with a phase-contrast microscopy. We observed sticky, viscous, transparent streaks of FIS in the fluid flowing down from the microposts, where the apparent property of the fluid was locally changed. The streaks are having a refractive index different from that of surrounding fluid, but they were hardly observed with bright field images. The streaks were mostly observed in the stagnation flow behind each micropost as well as the entry flow into the gap between microposts. The flow with the streaks was heterogeneous and highly unsteady. In consequence, the streaks entangle each other and form a knot, which were observed more frequently for cylindrical microposts than for slit-type obstacles in a microchannel. The FISs observed here were disintegrated in several minutes after the cessation of flow.

Tuesday 4:50 Verdun/Lachine GS4

NMR velocimetry of wormlike micelle solution flow in pipes and capillaries – apparent wall slip and shear banding

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Flow behavior of a series of wormlike micelle solutions in pipes is investigated. The objective of this body of work is to assess our ability to predict pressure drop for a given flow rate over a wide range of conditions. The flow behavior is analyzed by NMR velocimetry and classical capillary rheometry techniques. The wormlike micelle systems of interest are aqueous mixtures of SLE1S, SLE3S, and NaCl. Four compositions with different NaCl contents are used in this body of work, traversing up and back down the salt curve. Wormlike micelle microstructure is identified by cryo-TEM and rheological measurements. Results of flow behavior in circular cross sectional geometries (pipes and capillaries) are shown, including pressure drop versus flow rate behavior and NMR velocimetry. We observe classical parabolic velocity profiles at low Wi, apparent slip at pipe walls at high Wi, and shear banding in a limited number of conditions. We compare rheological properties derived from pipe and capillary flow experiments to rheological properties measured using rotational drag flows.

Tuesday 5:15 Verdun/Lachine GS5

Flow-induced gelation in a non-ionic wormlike micellar solution

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Surfactant molecules can self-assemble into various morphologies under proper combination of surfactant concentration, temperature, and flow conditions. In this work we consider the flow of a non-ionic micellar solution (precursor) through a microfluidic device containing microposts, with focus on their microstructural and rheological evolution. The precursor contains polyoxyethylene(20) sorbitan monooleate, also known as Tween-80 and the co-surfactant monolaurin (ML). The precursor is weakly viscoelasitc and shear thinning. When subjected to strain rates $\sim$10^{3}~s^{-1} and strain~$\sim$10^{3} under room temperature, non-ionic surfactant solution with a mixture of spherical and wormlike micelles can transition into stable, gel-like structures containing entangled, branched, and multi-connected micellar networks, evidenced by electron microscopy. An activation energy is needed for such structural transition. The necessary activation energy can be provided by tuning the thermodynamic properties of the micellar solution or by subjecting the solution to flow (i.e., our microfluidic strategies). The presence of spatial confinement and extension in the microfluidic flow induces entropic fluctuations, lowering the energy barrier between states, thus enabling the irreversible gelation from the non-ionic precursor solution. We also show that the rheological properties of the precursor are smaller than those of its gel-like structures. This rheological variation is associated with the microstructural evolution from spherical and wormlike micelles to an entangled and multi-connected micellar network.

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Tuesday 1:30 Outremont MB20

Flow induced crystallization of isotactic polypropylene

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Flow induced crystallization (FIC) has shown to be an interesting research area over the past four decades. Thread like precursors, resulting from applied stress on a melt for a certain amount of time, are a phenomenon which is widely found in industrial processing such as injection molding or film blowing. There are two criteria that need to be fulfilled in order to form these extended crystals. First, applying a shear rate faster than the stretch relaxation time of the melt, dictated by its molecular weight and polydispersity. Second, a critical specific work (Wc) needs to be applied to the melt in order to form sufficiently stable nuclei. Time sweep measurements have been performed at different degrees of undercooling and applied specific work, ranging from 0 MPa (quiescent crystallization) up to Wc, to study the crystallization kinetics of isotactic polypropylene. Time to reach tan(δ) = 1 was used as a comparison point, which allowed us to examine the transition from spherulitic nuclei to thread like row nuclei and determine Wc. This transition occurs whenever there is a change in nucleation rate, i.e. a time dependent change in slope. Rapid nucleation is a key factor for faster crystallization kinetics. As a result, the number density of spherulites in the material increases with increasing applied work, seen in polarized microscopy. Through DSC experiments it has been established that these extended structures are long-lived and have higher crystallization temperatures (T_C) compared to quiescent crystallization (T_{QC}). The relaxation time of these structures, time required for T_C to become equal T_{QC}, at temperatures above the spherulite melting point, was more than 20 hours. A transition in the relaxation time was found at temperatures approximately 40°C above the equilibrium melting temperature (193°C), where the memory of the sheared melt completely relaxes at much faster rate.

Tuesday 1:55 Outremont MB21

SAXS/WAXS studies of flow-induced crystallization of poly(1-butene) in shear flow

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Flow-induced crystallization of poly(1-butene) was studied in shear flow. Flow was produced using a Linkam shear cell that has been modified to allow x-ray access for in situ studies of polymer structure using synchrotron x-ray scattering techniques. After loading in the the shear cell, samples were first heated well into the melt, and then cooled to a crystallization temperature selected such that negligible quiescent crystallization would occur on reasonable time scales. A short burst of shear flow was then applied at various rates, after which simultaneous wide- and small-angle x-ray scattering (SAXS and WAXS) data were collected to study the resulting accelerated crystallization kinetics, as well as the morphology of the resulting crystallites (e.g. degree of crystallite orientation). SAXS and WAXS data provided generally self-consistent measures of the extent of crystallization, although WAXS data consistently reported a higher degree of crystallite orientation than SAXS. Average crystallite orientation was found to decrease over the course of crystallization. The impact of both deformation rate and total applied strain on the crystallization process were examined. The sample was also studied under similar flow conditions using (i) turbidity and (ii) linear viscoelasticity as probes of the developing crystallinity.

Tuesday 2:20 Outremont MB22

Stress overshoots in simple shear flow of entangled combs

Frank Snijkers[1], Dimitris Vlassopoulos[1], Taihyun Chang[2], Giovanni Ianniruberto[3], and Giuseppe Marrucci[3]
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We have investigated the transient response of entangled comb polymers in simple shear flow. The polymers were anionically synthesized combs, well-characterized via interaction chromatography, with entangled backbones an average of 29 branches of varying length. Using a cone-partitioned plate set-up we have observed that, beyond a certain shear rate, the start-up shear stress develops an overshoot which is associated with the backbone orientation and stretching. The peak strain became rate-independent and at a given rate it appeared to scale with the number of backbone entanglements when the dynamic dilution due to branches is accounted for. More importantly, for longer branches, within the rate-independent region the start-up shear stress displayed a double overshoot. With the aid of simulations, we have associated the faster, weaker overshoot with the withdrawal of branches into the backbone tube, in line with pom-pom dynamics. The excellent quantitative comparison between the simulations and experiments is encouraging.

Tuesday 2:45 Outremont MB23

Dielectric relaxation of monodisperse linear polyisoprene: Contribution of constraint release

Hiroshi Watanabe and Yumi Matsumiya
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Cis-polyisoprene (PI) has the type-A dipole so that the end-to-end fluctuation of PI chains results in slow dielectric relaxation. Dielectric and viscoelastic data of entangled linear PI are satisfactorily described by the full dynamic tube dilation (DTD) relationship and thus the constraint release (CR) mechanism underlying DTD contributes to the dielectric relaxation of PI. Nevertheless, recent modeling [Glomann et al. Macromolecules 2011, 44, 7430] and single-chain sliplink simulation [Pilyugina et al. Macromolecules 2012, 45, 5728] suggest that the CR mechanism has negligible influence on the dielectric relaxation time te of entangled linear PI, which somehow contradicts to the previous data. Thus, we revisited the classical problem, CR contribution to the dielectric relaxation of monodisperse linear PI. Specifically, we made dielectric and viscoelastic measurements for PI/PI blends in a wide range of the molecular weights of long and short components, M2 = 1.1M and M1 = 21k-179k, and with a small volume fraction of the short component, v1 = 0.1 and/or 0.2, to examine the CR contribution in the experimentally clearest way. It turned out that te of the short component was longer in the blends than in respective monodisperse bulk even for M1 = 179k. Furthermore, the viscoelastic and dielectric data of the short components (M1 = 43k) in the blend exhibited identical mode distribution and relaxation time, which confirmed that the CR mechanism was fully suppressed for these components in the blends. These results demonstrate, without any ambiguity, that the CR mechanism does contribute/accelerate the dielectric relaxation in monodisperse bulk PI even in the highly entangled regime (M1/Me = 36 for M1 = 179k). This CR-induced acceleration was found to be consistent with the empirical equations for the terminal relaxation time and CR time of monodisperse PI available in literature, as noted from a simple DTD analysis of the terminal relaxation process.

Tuesday 3:35 Outremont MB24

Rheological properties of Pd-diimine polyethylenes of complex chain architectures

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Chain architecture is an important chain parameter determining the physical properties, particularly rheological properties, and applications of polymer materials. The developments in Pd-diimine catalyst technology and its enabled polymerization technique have recently led to the successful design and synthesis of a novel class of polyethylenes of complex chain architectures. This allows the investigation of the effects of chain architecture on polymer rheological properties. In this presentation, we will discuss the melt rheological properties of a range of well-defined Pd-diimine polyethylenes of hyperbranched, star, block, and gradient architectures synthesized in our lab.

Tuesday 4:00 Outremont MB25

Non-kinematic approach to the Leonov model

Kwang Soo Cho
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Approximate dynamics of chain conformation is used to derive a nonlinear viscoelastic constitutive equation which belongs to the class of the Leonov model. A symmetric positive definite tensor called conformation tensor is introduced to describe deformation of the representative chain in polymer melt and its dynamics is derived from the Lengevin equation. The evolution equation of the conformation tensor is identical to that of the Leonov while the origin is not from kinematics but from dynamics of a polymer chain.

Tuesday 4:25 Outremont MB26

A priori predictions of the shear rheology of polymer melts

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The shear rheology of linear melts of arbitrary molecular weight distribution is now available in a completely a priori manner. This is made possible through the implementation of a novel dynamic Monte Carlo algorithm known as COMOFLO which combines the cooperative motion algorithm of Pakula with a shear biasing technique (Dorgan et. al. Macromolecules, 45(12) 8833-8840 (2012)). Using this technique, rheological properties are calculated as a function of shear rate and chain length. The viscosity and the first and second normal stress coefficients are calculated and found to be consistent with well-established experimental facts. The zero-shear viscosity scales linearly with low molecular weights and scales to the 3.5 power at higher molecular weights. This crossover in viscosity scaling occurs at the same chain lengths (N ~ 150) as the transition in chain dynamics from Rouse to Reptation. Because the simulations are conducted in the athermal limit, there are no parameter inputs. The known observable linear viscoelastic rheological properties of polymer melts are thus now available in a fully predictive fashion. Extensions of this predictive algorithm to polydisperse systems are discussed. Single peaked distributions of various breadths are compared to bimodal distributions and the results are shown to be in excellent agreement with the known experimental facts. The effects of molecular scale confinement may also be studied and the simulations demonstrate that decreasing the spacing between hard walls leads to faster molecular relaxation in the melt. Lower Rouse times and higher critical shear rates for shear thinning are observed under confinement.

Tuesday 4:50 Outremont MB27

Polymerisation-to-processing molecular rheology modelling of long chain branched polymers

Tom C. McLeish[1], Daniel J. Read[2], and Chinmay Das[2]
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A constant goal for molecular polymer rheology is the prediction of both linear and non-linear rheological response, and hence the performance of a polymer melt in processing conditions, directly from knowledge of the molecular weight distribution and branching structure. This is especially useful when polymerisation processes are also modelled, for then it is in principle possible to model, *in silico*, the sequence of experimental polymerisation and processing of a newly-designed melt. Early attempts at bringing the models required at the levels of polymersation and melt rheology have been made publically available in the "Branch-on-Branch" or "BoB" [1] software suite.

We present results for both Low Density Polyethylene and metallocene Long Chain Branched Polymers within this framework, drawing out some practical lessons on the designing-in of, for example, melt strength at chosen deformation rates and temperatures.

[1] D.J. Read, D. Auhl, C. Das, J. Den Doelder, M. Kapnistos, I. Vittorias and T.C.B. McLeish . "From Reaction to Rheology: Linked Molecular Models of Polymerisation Kinetics and Entangled Dynamics Predict Branched Polymer Structure and Flow", *Science*, **333**, 1871-1874 (2011).

Tuesday 5:15 Outremont MB28

Equilibrium rheology predictions of the mobile slip-link model

Jay D. Schieber[1], Tsutomu Indei[1], Marat Andreev[2], and Rudi Steenbakkers[1]
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We consider four criteria of acceptability for single-chain mean-field entangled polymer models: consistency with a multi-chain level of description, consistency with nonequilibrium thermodynamics, consistency with the stress-optic rule, and self-consistency between Green--Kubo predictions and linear viscoelastic predictions for infinitesimally driven systems. Each of these topics has been considered independently elsewhere. However, we are aware of no molecular entanglement model that satisfies all four criteria simultaneously, except a model used in this work. The discrete slip-link model (DSM) is able to predict linear viscoelasticity of monodisperse linear, polydisperse linear, and branched systems with just two adjustable parameters. The model also shows good agreement with most dielectric relaxation experiments and flows without parameter adjustment. In this work we show linear viscoelasticity predictions of Mobile Slip-link Model (MSM), a further modification of DSM. MSM satisfies all four criteria, and allow us to use molecular dynamics primitive path analisys to calculate all, but one adjustable parameters. The remaining parameter $\tau_{\rm K}$ determines all timescale in the model. Results produced by MSM are very close to previously obtained with DSM.

Symposium NF

Non-Newtonian Flows

Organizers: Ian A. Frigaard and Vivek Sharma

Tuesday 1:30 Mont-Royal/ Hampstead NF1

Displacement flow of yield stress fluids in highly inclined pipes

Kamran Alba[1], Seyyed Mohammad Taghavi[2], John de Bruyn[3], and Ian Frigaard[1]
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The results of an experimental study of buoyant miscible displacement flows of a yield-stress fluid (Carbopol) by a higher density Newtonian fluid along a long inclined pipe are presented. The focus is on the industrially interesting case where the yield stress is significantly larger than a typical viscous stress in the displacing fluid, but where buoyancy forces may be significant. Over the full range of pipe inclinations we find two distinct regimes called slump and centre-type displacements that were also identified in our earlier work on near-horizontal flows (S. M. Taghavi, K. Alba, M. Moyers-Gonzalez, and I. A. Frigaard, J. Non-Newtonian Fluid Mech. 167-168: 59-74, 2012). Interestingly, the occurrence of slump and center regimes is primarily governed by approximately the same ratio of Reynolds number to densimetric Froude number, Re/Fr, as in near-horizontal case (600<Re/Fr<800). This implies that the inclination angle does not directly determine the flow regime. We also observe a third regime which we refer to as turbulent-mixed flow. In this case, despite the existence of the yield stress, the flow is very similar to that for a Newtonian displacement when the mixing is very efficient. Under the category of the slump regime we do observe a range of exotic behaviour at higher inclinations associated with the progressive break-up of the Carbopol layer. We give a detailed description of these secondary regimes and their formation. In the absence of an imposed flow of the displacing fluid, i.e. lock exchange, we observe that flows may nonetheless develop under the action of buoyancy despite the yield stress. We discuss the underlying mechanisms and potential implications for the plug cementing process. Finally, the experimental data were characterized according to whether the displacement flows happen instantaneously or there exists a back flow. This is important for industrial applications, in which back flow is generally undesirable.

Tuesday 1:55 Mont-Royal/ Hampstead NF2

Utilizing an elasto-viscoplastic model to predict the downhole pressure profile after primary cementing

Flávio H. Marchesini and Rafael M. Oliveira
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The downhole pressure profile after primary cementing of an oil wellbore is investigated. The developed model considers the influence of (i) fluid loss to the geological formation, (ii) elasticity, thixotropy and structure development during gelation, and (iii) compressibility and shrinkage of the cement slurry. This is a one-dimensional model whose shear rates are estimated by vertical velocity and annular distance. The thixotropic elasto-viscoplastic model recently proposed by de Souza Mendes and Thompson, Rheologica Acta, 2013 is used to calculate shear stresses, which are then plugged into the momentum equation. This is coupled to an equation for pressure evolution derived from mass balance and compressibility considerations. The model is applied to current oil fields.

Tuesday 2:20 Mont-Royal/ Hampstead NF3

Finite element approximations for the flow of thixotropic elasto-viscoplastic materials through an abrupt expansion

Cleiton E. Fonseca[1], Fernanda B. Link[1], Sérgio Frey[1], Monica F. Naccache[2], and Paulo R. de Souza Mendes[2]
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We analyze the flow of elasto-viscoplastic thixotropic materials through an axisymmetric abrupt 1:4 expansion. The mass and momentum conservation equations are solved in conjunction with the equations of a recently proposed constitutive model for gels and other soft solids that exhibit elasticity while gelled, yield beyond a threshold applied stress, and are thixotropic. The constitutive model is composed of an Oldroyd-B-like differential equation for the stress tensor whose parameters are functions of a scalar parameter that gives the structuring level of the microstructure. This structure parameter is governed by an evolution equation that involves a microstructure buildup term and a breakdown term. The set of governing equations was solved by a four-field Galerkin least-squares-type method in terms of the structure parameter, extra-stress, pressure and velocity. For a wide range of the governing parameters, we determined the shape, size and location of the unyielded regions, as well as the fields of velocity, elastic strain, and strain rate. Among other findings, we observed that the effects of elasticity and thixotropy are analogous, in the sense that both cause the development length in the downstream channel to increase dramatically.

Tuesday 2:45 Mont-Royal/ Hampstead NF4

Residual deposits of yield stress fluids at the wall in Poiseuille flows along uneven channel

Ali Roustaei and Ian Frigaard
Mechanical Engineering Department, The University of British Columbia, Vancouver, BC, Canada

A slow channel flow of a yield stress fluid along a wavy walled channel undergoes a number of interesting qualitative transitions as the amplitude of the wave is increased. For small amplitude long wavelength wall perturbations the characteristic central unyielded plug remains intact, but perturbs in shape so that the plug is widest in the narrowest part of the channel; see [1]. At a first critical amplitude the central plug breaks [1,2]. After breaking, in the central part of the channel we find unyielded plugs around the symmetry points connected by pseudo-plug regions in which extensional stresses are sufficient large to yield the fluid. Here we study a second critical amplitude beyond which there appears a region of unyielded fluid that is attached to the wall in the widest part of the channel, i.e. a fouling layer of static fluid. We explore the characteristics of this fouling layer numerically for a range of different channel wall geometries, showing how the amplitude, channel aspect ratio and Bingham number interact to influence the size of the residual deposit. We offer some analytical insights into formation of the residual deposits and predictions of their size. This represents the first stages [3] in a longer study to understand the effects of uneven wellbore geometry on drilling and primary cementing processes in oil and gas well construction.

References: [1] I.A. Frigaard, and D.P. Ryan, "Flow of a visco-plastic fluid in a channel of slowly varying width" J. Non-Newtonian Fluid Mech. 123(1), pp. 67-83, (2004). [2] A. Putz, I. Frigaard & D.M. Martinez, "The lubrication paradox & use of regularisation methods for lubrication flows." J. non-Newt. Fluid Mech., 163(1-3), pp. 62-77, (2009). [3] A. Roustaei and I.A. Frigaard, "The occurrence of fouling layers in the flow of a yield stress fluid along a wavy-walled channel." Accepted for publication in J. non-Newt. Fluid Mech., to appear 2013.

Tuesday 3:35 Mont-Royal/ Hampstead NF5

A canonical framework for modeling elasto-viscoplasticity in complex fluids

Christopher J. Dimitriou and Gareth H. McKinley
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Guided by rheological measurements, we introduce a comprehensive framework for modeling elasto-viscoplasticity in soft solids and complex fluids. Elasto-viscoplastic materials are typically characterized by a linear (visco)elastic behavior at low stresses and a critical stress (or yield stress) above which the material irreversibly flows. The framework proposed here decomposes the material's deformation into a reversible elastic component, and an irreversible plastic component. It incorporates kinematic and isotropic hardening mechanisms to account for transient

yielding processes and/or thixotropy. We discuss a simple one-dimensional version of this kinematic hardening or 'KH' framework that is analytically tractable, as well as a more general fully three-dimensional, frame-invariant and thermodynamically-admissible representation. Predictions for several common rheological flow types and canonical experiments in shear and extension are provided. We discuss possible variants and extensions to account for complexities exhibited by real fluids, such as thixotropy, nonlinear elasticity below the yield point and non-zero normal stress differences. Comparisons of model predictions to experimental data are provided for two different fluids: A thixotropic waxy crude oil, and an "ideal" elasto-viscoplastic material consisting of a Carbopol microgel. This KH framework has several advantages over simpler models that are commonly used to describe yield stress fluids. First, the model can describe behavior over a wider range of common rheological test protocols. Second, it can eliminate the flow/no flow criterion inherent in many Bingham-like viscoplastic constitutive laws; this discontinuity often poses challenges for numerical simulations. Third, it provides a flexible constitutive framework that shares much in common with the familiar Oldroyd-B representation of polymer solution rheology but allows for additional complexities to be accounted for in elasto-visco-plastic material behavior, including thixotropy.

Tuesday 4:00 Mont-Royal/ Hampstead NF6

Stretch and relax: A filament calculation with yield stress properties

Yuriko Renardy[1] and Holly Grant[2]
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A filament with circular cross-sectional area is stretched by controlling the distance between the ends, and then stopped. The evolution of the filament radius in the presence of gravity and surface tension is studied when the constitutive model is Larson's viscoelastic partially extending strand convection model with a large relaxation time, combined with a Newtonian solvent. The results show phenomena with thixotropy and yield stress.

Tuesday 4:25 Mont-Royal/ Hampstead NF7

Computations of shear thickening liquid in stretching free surface flow using a simple generalized Newtonian constitutive model

J. Alex Lee[1], Sunilkumar Khandavalli[2], Jonathan Rothstein[2], and Matteo Pasquali[1]
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We present stretching liquid filament computations to model liquid transfer during a simplified gravure printing process. In this model, liquid is held between a cavity and a moving flat disk; and performance is measured in terms of the fraction of liquid removed from the cavity following break-up of the stretching filament. Inks often exhibit complex rheology due to the presence of polymers or particles, for example viscoelasticity, shear thinning, and shear thickening. Here we focus on shear thickening that occurs in nanoparticle solutions, wherein viscosity increases suddenly at a critical shear rate, and is otherwise shear thinning. To achieve this rheological behavior, we construct simple generalized Newtonian constitutive models from Carreau-like equations. We compute the flow with a standard ALE time-dependent finite element method. We show that computed free surface profile evolutions and liquid transfer fractions agree well with experimental results using aqueous silica nanoparticle-PPG suspensions. Visualization of the complete velocity, stress, and viscosity profiles in the liquid gives additional insight to the liquid transfer process. We explore parameter spaces not easily accessible by the experimental method, namely using smaller size scales (reduced importance of gravity), systematically varying rheological model parameters, and probing the effect of geometrical constraints.

Tuesday 4:50 Mont-Royal/ Hampstead NF8

Bifurcation phenomena in strong extensional flows

Filipe A. Cruz[1], Robert J. Poole[2], Alexandre M. Afonso[1], Fernando T. Pinho[3], Paulo J. Oliveira[4], and Manuel A. Alves[1]
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Previously, our group predicted numerically the existence of purely elastic flow instabilities in a cross-slot geometry using the upper-convected Maxwell model, via a finite-volume method [Poole et al., Phys Rev Lett 99(16):164503, 2007]. A first critical Deborah number ($De_{CR}\approx0.31$) was identified for the transition from steady symmetric to steady asymmetric creeping flow, and at higher *De* a second instability occurs leading to a time-dependent flow. In this presentation, we focus on the first (steady) flow transition, and further critical Deborah numbers are given for Oldroyd-B ($De_{CR}\approx0.35$, at solvent viscosity ratio $\beta=1/9$) and simplified linear Phan-Thien-Tanner ($De_{CR}\approx0.50$ at $\beta=1/9$ and extensibility parameter, $\varepsilon=0.02$) fluids.

Possible causes for differing critical Deborah numbers are discussed as well as clues towards a generalized purely elastic flow transition criterion.

Tuesday 5:15 Mont-Royal/ Hampstead NF9

Homogeneous planar elongational flow and elastic instabilities in an optimized-shape cross-slot extensional rheometer

Simon J. Haward[1] and Gareth H. McKinley[2]
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A cross-slot flow geometry, with a shape that has been optimized by numerical simulation of the fluid kinematics, is fabricated using wire electro-discharge machining and subsequently employed to measure the extensional viscosity of a range of dilute and semi-dilute polymer solutions of different molecular architectures. MicroPIV is used to verify the homogeneity of the kinematics and full-field birefringence microscopy is used to monitor the evolution and growth of macromolecular anisotropy along the stagnation point streamline. We observe the formation of a strong and uniform birefringent strand when the dimensionless flow strength exceeds a critical Weissenberg number, Wi 0.5. Birefringence and bulk pressure drop measurements in this Optimized Shape Cross-slot Extensional Rheometer (OSCER) provide self-consistent estimates of the planar extensional viscosity of viscoelastic test fluids over a wide range of deformation rates (up to 600 s-1). Measurements with a monodisperse dilute polymer solution are also in close agreement with numerical simulations performed using a finitely extensible non-linear elastic (FENE) dumbbell model. As the imposed extension rate in the OSCER device is increased the homogeneous planar elongational flow ultimately becomes unstable. High-frame rate video-imaging of the birefringence field is used to construct space-time diagrams of the evolution in the flow for seven different polymer solutions and to construct the first stability diagram for planar extensional flows in cross-slot devices. The mode of instability is found to depend on the elasticity number (El = Wi/Re) of the fluid, with a steady symmetry-breaking purely-elastic bifurcation observed at high El >> 1, and time-dependent three-dimensional inertio-elastic instabilities dominant for El < 1.

Symposium BM

Rheology and Processing of Bio-based Materials

Organizers: Michel Huneault and James J. Feng

Tuesday 1:30 Côte-St-Luc BM6

A new extended non-homogeneous constitutive model for human blood

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The nature of blood can be categorized as being either Newtonian or non-Newtonian. The assumption of Newtonian behaviour is acceptable in high shear rate flows, such as flow through larger arteries. It is not, however, valid when the shear rate is low, typically less than 100^{-1}. These include, for normal blood, slugish flow in the venous system and parts of the arterial vasculature where the geometry has been altered and RBC aggregates become more stable, such as downstream of a stenosis, inside a saccular aneurysm.

The use of computational fluid dynamics (CFD) techniques is becoming increasingly in cardiovascular research. It is an important tool in the quest to better understand blood flow characteristics, wall shear stresses, and recirculation zones in the arterial wall regions which are usually very difficult to obtain in vivo. The major challenge is to develop sound mathematical models and efficient and stable numerical schemes in order to obtain accurate numerical solutions for the governing equations.

In this study, we use a new constitutive equation for whole human blood [M. A. Moyers-Gonzalez, R. G. Owens and J. Fang, A non-homogeneous constitutive model for human blood. Part I: Model derivation and steady flow. J. Fluid Mech., 617 (2008) 327-354) in the context of Spectral/hp element methods. In this model, the local shear viscosity is determined in terms of both the local shear-rate and the average rouleau size. The above constitutive model is extended in scope to include both low and high shear stress flows. The numerical results of this study are compared with those obtained by Moyers-Gonzalez et al.

Tuesday 1:55 Côte-St-Luc BM7

A constitutive model for the nonlinear viscoelastic behavior of the fibrin network in blood clots

Thomas van Kempen[1], Frans van de Vosse[1], and Gerrit Peters[2]
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[2]Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5612AZ, The Netherlands

Blood clots form to prevent blood loss in case of a vascular injury but their failure has serious consequences such as stroke and thrombosis. The main structural component of the blood clot is fibrin, a fibrous network that develops within the clot and is therefore of major importance for its mechanical functioning. When subjected to large deformations, fibrin shows nonlinear viscoelastic behavior which is expected to be important for its physiological functioning. Current models are not able to describe this behavior. Therefore, a constitutive model for the nonlinear viscoelastic behavior of the fibrin network is developed. Large amplitude oscillatory shear (LAOS) measurements are used to study the rich nonlinear response of fibrin and as a validation of the model. The results are analyzed in terms of strain vs. stress curves, i.e. so-called Lissajous plots. An extended Kelvin-Voigt model is used. At increasing strain the networks stiffens and the viscous dissipation increases which is modeled using a deformation-dependent modulus and viscosity. Successive deformation cycles lead to an irreversible softening over time (thixotropic behavior) that is modeled by using a network integrity fraction (NIF). From transient LAOS data, an evolution equation for the NIF is proposed that takes into account the deformation the network has experienced. The model describes the rich nonlinear thixotropic behavior of the fibrin network and is at the same time relatively simple to be suitable for advanced numerical simulations of blood clot formation in arteries.

Tuesday 2:20 Côte-St-Luc BM8

Research review on molecular dynamics and rheological properties of the gel of the deoxy-hemoglobin S molecules in sickle cell anemia

Francis E. Mensah
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Sickle Cell Disease also called Drepanocytosis, is an inherited disease which affects many people worldwide. In this research, we consider blood as a fluid and we investigate the characteristics of the sickle cell molecules in terms of population dynamics using Volterra integro-differential equation. Then, we make use of the dynamical system approach to study the mathematical model of the polymerization of the deoxy-hemoglobin S molecules in sickle cells anemia. Finally, we propose some theoretical models to describe some steady rheological properties of the gel of the Deoxy-HbS molecules in a simple shear flow.

Tuesday 2:45 Côte-St-Luc BM9

Segregation of particles sujbect to magnetic forces in cellular blood flow in a model microvessel

Jonathan B. Freund
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The transport of nanometer-scale particles by magnetic forces in a small blood vessel is studied using a simulation model that explicitly includes hydrodynamic interactions with realistically deformable red blood cells. Such a configuration is relevant to targeted drug or hyperthermia delivery, for which transport to the vessel wall is essential for localizing therapy. In the absence of magnetic forces, it is seen that interactions with the unsteadily flowing red cells cause lateral particle velocity fluctuations with an approximately normal distribution and variance of about one-tenth that of the mean flow speed. The resulting dispersion is over 100 times faster than expected for Brownian diffusion, which we neglect. Magnetic forces relative to the drag force on a hypothetically fixed particle at the vessel center are selected to range from 0.006 to 0.204. The stronger forces quickly drive the magnetic particles to the vessel wall, though in this case the red cells impede margination; for weaker forces, many of the particles are marginated more quickly than might be predicted for a homogeneous fluid by the apparently chaotic stirring induced by the motions of the red cells. A corresponding non-dimensional parameter, which is based on the characteristic fluctuation velocity rather than the centerline velocity, explains the switch-over between these behaviors. Most surprisingly, forces that are applied parallel to the vessel are seen to have a strong effect on the segregation and margination speed. This is due the microstructure of the blood cells, which take on a streamwise-asymmetric orientation. In essence, the cells in this configuration act as low-Reynolds-number analogs of turning vanes, causing streamwise accelerated particles to be directed toward the vessel center and streamwise decelerated particles to be directed toward the vessel wall.

Symposium SG

Solids, Glasses and Composites

Organizers: Marianna Kontopoulou and Eliot Fried

Tuesday 3:35 Côte-St-Luc SG1

Formation of fractal-like structure in organoclay based polypropylene nanocomposites

Trystan Domenech, Riadh Zouari, Edith Peuvrel-Disdier, and Bruno Vergnes
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We present the structural features of dispersion of organoclay in a polypropylene melt investigated by shear rheology. The addition of maleated polypropylene as a compatibilizer leads to a mixed intercalated-exfoliated nanocomposite structure with solid-like behavior above the percolation threshold. Scaling behavior of the nanocomposite linear viscoelastic properties based on apparent yield stress and critical strain measurements enables to assess the fractal dimension df of the network formed by the anisotropic clay particles within the matrix. The network structure induces a thixotropic behavior which manifests by solid-like behavior accentuation over time under quiescent conditions and sensitivity to large deformations. Formation kinetics of the fractal network structure at rest is discussed through linear and nonlinear rheological investigations. A two step process is observed for clay network reorganization over annealing time, with pronounced transition around 104 s. These phenomena, which picture a non-equilibrium state where interparticle attractions favor disorientation of the platelets and network growth, are strongly coupled to the dispersion state of the organoclay within the polymer matrix.

Tuesday 4:00 Côte-St-Luc SG2

Varying effects of extrusion on structure and rheology of polypropylene-layered silicate nanocomposites

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It is well known that thermal annealing of polymer layered silicate nanocomposites can lead to aggregation of nanoparticles, changing a well dispersed structure to a highly intercalated structure or worse with face-to-edge aggregation of nanolayers. The objective of this work was to investigate the effect of melt extrusion on nanocomposite structure and rheology with additional treatment of organically modified layered silicates. Two different organically modified layered silicate were treated with an aminoalkyl dimethoxy silane in a methanol-water mixture; in one case, the silanols reacted only at the nanolayer edges while in the other case, the silanols entered the interlayer galleries. Nanocomposites were prepared by melt compounding polypropylene and maleated polypropylene with these two silane treated layered silicates. Samples of the nanocomposites were extruded through a 1 mm diameter capillary die with L/D = 30 mounted in a Dynisco LCR 6000 rheometer at a shear rate of 500 s^{-1}. The extruded specimens as well as the original compounds were characterized in small amplitude oscillatory shear at 180 C. Transmission electron micrographs were also obtained of the compounds before and after extrusion. These revealed some restacking and edge-to-edge aggregation in the extruded compound with edge treated nanolayers; in the other compound with silanols penetrating the galleries, there was extensive face-to-edge aggregation. The changes in storage shear modulus G' were found to be quite different for the two composites: an increase in the low frequency plateau was observed with edge treated nanolayers while a sharp drop was observed in the other case. These differences may be attributed to different balances between the polymer-particle interactions and particle-particle interactions. This was quantified with fits to a model developed from the one proposed by Sarvestani (2008) for the dynamic moduli of chains attached reversibly to nanoparticles.

Tuesday 4:25 Côte-St-Luc SG3

Relationship between rheological and electrical percolation of nanocomposites based on iPP and TiO_2

Ahmad Zohrevand[1], Abdellah Ajji[1], and Frej Mighri[2]
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The aim of the present work is to investigate microstructure, electrical conductivity and rheological properties of the nanocomposites based on isotactic polypropylene (iPP) and semiconductor spherical nanoparticles of TiO_2. Attempts were made to find a relation between electrical percolation threshold (in the solid state) and rheological percolation threshold (in the melt state). Compatibilized and uncompatibilized iPP/TiO_2 nanocomposites were prepared by twin screw extrusion. Analyzing DC electrical conductivity of the samples revealed a lower percolation threshold for uncompatiblized nanocomposites. On the other hand, frequency and strain sweep experiments showed the same behavior for rheological percolation threshold. Liquid-solid transition in the uncompatibilized samples occurred at lower TiO_2 content compared to the compatibilized ones. A power-law relation between electrical/rheological properties and TiO_2 volume fraction was used to quantify the percolation threshold. Scaling analyses of the results of strain sweep tests resulted in a lower value of fractal number d_f for the uncompatibilized samples which was in agreement with SEM and AFM morphological observations.

Tuesday 4:50 Côte-St-Luc SG4

Morphology and viscoelastic properties of ethylene-octene copolymer/nanosilica composites with varying polymer/filler interactions

Mathieu Bailly[1], Kyle Petrie[1], Marianna Kontopoulou[1], Peng Xiang[2], and Zhibin Ye[2]
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Ethylene-octene copolymer (EOC)/ nanosilica composites were prepared by melt compounding. The effects of the specific surface area (SSA) of the silica on the microstructure and the LVE properties were investigated with and without a maleated EOC compatibilizer. In the absence of compatibilizer, increasing SSA resulted in the presence of larger silica aggregates, because of increased probability of hydrogen bonding between filler particles that resulted in enhanced filler/filler interactions. The increased propensity for aggregation was revealed by time sweeps, as well by the increased strain sensitivity in stress sweeps. The viscoelastic properties in the terminal region were influenced substantially by the state of dispersion, as increasing SSA resulted in more significant deviations from terminal flow. A combination of creep/recovery and oscillatory measurements was implemented to further differentiate the responses. When a maleated EOC compatibilizer was added to the matrix, the amount of polymer physically bound to the nanoparticles following compounding was higher than in the non-compatibilized samples due to the presence of enhanced polymer/filler interactions consisting of hydrogen bonding between the silanol groups and the anhydride group of the compatibilizer. The SSA of the particles had no effect on the viscoelastic properties of the compatibilized composites. Furthermore the effects of grafting polyethylene (PE) brushes of varying brush density and length on the particles were investigated. The improved dispersion and interfacial adhesion of the grafted particles resulted in a reduction in the LVE properties with respect to the unmodified composite. A two phase model, which takes into account the hydrodynamic effect of the filler, as well as interfacial effects between polymer and filler has been implemented to obtain insight on the extent of polymer/filler interactions established between the polymer matrix and the filler in the cases described above.

Tuesday 5:15 Côte-St-Luc SG5

Rheological behavior of compatibilized polypropylene/flax fibre composites

Helia Sojoudiasli, Pierre Carreau, and Marie-Claude Heuzey
Chemical Engineering, École Polytechnique de Montréal, Montreal, Canada

Low density, availability and high specific modulus make natural fibres appropriate substitutes for synthetic fillers. Despite these overall unique properties, their hydrophilicity makes them incompatible with hydrophobic polymers and represents their most predominant weakness. In this study composites of polypropylene (PP) with flax fibres have been investigated in terms of rheological and mechanical properties. To overcome the incompatibility between flax fibres and PP, different commercial compatibilizers with maleic anhydride grafted on polypropylene (PP-g-MA) have been used. Their efficiency of in terms of melt flow index (MFI) and MA content for reinforcing the PP/flax fibre interface has been investigated. Rheological characterization in transient, steady and small amplitude oscillatory shear flow has been carried out to provide fundamental knowledge about the effect of the various compatiblizers. It has been observed that at low shear rates the steady shear viscosity of the composites increased markedly with fibre content, while at high shear rates due to the orientation of the fibres, the viscosity became almost independent of flax fibre content. In transient flow the composites showed large stress overshoots and delayed overshoots under reversal flow as a result of fibre orientation, and the effect of strain on fibre orientation in shear flow has been examined using a Linkam optical shearing cell. It has been observed that the optimum content of compatibilizer depends on the MA content and MFI. Adding a compatibilizer with a very high MFI caused a large decrease in viscosity. Finally, the efficiency of each compatibilizer in improving the tensile properties of the composites has been investigated.

Wednesday Morning

Symposium PL

Plenary Lectures

Wednesday 8:30 Westmount PL3

Rheological characterization of polymer nanocomposites

Pierre Carreau
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Polymer nanocomposites (PNCs) are materials composed of a polymer matrix filled with nanometer-size particles. The use of 2-6 wt% nanoparticles (compared to 20-30 wt% in the case of conventional composites) results in increased stiffness, strength, barrier properties as well as improved heat resistance. In this presentation we will show how rheological methods can be advantageously used to obtain structure-property relationships of PNCs. Key results on the rheological characterization of polyethylene terephthalate (PET) and polylactide (PLA) nanocomposites based on organo-modified clays will be presented. In particular, we will show how chain extenders can be used to control the molecular weight of the matrix and improve the mechanical and barrier properties.

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Wednesday 10:00 Westmount SC29

Universal scaling of microscopic and macroscopic behavior in spherical non-colloidal suspensions with a non-Newtonian fluid matrix

Nicos S. Martys[1], Didier Lootens[2], William L. George[1], Pascal Hébraud[3], and Maxime Liard[3]
[1]Materials and Construction Research Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States; [2]Sika Technology A.G., Zurich CH-8048, Switzerland; [3]IPCMS, Strasbourg 67034, France

It has been observed that flow curves (viscosity vs shear-rate) of spherical non-colloidal particles suspended in a non-Newtonian fluid matrix can be rescaled so as to collapse onto the flow curve of the matrix fluid. This result is surprising given the broad range and spatial heterogeneity of localized shear rates and viscosity in such systems. In this presentation, results from experiment and computational modeling are presented that examine the microscopic origins of this scaling behavior. We consider the cases of shear thinning, Newtonian and shear thickening matrix fluids. Over a wide range volume fractions (5% to 50%) it is shown that the distribution of localized shear rates can be collapsed onto a single universal curve. The scaling parameters for rescaling the shear rate distributions can be analytically related to the macroscopic rescaling parameters for the viscosity. We discuss the application of this scaling ansatz to predict the macroscopic behavior of suspensions from measurements of the matrix fluid alone. Finally, this analysis is extended to suspensions composed of non-spherical particles.

Wednesday 10:25 Westmount SC30

Kinetic theory based models for high concentrated suspensions in generic suspendant fluids

Emmanuelle Abisset-Chavanne[1], Rabih Mezher[1], Julien Ferec[2], Gilles Ausias[2], and Francisco Chinesta[1]
[1]GeM-Ecole Centrale Nantes, Nantes 44300, France; [2]LIMATB, Université de Bretagne-Sud, Lorient, France

The prediction of slender particles suspensions behaviour and properties is, even today, widely based on the Jeffery's equation proposed in 1922. The problem is that this equation has been developed assuming a large number of hypothesis and in particular the fact that the suspendant fluid must be Newtonian and the concentration of particles must be low. In a view of modelling the rheological behaviour of more complex systems, namely high concentrated suspensions in a viscoelastic fluid, the Jeffery's equation, or derived ones, are no more sufficient. To tackle this issue, a strategy based on the kinetic theory has been recently developed in order to derive a generic formulation for slender particles suspensions models at the mesoscale. Microstructural models that take into account the non-newtonian nature of the fluid and the particles/particle interactions are introduced in a kinetic description of the suspension. This allows to derive a mesoscopic model able to take into account the different natures of the suspendant fluid (Newtonian/non-newtonian) and the evolution of the microstructure for dilute and high-concentrated suspensions. In the work proposed here, the focus is made on the modelling of high concentrated suspensions experiencing the formation of aggregates composed of entangled particles. The approach used to derive such a model is described, and in particular the work performed to introduce the suspension elasticity due to the microstructure. The model proposed is finally identified from experimental results performed in Cambridge.

Wednesday 10:50 Westmount SC31

Mesoscale simulation of colloidal suspensions at equilibrium

Safa Jamali, Arman Boromand, and Joao Maia
Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7038, United States

Dissipative Particle Dynamics as a particulate simulation method was proposed first in 1992 [1] to study the dynamics of suspensions using three different types of potentials: A conservative force to represent the extent of pressure between particles, a Dissipative force to act like the viscosity and a Random force to introduce thermal fluctuations in the system. However the proposed method failed to capture shear properties of suspensions because it lacked a potential to reproduce lubrication forces and a clear definition for the colloid surface. Recently we reported [2] a modified DPD method which defines colloidal particles as particles with hard core and a dissipative coat to represent the stabilized layer in real suspensions. An additional lubrication force was introduced to include the short-range hydrodynamics that are not captured in original DPD. The model was found to be able to reproduce shear properties of suspensions for a wide range of different systems, from monodisperse to bimodal with different volume fractions, compositions and size ratios. In the present work equilibrium properties of suspensions are studied. The previous DPD model is further modified with a parameter to enable accurate control over the thickness of the stabilized layer. Zero shear viscosity measurements have been performed for suspensions with different characteristics and the results are compared to theoretical predictions. Finally, the equilibrium behavior of colloidal suspensions is compared to emulsions of the same size and properties.

[1] Hoogerbrugge, P.J. and J.M.V.A. Koelman, Simulating Microscopic Hydrodynamic Phenomena with Dissipative Particle Dynamics. Europhysics Letters, 1992. 19(3): p. 155-160. [2] Jamali, S., M. Yamanoi, and J. Maia, Bridging the gap between microstructure and macroscopic behavior of monodisperse and bimodal colloidal suspensions. Soft Matter, 2013. 9(5): p. 1506-1515.

Wednesday 11:15 Westmount SC32

Numerical studies of inertial suspensions of non-Brownian rigid spheres: Steady and periodic shear

Luca Brandt[1], Jean Rabault[2], and Francesco Picano[1]
[1]KTH Mechanics, Stockholm, Sweden; [2]Ecole Polytechnique, Palaiseau, France

Concentrated suspensions of non-Brownian spheres in Newtonian fluids have been extensively studied in the laminar regime at vanishing inertia focusing on the rheological properties. However, in several applications, flows of suspension occur in turbulent conditions where unsteadiness and inertia become relevant. To fill this gap, we investigate the effects of an oscillatory shear rate. We consider a suspension at 30% of volume fraction sheared in a Couette cell whose walls move with a sinusoidal law at a given frequency. The system depends on two parameters: the particle Reynolds number that accounts for the relevance of inertia and the ratio between the system frequency and the maximun shear rate. Several fully resolved Direct Numerical Simulations have been performed changing these parameters. The complex viscosity, mean particle concentration and velocity characterize the macroscopic behavior of the system. The microscopic behavior is analyzed by looking at the pair distribution function. Different effects have been observed as shear thickening, elasticity, strong microstructure anisotropy and particle layering. The effective viscosity is found to increase with the shear rate at fixed system frequency, i.e. shear-thickening, but also to increase with the system frequency at given shear rate. Nonetheless, the viscosity growth rate with the oscillation frequency is found to be smaller than what observed for an oscillatory laminar Couette flow without particles. We show that at low frequencies finite inertia induces the formation of shadow regions behind each particle where there is a low probability to find a second particle. The shear-thickening is then explained as an increase of the effective volume fractions that accounts for these regions. Concerning the effect of the frequency, the observed phenomena are related to the thickness of the momentum diffusion layer near the wall, this in turn function of the system frequency.

Wednesday 11:40 Westmount SC33

Secondary convection due to second normal stress differences: A new mechanism for the mass transport of solutes in the pressure-driven flow of concentrated, non-colloidal suspensions

Arun Ramachandran
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A mechanism for enhancement in the mass transfer rate of solutes in flowing, concentrated suspensions that is often cited in the literature is the self-diffusion of particles arising from shear-induced interparticle interactions. Recently, it was demonstrated by Zrehen and Ramachandran [Phys. Rev. Lett. 110, 018306 (2013)] that the pressure-driven flow of suspensions through non-axisymmetric geometries is not unidirectional; the main flow is accompanied by secondary currents within the cross-section of the conduit, driven by second normal stress differences. This secondary convection represents a new and heretofore unexplored, advective mechanism for mass transfer of solutes normal to the primary streamlines in flowing suspensions, and is investigated in this paper via simulations. For small particle sizes, the enhancement of solute diffusivity by shear-induced self-diffusion is weak. However, the magnitude of the secondary currents is unaffected by particle size. Thus, for suspensions with particles much smaller than the conduit size, secondary convection, and not shear-induced self-diffusion, can be the dominant mechanism for shear-induced enhancement of mass transfer. In the limit where shear-induced self-diffusion is the dominant diffusive mode of mass transfer, secondary convection can provide additional enhancement of mass transfer over that due to self-diffusion, possibly doubling the augmentation in some geometries. The relevance of this new mechanism of mass transfer is in the improved modeling of the transport of high molecular weight solutes in suspension flows. This mechanism also suggests the possibility of exploiting conduit geometry to improve the mass transfer rate of solutes.

Symposium GS

Gels and Self-assembled Systems

Organizers: Jai Pathak and Matthew E. Helgeson

Wednesday 10:00 Verdun/Lachine GS6

Dynamic rheology and microstructure of shear-banding wormlike micellar solutions using 1-2 plane flow-SANS

A. Kate Gurnon[1], Carlos R. Lopez-Barron[2], Lionel Porcar[3], and Norman J. Wagner[4]

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Polymer-like or worm-like micelles are models for understanding polymer physics and are of interest across a broad range of applications ranging from enhanced oil recovery to many consumer products. A key phenomenon is the ability to formulate PLM solutions that exhibit a "breaking viscosity", such that they flow rapidly upon a sufficient applied stress. Prior investigations have elucidated the shear banding responsible for this viscosity behavior, yet our understanding of the dynamic rheology is incomplete. To address this, flow start-up and large amplitude oscillatory shear (LAOS) measurements have revealed intriguing, nonlinear dynamic rheological behavior. In this work we study this nonlinear dynamic rheology and understand its significance and source by measuring the microstructure of the PLMs during deformation using newly developed instrumentation implemented on SANS beamlines at the ILL Grenoble and the NCNR, NIST. A well-characterized formulation (CpCl/NaSal) (2:1 molar ratio) with 0.5 M NaCl in D2O is studied. The microstructure on the segmental length scale is measured during LAOS and flow start-up via a newly developed method of time-resolved SANS [C. R. Lopez-Barron et al. PRL. 2012, 108 , 897)]. This enables both time and spatial resolution of the microstructure during oscillatory flow. Measurements in the velocity -velocity gradient (1-2) plane of shear are used to quantitatively define the microstucture and predict the local stresses. We attribute the anomalous rheology observed in LAOS to an apparent shear-induced phase separation (SIPS) that occurs at longer length scales than those measured during SANS, but which can be observed as a "butterfly pattern" during a complementary rheo-small angle light scattering methods (SALS) [P. Thareja et al. JOR 2010, 55 , 1375]. The techniques used here elucidate the microstructure responsible for the intriguing and useful nonlinear dynamic rheology. These measurements are invaluable for testing rheological constitutive models.

Wednesday 10:25 Verdun/Lachine GS7

Aging and temperature studies of flow-induced structured phase in wormlike micellar solutions

Joshua J. Cardiel[1], Tonggu Lige[2], Wang Liguo[2], and Amy Shen[1]

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Surfactant molecules can self-assemble into various morphologies under proper combinations of ionic strength, temperature, and flow conditions. Flow-induced structure formation has been reported in solutions of wormlike micelles; however, until now these structures were all temporary and would disintegrate upon cessation of the flow. Usually these reversible flow-induced structures would form under shear flow above a critical shear rate [1]. Irreversible micellar structures were first reported by Vasudevan et al. [2] when a semi-dilute wormlike micellar solution passing through a microfluidic tapered channel packed with glass beads (20-100 µm in diameter). Cardiel et al. [3] recently showed the formation of these irreversible flow-induced structured phases (FISP) in both ionic semi-dilute shear thinning and shear thickening wormlike micellar solutions (CTAB/NaSal). They observed that the FISPs consist of highly entangled, branched and multi-connected micellar bundles. In this work, we study the aging behavior of the FISP by characterizing the rheological properties of the FISP over time (zero shear viscosity, elastic modulus and relaxation time). We also observed that the FISP disintegrated at temperatures above 45 C. We correlate the aging and temperature studies of the FISP to their thermodynamic properties (bending modulus, saddle-splay constant and free-energy.

References: [1] Berret, J.F. Molecular Gels 2006, 667-720. [2] Vasudevan, M.; Buse, B.; Lu D.L.; Krishna, H.; Kalyanaraman, R.; Shen, A.Q.; Khomami, B.;Sureshkumar, R. Nat. Mat. 2010 9, 436-441. [3] Cardiel, J.J; Dohnalkova, A.C.; Dubash, N.; Zhao, Y.; Cheung, P.; Shen, A.Q. PNAS 2013 doi:10.1073/pnas.1215353110.

Wednesday 10:50 Verdun/Lachine GS8

Transient dynamics of a thermodynamically consistent model for wormlike micellar solutions

Natalie Germann[1], L. P. Cook[1], Antony N. Beris[2], and Norman J. Wagner[2]

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Wormlike micelles are self-assemblies of surfactant molecules. They are used in a variety of applications including detergents, personal care products as well as rheological modifiers. When undergoing strong shearing deformations, concentrated solutions of wormlike micelles can develop inhomogeneities in the flow field, including multiple localized bands with different shear rates, known as shear bands. Recently, we developed a thermodynamically consistent model for wormlike micellar solutions [1]. In this talk, we present sample calculations for startup shear flow performed in a concentric Taylor-Couette device. A semi-implicit preconditioned Newton-Krylov solver was used for the simulation. Like the Vasquez-Cook-McKinley model [2], the new model can predict multiple shear bands at a nonzero Reynolds number. A sensitivity analysis of the model parameters will be presented. Special focus will be given to the influence of the reaction rates and the viscoelasticity of the micelles on their rheology and microstructure.

[1] N. Germann, L. P. Cook, and A. N. Beris. Nonequilibrium thermodynamic modeling of the structure and rheology of concentrated micellar solutions, J. Non-Newt. Fluid Mech., (196):51-57, 2013. [2] P. A. Vasquez, G. H. McKinley, and L. P. Cook. A network scission model for wormlike micellar solutions: I. Model formulation and viscometric flow predictions. J. Non.-Newt. Fluid Mech., 144(2-3):122 -139, 2007.

Wednesday 11:15 Verdun/Lachine GS9

A free-energy density for wormlike micelles

Meisam Asgari[1], Brian Seguin[2], and Eliot Fried[1]

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Considerable attention has been paid to the rheological properties of micellar surfactant-based solutions in recent years. An important property of surfactant molecules is their ability to assemble spontaneously in solution. Self-assembly provides a fundamental mechanism for building complex materials. One of the most important structures formed by the self-assembly of surfactant molecules is the wormlike micelle. We develop the free-energy density for wormlike micelles based on microphysical considerations that take into account the interaction of the molecules comprising the micelle. What results is an expression for the free-energy density of a wormlike micelle in terms of the curvature and torsion of its centerline and their derivatives with respect to the arc-length.

Wednesday 11:40 Verdun/Lachine GS10

Creep, fracture and yielding of protein gels

Christophe Perge[1], Mathieu Leocmach[2], Nicolas Taberlet[2], Thibaut Divoux[3], and Sebastien Manneville[1]

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We report on experiments combining rheology, ultrasonic imaging and direct visualization in acid-induced casein gels. These gels behave as yield stress materials, but exhibit two major differences with classic soft glassy materials such as foams, microgels or emulsions. First, their microstructure is extremely loose and the yield stress results purely from strong attractive interactions controlled by the pH, not from a jammed collection of soft objects. Second, their yielding process is irreversible. Up to now these gels have been mainly studied under uniaxial compression or imposed shear rate, but their stress-controlled fluidization dynamics remain unknown. Here we show that under a steady imposed shear stress casein gels display a robust creep regime reminiscent of Andrade's creep in amorphous solids: the shear rate slowly decreases as a power law of time over several decades. At the end of this creep regime a fracture pattern progressively develops. Fractures are oriented along the vorticity direction with a well-defined wavelength in the azimuthal direction. They grow until the material fails and is rapidly fluidized at very large shear rates. Ultrasonic imaging allows us to follow both the creep regime and the fracture growth up to complete fluidization. Interestingly, the failure time is shown to diverge as a power law of the applied shear stress. Extensive measurements reveal that the power-law exponent only depends on the gel microstructure, whereas the cell geometry only affects the power-law prefactor. Ongoing microscopic investigation tends to reveal a strong correlation between pre-existing microcracks and the failure time scaling law.

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Wednesday 10:00 Outremont MB29

A coarse-grained model for entangled polymer dynamics: Comparison with experimental rheological data

Abelardo Ramirez-Hernandez[1] and Juan J. de Pablo[2]
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In recent years, coarse-grained models have emerged as a useful tool to describe the physics of soft materials at length and time scales unattainable by using fully atomistic models. This is particularly true for polymeric melts where their rheological properties span dynamic responses ranging from milliseconds to hours or days. The drawback to this approach is that, soft effective interaction potentials are tipically used, making possible the violation of the local non-crossability constraint, thus erasing the effects of entanglements on dynamics. In this work we use the theoretically informed entangled polymer simulations (TIEPOS) approach for multicomponent polymeric systems to predict the linear and non-linear response of pure homopolymers and blends of entangled systems. In this model, the topological effect of non-crossability of polymers is described by effective fluctuating interactions, mediated by slip-springs, between neighboring pairs of polymeric molecules. We performed a comparison between simulation predictions and experimental data for a series of well-characterized linear polymeric melts. Our results are shown to be in quantitative agreement both in linear and non-linear rheology. The agreement between simulations and experimental data suggests that the main relaxation mechanisms that arise in entangled polymers are correctly captured by the proposed approach. We generalize this approach to explore the effect of nanoparticles on the rheology of homopolymers as well as on the rheology of nanostructured polymeric materials.

Wednesday 10:25 Outremont MB30

Atomistic simulation of dynamics of individual molecules in entangled polymers undergoing homogenous shear flow

Hadi Nafar, Brian J. Edwards, and Bamin Khomami
Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996-2200, United States

Nonequilibrium molecular dynamics (NEMD) simulations of entangled linear polyethylene were performed to investigate the chain dynamics over a wide range of Weissenberg numbers (Wi). We discuss results for the probability distribution of the chain end-to-end vector, characteristic times of the system, number and life time of entanglements, chain self-diffusion coefficient and disengagement time, all as a function of Wi. Specifically, it is shown that the probability distribution function of the end-to-end vector at high Wi is bimodal with two peaks associated with "vorticity excursions" and stretching of the chains. To understand the underlying physics of the aforementioned phenomenon, the relevant system time scales were determined. Specifically, the autocorrelation function of the unit end-to-end vector showed a periodic behavior at high Wi which is associated with the onset of "vorticity excursion" of individual chains within a background of highly stretched chains. The Rouse (T_R) and rotational (T_{rot}) relaxation times of the system were extracted by fitting a functional form of $A\exp(-t/T_R)\cos(2\pi t/T_{rot})$ to the autocorrelation function data. It is shown that the Rouse time calculated using this method is considerably different than the one calculated using a stretched exponential (as in previous works) for all shear rates undergoing the "vorticity excursion". Both the Rouse and rotational relaxation times exhibited a shear-thinning behavior that scaled as $Wi^{-0.75}$ at high Wi. The number and lifetime of entanglements, which is related to the average time of creation and destruction of entanglements, was also computed as a function Wi. It is shown that this characteristic timescale has a shear-thinning behavior which scaled as $Wi^{-0.63}$ at high Wi. The implications of these findings will be discussed in this presentation with regard to convective constraint release and contour fluctuations in advanced reptation theories and slip link simulations.

Wednesday 10:50 Outremont MB31

Inference of polymer structure by simultaneous analysis of chromatographic and rheological measurements

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

The need to combine knowledge of synthesis, chromatography and rheology to infer the structure and composition of blends of branched polymer has been highlighted by recent TGIC experiments. In this work, a Bayesian framework to perform this integration of "heterogeneous" data sources and models is presented. Preliminary results on a linear polymer intentionally contaminated with a small amount of high molecular weight tail are reported. As expected, it is found that chromatography alone lacks the resolution to resolve the tail, while rheology alone identifies multiple structures consistent with the experimental data, but cannot discriminate between them. These difficulties are resolved when the two data sources are combined.

Wednesday 11:15 Outremont MB32

Dominance of intermolecular friction in fast deformation of polymer melts close to T_g, breaking away from the rubber elasticity model

Hao Sun[1] and Shi-Qing Wang[2]
[1]University of Akron, Akron, OH 44325, United States; [2]Polymer Science, University of Akron, Akron, OH 44325, United States

Transient (nonlinear) responses of entangled polymers to startup deformation always show a transition from the initial elastic deformation to irreversible deformation (flow) [1-3]. This yielding behavior varies with the applied rate: at a higher rate the entanglement network can be strained to a higher degree before the chain disentanglement causes a breakdown. In this work, we subject various entangled melts including polystyrene to startup uniaxial extension and simple shear respectively at temperatures close to the glass transition temperature. The theological response is found to deviate significantly from the rubbery elastic deformation that is familiar at higher temperatures. To model this behavior, we have to acknowledge significant contributions to the mechanical stress arising from intermolecular friction.

[1] S. Q. Wang, S. Ravindranath, Y. Wang and P. Boukany, J. Chem. Phys. 127, 064903 (2007). [2] Y. Y. Wang and S. Q. Wang, J. Rheol. 53, 1389 (2009). [3] S. Q. Wang, S. Ravindranath and P. E. Boukany, Macromolecules 44, 183 (2011).

Wednesday 11:40 Outremont MB33

Linear viscoelasticity of polyether-ester-sulfonate copolymer ionomers

Quan Chen, Gregory J. Tudryn, Huai-Suen Shiau, and Ralph H. Colby
Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

Linear viscoelastic properties were examined for copolyester ionomers synthesized via condensation of sulfonated phthalates with mixtures of poly(ethylene glycol) (placing a segment of M = 600 PEO in the chain) and poly(tetramethylene glycol) (yielding M = 650 PTMO) of systematically varying ratios. The copolymers exhibited microphase separation as confirmed in SAXS measurements. Since PEO has superior specific ion solvating ability compared to that of PTMO, increasing the PTMO fraction increases the ionic association lifetime and delays the LVE terminal relaxation, creating a rubbery plateau. The degree of this delay enables an evaluation of the activation energy that increases with PTMO fraction, which is in accordance with ab initio calculations. For ionomers rich in PEO, the ions primarily reside in the PEO-rich microphase and the activation energy and delay are similar to the PEO-based ionomers. In contrast, the ionomers rich in PTMO are forced to have ion aggregates in the PTMO-rich phase with significantly stronger activation energy, causing the delay in terminal response covering many decades in time.

Symposium NF

Non-Newtonian Flows

Organizers: Ian A. Frigaard and Vivek Sharma

Wednesday 10:00 Mont-Royal/ Hampstead NF10

Different scaling laws for the thinning of a weakly elastic jet

Wouter Mathues[1], Claire McIlroy[2], Oliver G. Harlen[2], and Christian Clasen[1]
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Weakly viscoelastic jets are encountered in a wide variety of applications from ink jet printing to spraying of fertilizers. Understanding the breakup dynamics of a weakly viscoelastic jets is therefore of great importance. In case that elastic stresses in a jet are sufficient to balance the surface tension driving the breaking process, the filament diameter D decreases exponentially with time (D ~ exp(-t/3?), which is employed to extract the relaxation time ? in CaBER type experiments or with advanced extensional jetting rheometers as the recently proposed ROJER [1]. However, recent investigations [2] have shown that for jetting at lower Weber numbers, close to the dripping-jetting transition, a different scaling of D ~ exp(-t/2?) is theoretically possible based on the assumption of constant axial force during the thinning process. In this paper, studying the breaking dynamics of a dilute, weakly elastic polyethylene oxide solution in jetting and static capillary breakup with high resolution high-speed imaging, we show that D ~ exp(-t/2?) is experimentally observed, and explore the range of We for which this scaling holds. Furthermore we demonstrate with numerical simulations how the transition between the two scalings depends on the wavelength of the instability on the jet. We observe both in experiment and simulation that a jet thinning with D ~ exp(-t/2?) does not exhibit a self-similar structure of the corner region where the thinning filament connects to the drop as it is generally observed for a filament with an axial tension decaying with the filament radius [3]. The actual evolution of the axial forces in a with D ~ exp(-t/2?) thinning jet is determined with numerical simulations and the differences to the self-similar thinning are pointed out.

[1] Ardekani, A.M., V. Sharma, and G.H. McKinley, Journal of Fluid Mechanics, 2010. 665: p. 46-56. [2] Clasen, C., et al., Journal of Fluid Mechanics, 2009. 636: p. 5-40. [3] Clasen, C., et al., Journal of Fluid Mechanics, 2006. 556: p. 283-308.

Wednesday 10:25 Mont-Royal/ Hampstead NF11

Drop-on-demand printing of complex liquids

Neil F. Morrison and Oliver G. Harlen
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We investigate the influence of fluid properties on jet breakup in the context of drop-on-demand inkjet printing. In drop-on-demand printing, each drop remains connected to the printhead by a ligament which thins while the drop is in flight. Upon pinch-off the severed ligament may recoil into the leading drop, or it may fragment into `satellite drops' which reduce printing resolution. A key goal of inkjet research is to prevent or impede the creation of satellite drops without compromizing on printing speed. Viscoelastic and shear-thinning fluids may, in rather different ways, exhibit enhanced resistance to fragmentation in jetting flows compared to Newtonian fluids of similar viscosity. In this work we seek to explore and exploit this behaviour with the aim of reducing the number and net volume of satellites produced when printing at a prescribed drop velocity. Using Lagrangian finite-element simulations under realistic industrial inkjet conditions, we consider non-Newtonian fluid models which incorporate both viscoelastic and thixotropic effects simultaneously. We discuss how appropriate values of the rheological parameters may be chosen so as to optimize the fluid's transient viscosity at different key stages of a drop-on-demand flow cycle, and how our results may be beneficial to industrial and commercial applications of inkjet technology.

Wednesday 10:50 Mont-Royal/ Hampstead NF12

Reconstructed dynamics of in situ mechanical pressure fluctuations during the extrusion flow of polymer melts

Roland Kádár, Ingo F. C. Naue, and Manfred Wilhelm
Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology - KIT, Karlsruhe, Germany

The flow of polymer melts during extrusion is investigated in this work. High sensitivity mechanical pressure transducers distributed along the die length are used to study the onset of mechanical pressure fluctuations due to extrusion instabilities and their propagation inside the extrusion die. Flush mounted and 'buried' transducer configurations, to create the 'hole effect', are used for a variety of melts having different molecular properties and topologies. The data analysis is mainly concerned with the nonlinear (reconstructed) dynamics of in situ mechanical pressure fluctuations during the observed transition sequences, i.e. the chaotic character of the extrudate patterns. A capillary rheometer featuring a custom slit die equipped with four high sensitivity pressure transducers with three of them regularly distributed and flush mounted along the channel length and the fourth opposing one of the other three. The position of the latter can be adjusted in order to create the 'hole effect' as an estimation of the normal forces. Complementary, an online visualization system is positioned at the die exit. The optical system is used to determine the die swelling as well as for extrusion regime monitoring through spatio-temporal imaging. Furthermore, an axial load is applied on the extrudate using a Rheotens accessory and the effects of increasing draw ratios are thus considered. The in situ mechanical pressure data and the spatio-temporal diagrams are then used for process/flow characterization. The characteristic frequencies of instabilities are determined for the analyzed Weissenberg numbers using a variety of experimental input parameters and protocols. Pressure bifurcation diagrams, reconstructed attractors, and the divergence of trajectories in the reconstructed space space, i.e. maximal Lyapunov exponents, are considered in relation to the normal stress differences, for the transient detection of the onset of instabilities and to differentiate between melts with different molecular properties.

Wednesday 11:15 Mont-Royal/ Hampstead NF13

Consequences of stress-concentration coupling in the flow of polymer solutions

Michael Cromer, Yassine Dhane, Glenn Fredrickson, and L G. Leal
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We have recently revealed, through a two-fluid model formalism, that shear banding is possible in the flow of polymer solutions driven by polymer migration up stress gradients via the Helfand-Fredrickson coupling mechanism. In this talk we delve further into the analysis of this phenomenon, in particular the scaling of the interfacial layer between bands as well as what controls the number of bands. As an extension of this work we consider flows beyond the simplest case of planar shear. In particular we will look at two additional flows, one rate and the other stress driven. 1. How does the introduction of curved streamlines affect the shear-rate driven flow? We consider the case of a circular Taylor-Couette cell in which a geometric bias now exists to determine the location and number of bands. A particularly interesting question is whether elastic recoil (negative velocity) due to the stress overshoot is possible for polymeric materials. 2. How does the flow change when it is stress-driven? Here we consider the pressure-driven flow through a rectilinear channel. The main questions are whether the new banding instability results in spurt and, if so, can this explain the experimentally observed spurt phenomenon, which is currently attributed to slip?

Wednesday 11:40 Mont-Royal/ Hampstead NF14

Numerical study of secondary flows of FENE rheological models in curved ducts

Joana M. Malheiro[1], Paulo J. Oliveira[1], and Fernando T. Pinho[2]
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The study of non-Newtonian fluid flows in curved ducts has great interest due to the complex secondary flows generated in the cross-section of the ducts. This secondary flow is important to many industrial and engineering applications because it tends to increase mixing, mass and heat transfer, with either Newtonian or non-Newtonian fluids. In an attempt to better understand the development of those secondary flows and to assess the relative contributions of elastic and inertia forces many studies have been published assuming different rheological models to describe complex fluid behavior. Among the many available rheological models those which have received less attention in this type of flow are the FENE-type models (Finite Extensible Nonlinear Elastic), which are frequently employed in numerical simulation studies of viscoelastic flows because they give a reasonable description of the rheology of diluted and semi-diluted polymer solutions. An additional factor adding complexity to the generation of the secondary flows in curves is related to the geometry of the curved channel. Choosing either a square or a rectangular cross-sectional channel is known to be important for flow development because the flat walls have been shown to enhance such secondary flow development. We investigate, by means of numerical simulations, the development of secondary flow through a 180? curved duct having a square cross-section, of viscoelastic fluids described by three FENE-type models: the FENE-P(Peterlin approximation), the FENE-CR(Chilcott and Rallison approximation) and the FENE-MCR(modified form of the previous). The flow and constitutive equations were solved numerically with a finite-volume method, for various Reynolds and Weissenberg numbers and for a range of values of the dimensionless model parameters (retardation ratio and extensibility parameter). The results of these simulations show complex changes of the three-dimensional flow, but also reveal similarities in the flow development for different rheological models.

Symposium SG

Solids, Glasses and Composites

Organizers: Marianna Kontopoulou and Eliot Fried

Wednesday 10:00 Côte-St-Luc SG6

The role of concentration on shear stress growth and orientation evolution of long glass fiber suspensions

Mark J. Cieslinski[1], John T. Hofmann[2], and Donald G. Baird[1]

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Measuring the rheological response of concentrated fiber suspensions within a well-defined flow field can give insight to the orientation evolution of fibers in complex industrial processes such as injection molding. A sliding plate rheometer allows for measurements of the shear stress growth at the startup of shear flow which is primarily caused by fiber orientation evolution. In order to associate the rheological behavior to the evolution of orientation both a stress tensor and an orientation model are required. In the case of long fibers (i.e. lengths > 1mm) a modification of the Bead-Rod orientation model for dilute solutions was adapted to concentrated systems and used to capture the semi-flexible nature of long fibers by representing a fiber as two adjoined vectors. Empirical modifications to the Lipscomb stress tensor, which was developed for short rigid fibers, were made in an effort to extend its application to long fibers. The aim of this work is to assess the capacity to which these models reflect changes in the orientation evolution in long fiber suspensions. Investigation into concentration effects of long glass fiber in polypropylene allows for continued evaluation of current models. Measured fiber orientation values taken at different times during the flow are compared with the rheological response to give insight to the primary factors influencing stress in long fiber composites. Furthermore, the results from the sliding plate device are compared against the behavior of fiber suspensions of various concentrations in model injection molding flows.

Wednesday 10:25 Côte-St-Luc SG7

Modeling yielding and strain hardening in glassy polymers

Ronald G. Larson and Weizhong Zou

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Strain hardening has long been an observed feature of polymer glasses in extension; explanations to date have often been phenomenological. Ediger and coworkers (Lee et al. Science 323, 231, 2009) have shown in experiments on PMMA glasses that, in addition to strain hardening, polymeric glasses show a remarkable non-monotonicity in the segmental relaxation time both in loading and unloading of stress. Earlier, we developed a simple constitutive equation that combines recent theories for yielding in simple glasses (Brader et al. PNAS, 106, 15186, 2009) to represent local segmental modes in the polymer, with a dumbbell model for the slow polymer relaxation modes (S.M. Fielding, R.G. Larson, and M.E. Cates, Phys. Rev. Lett., 108.048301, 2012). For a polymer glass under uniaxial loading, the model predicts that the liquefaction of the segmental modes permits strain hardening of the polymer modes to emerge, and once this emerges, it slows the deformation of the material under constant load enough to partially re-vitrify the segmental modes even though the sample remains under stress. However, the model fails to predict the small recoil observed when stress is unloaded from the sample, instead predicting almost complete recoil. Here, we trace this problem with the model to the use of a single-mode dumbbell model, and extend the model by including multi-bead chain dynamics in place of the over-simplified dumbbell. We use a novel combination of a schematic model for the glass with Brownian dynamics simulations for the multi-bead chain to predict both creep and recoil. We show that the multi-bead model predicts similar effects as the dumbbell during creep, in agreement with experiments, and that it greatly reduces the overly large recoil obtained from the dumbbell model during recoil. The resulting model appears to be a very promising one for predicting creep and recoil in glassy polymers and can be easily applied to other deformation histories, including shear.

Wednesday 10:50 Côte-St-Luc SG8

Time-strain superposition in soft glasses

Samanvaya Srivastava and Lynden A. Archer
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Soft glassy materials are typified by large relaxation times and thus it is imperative to probe their long time responses. Most of these systems are athermal, and thus the conventional time-temperature superposition (TTS) approach has not proven to be suitable for accessing long time behaviors. We report a simple time-strain superposition (TSS) procedure that can be used instead to create rheological maps of soft glassy dynamics spanning over unprecedented time-scales. Experimental results from model soft nanoparticle suspensions as well as self-suspended nanoparticle fluids are presented. The roles of temperature and strain in assisting the relaxation in materials that exhibit TTS and TSS, respectively, are found to be analogous; the shift factors are shown to exhibit a WLF like dependence on strain in TSS. The generality of the approach is confirmed by theoretical calculations using the soft glassy rheology (SGR) model that also predict similar behavior, thus suggesting that time-strain superposition is a generic feature of all soft glasses.

Wednesday 11:15 Côte-St-Luc SG9

Rheological hysteresis in soft glassy materials

Thibaut Divoux[1], Vincent Grenard[2], and Sebastien Manneville[2]
[1]Centre de Recherche Paul Pascal, Bordeaux, France; [2]Physics, Ecole Normale Superieure de Lyon, Lyon, France

The nonlinear rheology of a soft glassy material is captured by its constitutive relation, shear stress versus shear rate, which is most generally obtained by sweeping up or down the shear rate over a finite temporal window. For a huge amount of complex fluids, the up and down sweeps do not superimpose and define a rheological hysteresis loop. By means of extensive rheometry coupled to time-resolved velocimetry, we unravel the local scenario involved in rheological hysteresis for various types of well-studied soft materials. We introduce two observables that quantify the hysteresis in macroscopic rheology and local velocimetry, respectively, as a function of the sweep rate δt^{-1}. Strikingly, both observables present a robust maximum with δt, which defines a single material-dependent time scale that grows continuously from vanishingly small values in simple yield stress fluids to large values for strongly time-dependent materials. In line with recent theoretical arguments, these experimental results hint at a universal time scale-based framework for soft glassy materials, where inhomogeneous flows characterized by shear bands and/or pluglike flow play a central role.

Wednesday 11:40 Côte-St-Luc SG10

Determination of the glass transition of sub-micron polymer films on a silicon wafer by DMA

Catheryn L. Jackson[1], Robert C. Cieslinski[2], Abhishek L. Roy[3], and Owendi Ongayi[4]
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Measuring the glass transition temperature, Tg, of polymer films in the range of 50-500 nm in thickness is very difficult and non-routine. Tg determination is important for polymer films used in commercial applications such as reverse osmosis (RO) membranes and electronic materials. Various methods have been used to determine Tg in thin films, including X-ray reflectivity, ellipsometry, a nanobubble inflation method using atomic force microscospy (AFM), positron annihilation spectroscopy and thermal AFM probe type measurements, but these methods require specialized equipment. Differential scanning calorimetry (DSC) has been applied to powders of scraped thin films, but consolidation and annealing that might occur in the pan is uncontrolled and may negate any effect seen due to film thickness. We report results for reference polymers, including polystyrene (PS), and examples of commercial polymers used as ultra-thin films using a dynamic mechanical analyzer (DMA) in the 3-point bending mode with a silicon wafer support. The peak tan d temperature is reported, which is related to the polymer Tg and effects due to confinement and film thickness are addressed.

Wednesday Afternoon

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Wednesday 1:30 Westmount SC34

Bond strength in colloidal gels measured from thermal rupture force distributions

Kathryn A. Whitaker[1], Lilian C. Hsiao[2], Michael J. Solomon[2], and Eric M. Furst[1]
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Optical tweezers were used to measure the thermal rupture forces between two particles suspended in solvent containing polymer depletant. Dilute suspensions of fluorescent poly(methyl methacrylate) spheres were suspended in 75% (v/v) cyclohexane and 25% (v/v) cyclohexyl bromide. The concentration c of non-adsorbing polystyrene depletant (Mw = 900,000) ranged from 0.0-15.3 mg/mL. The tweezers were used to bring particle pairs into contact and then pull them apart at load rates between 7-11 pN/s. By averaging the particle trajectories over many approach and retraction cycles, we calculate the cumulative probability distribution of the particles being bound together as a function of applied force [1]. This distribution is representative of the thermal forces that cause bond breaking in colloidal depletion gels. The rupture force increased linearly with increasing polymer concentration, in agreement with the Asakura-Oosawa (AO) model, up to the polymer concentration c = 6.6 mg/mL. Beyond this concentration, the pair interactions and corresponding rupture forces exhibit significantly more variance, suggesting that the AO model no longer captures the bond strength. We compare the interparticle force measurements with the linear viscoelasticity and local dynamics of colloidal gels (f = 0.20, c = 5.3-15.9 mg/mL).

[1] Swan, J., Shindel, M. and Furst, E. M., Phys. Rev. Lett., 109, 198302 (2012)

Wednesday 1:55 Westmount SC35

Microrheology of soft particle pastes: Forced motion of a tagged particle in a jammed suspension

Lavanya Mohan[1], Michel Cloitre[2], and Roger Bonnecaze[1]
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Soft particle pastes like microgels and compressed emulsions are densely packed, disordered suspensions of soft and deformable particles. The particles are jammed beyond random close packing (f >0.64). They behave like weak elastic solids at rest and low stresses but flow like liquids above the yield stress and this unique feature makes them useful as advanced rheological additives to process materials including high-performance coatings, textured food and personal care products. To relate the particle scale behavior to the macroscopic rheology we study the forced motion of a tagged particle through jammed suspensions with the help of particle scale simulations. A random particle is chosen and a known constant external force is applied on it and its motion in response is tracked. At small forces the particles are trapped in cages which resists the external force whereas at larger forces the tagged particle breaks free of the cage. This provides the microscopic evidence of yielding behavior in these materials. The average velocities of these particles in response to the applied forces are computed and the microscopic mobilities of these particles are extracted from them. The maximum distance through which the effect of the disturbance caused by this single tagged particle travels is also computed to determine the effectiveness of the particle-particle facet network present in these materials in transmission of localized microscopic forces. The simulations are performed with different packing fractions to understand the effect of volume fraction which gives information about the "microscopic cage strength" at different packing densities. The simulations thus provide means to probe the mirco and nano scale microstructure and properties of these materials including particle scale mobilities, transmission of localized disturbances and cage strength.

Wednesday 2:20 Westmount SC36

Capillary driven percolating networks in ternary particulate suspensions

Trystan Domenech and Sachin Velankar
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We investigate the effect of capillary bridging in ternary blend systems composed of a pair of immiscible molten polymers and spherical silica particles in the few-micron range. Particles are dispersed in the majority phase polymer (dubbed the "primary fluid") under molten conditions. The effects of melt-blending a small amount of the secondary immiscible polymer are examined by optical and electron microscopy. In the absence of the secondary fluid, the particles are uniformly dispersed with little or no aggregation. With addition of secondary fluid, we note a dual morphology: the secondary fluid is either in the form of dispersed drops containing a high particle loading, or in the form of capillary bridges connecting the particles into a volume-spanning "pendular" network. The pendular network appears even at particle loadings of 10 vol% suggesting that capillary bridging lowers the percolation threshold of the suspension. These structural changes are accompanied by major rheological changes: Linear viscoelastic properties change from Newtonian behavior in the absence of secondary fluid to solid-like behavior in the case of ternary blends. Additionally, large deformation experiments show the emergence of yield-like behavior for the ternary blends. The flow history and the preparation method used to prepare the ternary blends has a major influence on the structure and the rheological properties.

Wednesday 2:45 Westmount SC37

Shear-induced structuration of suspensions of attractive particles

Nicolas Taberlet[1], Vincent Grenard[2], and Sebastien Manneville[3]
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Colloidal gels of carbon black particles in a mineral oil are studied. When such gels are sheared between parallel plates with a narrow gap (typically less than 1 mm) the particles do not remain homogeneously distributed but instead arrange into highly anisotropic structures perpendicular to the shear direction. A similar behavior has been reported in other attractive systems (flocculated emulsions, carbon nanotube suspensions and clay gels). Here we investigate this structuring experimentally through simultaneous rheological measurements and optical observations. We study the formation and stability of those shear-induced structures by varying the particle concentration, the gap width and the shear rate. Similar results were obtained using a suspension of hollow glass beads in mineral oil rendered attractive with a small concentration of water through capillarity-induced interactions. Numerical simulations of attractive particles in a newtonian fluid were also performed. The simulation configuration is the same as in the experiment: the fluid is sheared at constant shear rate between two plates. The interactions between particles are modelled by a Lennard-Jones potential and the fluid is taken into account by assuming a linear velocity profile and simply adding a viscous drag force on the particles. We observe a critical shear rate under which structuring into vorticity-aligned flocs occurs. This critical shear rate scales as a power-law of the gap width with an exponent -2.4. We have checked that several attractive potentials combined with hard-sphere repulsion qualitatively yield the same results.

Ref : Grenard, Taberlet and Manneville, Soft Matter, 2011, 7, 3920-3928

Wednesday 3:35 Westmount SC38

Size segregation in sheared two-dimensional polydisperse foam

Hadi Mohammadigoushki and James J. Feng
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We report experiments on simple shear flow of two-dimensional bidisperse and polydisperse foams in a Couette device. The bubbles segregate according to their sizes, with larger ones in the middle of the gap and smaller ones closer to the walls, when the shear rate and the bubble size ratio are each above a threshold. The spatial distribution of the larger bubbles becomes flatter across the gap as its area fraction increases. To explain these observations, we adapt a model for monodisperse emulsions that predicts the spatial distribution of droplets as an outcome of the competition between migration away from the walls and shear-induced diffusion. The dense packing of bubbles in our foam intensifies bubble-bubble interaction, which manifests itself both in lateral migration due to wall repulsion and in collision-induced diffusion. After accounting for this difference via an effective capillary number based on the deformation of the bubbles, the model predicts the observed bubble distributions accurately.

Wednesday 4:00 Westmount SC39

Behavior of a static bubble in a yield stress fluid

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Non-bearing materials currently used in building applications (walls or bulkheads) are generally formed by panels or blocks. Such materials require good thermal performances and minimal mechanical strength. We focus on calcium sulfate foams containing a large amount of air trapped in bubbles. The foam production starts with fluid suspension obtained by quick mixing of water, mineral binder and surfactants. Foaming is applied before the quick setting of the mineral matrix. To study the interaction between foaming and rheological properties evolution, we use a transparent fluid model (dispersion of carbopol 676 in water). The air bubbles stability in yield stress polymer gel is analyzed by picture processing. Bubbles are inserted with a variable volume using a syringe for injection controlling gas pressure. We start with the study of single bubble in different carbopols gels to model the effect of rheological properties evolution (setting effect). As expected, bubbles sizes and internal pressure evolve according to thermodynamical laws. During injection, bubble growing depends on various parameters: yield stress, injected volume and pressure, sphericity... Experiments are conducted in several conditions to determine the parameters influences on bubble shape and volume. This lead to the identification of rheological behavior linking pressure, bubble geometry and yield stress in static condition. The foam stability is mostly conditioned by coalescence phenomena. It consists on the fusion of two bubbles in contact after the separating diaphragm destruction. Experiments reveal that a small amount of surfactants is needed to preserve foam structure. Coalescence phenomenon is studied on Carbopol gel following the meet conditions of two injected bubbles. The type and the surfactants amount generate a wide range of configuration. Results leads to a better understand of the foams stability at fresh state. It gives us tools to optimize the formulation regarding mechanical and thermal properties targets.

Wednesday 4:25 Westmount SC40

Particle sedimentation in emulsions under flow

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The sedimentation velocity of particles in oil-in-water emulsions under various flows that are orthogonal to the sedimentation direction has been measured using a CCD camera and an automatic particle tracking software. Of particular interest is the effect of different flow parameters on the sedimentation rate. The studied parameters include the strain magnitude of oscillatory shear, the strain rate of continuous shear, and strength of the extensional shear. The effects of various emulsion properties on the sedimentation rate are also investigated. The interplay between the sedimentation rate, flow conditions, and emulsion properties is discussed.

Wednesday 4:50 Westmount SC41

Bubble migration in two-dimensional foam under inhomogeneous shear: Effects of non-Newtonian rheology

Hadi Mohammadigoushki and James J. Feng
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When sheared in a wide-gap Couette device, a two-dimensional foam exhibits bubble migration behavior that differs from that in a narrow-gap Couette cell. A larger bubble in an otherwise monodisperse foam migrates away from the walls toward an equilibrium position that is between the inner cylinder and the center of the gap. This deviation from the center of the gap cannot be explained by the nonuniform shear-rate profile nor the curvature of streamlines. We believe it to be a manifestation of the non-Newtonian rheology of the foam as a continuum, with pronounced shear thinning and normal stress differences. The effects of these two factors on the lateral migration of a single bubble are then examined separately by using xanthan gum solutions and Boger fluids. Shear-thinning is shown to drive the bubble toward the outer wall, while the first normal stress difference has the opposite effect. The behavior of a large bubble in a two-dimensional foam can be understood from the competition between the opposing effects.

Symposium GS

Gels and Self-assembled Systems

Organizers: Jai Pathak and Matthew E. Helgeson

Wednesday 1:30 Verdun/Lachine GS11

Equilibrium configurations of high density lipoproteins

Aisa Biria and Eliot Fried
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A High-Density-Lipoprotein (HDL) consists of an assembly of phospholipid molecules in a lipid bilayer, and a belt of a protein polymer chain. The hydrophilic head groups of the phospholipid molecules are in contact with the exterior aqueous environment and shield the interior hydrophobic tails from that environment. This special configuration makes lipoproteins a suitable carrier for fats such as triglycerides and cholesterol esters in the blood stream. In our study, the free energy of the HDL consists of the bending energy of the lipid bilayer surface in form of the Canham-Helfrich energy, and the line energy of the chiral protein loop, which depends on its curvature and torsion. We derive the shape equations and boundary conditions governing the equilibrium of the HDL by using variational methods. Next, we employ numerical schemes to solve these equations and obtain various equilibrium configurations.

Wednesday 1:55 Verdun/Lachine GS12

Molecular features inferred from macroscopic rheology: Asymptotically-nonlinear material functions of LAOStrain (large-amplitude oscillatory shear strain)

N Ashwin K. Bharadwaj and Randy H. Ewoldt
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We examine a self-healing transient polymeric network formed by ion-assisted thermoreversible crosslinks (poly-vinyl alcohol (PVA) and sodium tetra borate (Borax) in water). We demonstrate that molecular features such as polymer persistence length can be inferred from macroscopic nonlinear rheological measurements. This is accomplished using the newly defined asymptotic material functions of large-amplitude oscillatory shear strain (LAOStrain), firstly by deriving a new analytical result for a transient network constitutive model subject to LAOStrain, followed by experimental measurement of the four asymptotically-nonlinear LAOStrain material functions. Nonlinear material functions, in general, would cover a high-dimensional space, but asymptotically nonlinear measures are low-dimensional fingerprints, depending only on frequency and not amplitude. To give our results context, we survey other constitutive models with available analytical solutions. We consider constitutive models across various material classes: the corotational Maxwell model, Giesekus model, and other specific models for polymer melts, rod-like polymer solutions, and emulsions. Only the newly derived result for a nonlinear-elastic transient network can

qualitatively describe the experimental data, with the added benefit of inferring material microstructure by quantitatively fitting the nonlinear parameter.

Wednesday 2:20 Verdun/Lachine GS13

Stochastic modeling and simulations of transient networks: Soft materials, gels and concentrated surfactants

Yun Zeng[1], L. P. Cook[1], and Lin Zhou[2]

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Many polydisperse entangled materials such as physically cross-linked gels, biopolymer networks, and concentrated surfactants exhibit "slow" relaxation process (power-law-like rather than exponential). Such power-law-like viscoelastic responses can be captured at the macroscale, by a "fractional" Maxwell model. Cates (Macromolecules 1987) modeled the regime in which the time scales for reptation and breaking/reforming are not well separated and found a stretched exponential stress relaxation. Our modeling is at the mesoscale, in order to avoid closure approximations, and works towards capturing the power-law relaxation process.

We consider stochastic models in which the transient network is composed of inter-connected and dangling elastically active chains (bead-spring dumbbells). In these meso-scale models the Fokker-Planck equation is formulated for each chain/dumbbell, and coupled with a kinetic model for the attachment/detachment processes. Classically, the attachment/detachment rates are governed by exponential distributions. In this work, models are extended to include alternative attachment/detachment mechanisms, nonlinear intermolecular forces, polydispersity and meso-scale interactions among the network components.

Wednesday 2:45 Verdun/Lachine GS14

Linear viscoelasticity and swelling of complex coacervates formed from mixing aqueous solutions of polyanions and polycations

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Combining near equimolar amounts of poly(diallyldimethylammonium chloride) to sodium poly(isobutylene-alt-maleate) results in formation of a polyelectrolyte complex (PE-complex) that precipitates from solution as a liquid coacervate with roughly 15 wt% of each polyion and 70 wt% water. Zeta-potential titrations conclude that these PE-complex coacervates are nearly charge-neutral, with similar stoichiometry regardless of the order and exact amounts of additions. Swelling and linear viscoelasticity (LVE) are studied at different salt concentrations in the surrounding solution. The enhanced swelling observed at high salt concentration suggests these coacervates behave like polyampholyte gels, with salt screening charge attractions. However, the stronger swelling at very low salt concentrations suggests the coacervates also act like polyelectrolyte gels, owing to a weak net charge. Linear viscoelastic oscillatory shear measurements indicate that the coacervates are viscoelastic liquids and that increasing ionic strength of the medium weakens the electrostatic interactions holding the polyelectrolyte network together, lowering the relaxation time and viscosity. We use the time-salt superposition idea recently proposed by Spruijt, et al. to access timescale ranges otherwise inaccessible, by constructing master curves and use a simple sticky Rouse model to understand the LVE for these soft materials, including the effect of polyanion chain length.

Wednesday 3:35 Verdun/Lachine GS15

Dynamics and microstructure of metallo-supramolecular networks

Hadi Goldansaz[1], Dietmar Auhl[2], Christian Bailly[1], and Evelyne van Ruymbeke[1]

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Supramolecular polymers are large synthetic molecules, which can self-assemble into well defined architectures via highly directional non-covalent interactions to form macromolecules with desired configurations and properties. Metal-ligand coordination chemistry has been used to prepare a wide range of stimuli-responsive supramolecular architectures with varying hierarchical structures based on the diversity of metal-ligand systems and ease of tuning the interaction strength [1]. In this study poly ethylene-oxide (PEO) is employed as a model polymer system to test the dynamics and stimuli responsive behavior of the transient metallo-supramolecular networks. The strength and characteristic terminal relaxation time of the network proved to be enormously sensitive to the metal ion concentration. Investigations on the terpyridine end-functionalized supramolecular PEO networks using Nickel(II) chloride salt revealed that formation of the metal-bis-terpyridine complexes is favored up to the stoichiometric concentration of the metal ions and mono-complexes are formed at superior concentrations which lead to a decrease of viscoelastic properties of the network [2]. However this trend is replaced at concentrations higher than 2 times the stoichiomety in which very strong gel like behavior is observed that exhibits several orders of magnitude higher elasticity and viscosity by comparing with the stoichiometric composition. Combined rheological, dielectric and microstructure studies illustrated that interactions between Ni(II) ions and polymeric precursor backbone are responsible for such dramatic gel-like behavior, in which metal ions act as physical cross linking agents.

[1] L. Brunsveld , B.J. Folmer, E.W. Meijer, R.P. Sijbesma. Chemical reviews (2001),101(12),4071. [2] P. Guillet,C. Mugemana, F.J. Stadler, U.S. Schubert, C.A. Fustin, C. Bailly, J.F. Gohy, Soft Matter (2009) 5,3409.

Wednesday 4:00 Verdun/Lachine GS16

Viscoelasticity and shear-induced structure in nanoemulsion transient gels

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Chemical Engineering, UC Santa Barbara, Santa Barbara, CA 93106, United States

Nanoemulsions have been considered for a range of advanced applications where fine control over their rheological properties is desired, independent of their colloidal stability. To address this issue, we have developed a scheme for imparting thermoreversible viscoelasticity to model oil-in-water nanoemulsions. Specifically, polymer-surfactant complexation in the aqueous phase and subsequent association of said complexes with nanoemulsion droplets lead to a gel-like transient network at low temperatures. Interestingly, the gels exhibit Maxwell-like viscoelasticity that follows time-temperature superposition (TTS) over a wide temperature range - the first time such behavior has been observed in emulsions. Small angle scattering measurements show that the low-temperature gelation arises entirely from the dynamics of the system, with no observable changes in suspension microstructure. Further TTS measurements show, despite a complex dependence of the linear viscoelasticity on fluid composition, a remarkably simple correlation between the linear viscoelasticity and the energetics of polymer-surfactant complexation. This result is directly reconciled with temporary network theory to give direct measurement of the association energy of network junctions. Finally, we demonstrate that the nonlinear rheology of the nanoemulsion transient gels exhibits strong shear thinning and shear banding. Rheo-SANS measurements indicate that this behavior arises due to the formation of shear-induced structure of the droplet phase, which we hypothesize is related to the nonlinear deformation of the transient polymer network. Overall, these studies demonstrate polymer-surfactant complexation as a highly generic mechanism to control both the linear and non-linear rheology of nanoemulsions, which could be exploited to design new materials with dynamically controlled rheology.

Wednesday 4:25 Verdun/Lachine GS17

Rheological observations near the gel point

H. Henning Winter
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Material states in the vicinity of the gel point exhibit exceptional properties which can be important for practical applications. An example is polymer processing while passing through the gel point. Other examples are materials that are used when near the gel point (adhesives, food materials, toners, ..). While they all share the same property at the gel point (powerlaw relaxation modulus, G(t)=S t-n for t >lamda,0), the transition behavior is less clear. An attempt will be made to classify common rheological features in the transition behavior and to show differences.

Wednesday 4:50 Verdun/Lachine GS18

Gelation and crosslinking in multi-functional thiol and multi-functional acrylate systems involving an in situ comonomer catalyst

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Thiol-acrylate polymerization is rapid and solvent-free, yielding materials with high conversion and uniform crosslink densities, which are beneficial in biomaterial applications. Unfortunately, most thiol-acrylate systems form via free-radical photopolymerization, requiring an external light source and photoinitiator. Additionally, radicals may remain in the final product and leach into the body. A tertiary amine can act as an *in situ* catalyst/comonomer to initiate a step growth polymerization without photoinitiator or external light, while retaining the benefits of photopolymerized systems. Fourier transform mechanical spectroscopy (FTMS), was used to monitor the gelation mechanism, while the Winter-Chambon criteria were used to determine the gel point, relaxation exponent (n), and fractal dimension as a function of *in situ* catalyst/comonomer concentration. Crosslinking occurred more quickly as catalyst concentration increased until a critical concentration of 22 mol%, where the gel time lengthened. Monitoring the change in strain over time provided an alternate method to estimate gel times within 10% error. Using rheology and Fourier transform infrared spectroscopy (FTIR), experimental conversion at the gel point for 16.1 mol% catalyst was calculated as 0.55, verifying the theoretical value of 0.57 calculated using Flory-Stockmayer's statistical approach. Relaxation exponents of 0.97 and fractal dimensions of 1.3 were calculated for all samples, consistent with coarse-grained discontinuous molecular dynamics (DMD) simulations. The elevated value of n may be due to the low molecular weight prepolymer. The fractal dimension and n were invariable over all systems studied, suggesting the crosslinking mechanism remains unaffected by changes in catalyst concentration, allowing the gel time to be tailored by simply modulating the catalyst concentration.

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Wednesday 1:30 Outremont MB34

Not all slip is the same

John R. Dorgan and Nicholas A. Rorrer
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New molecular scale insight into polymer slip and cross-flow migration effects is available using the recently developed COMOFLO algorithm (Dorgan et. al. PRL 110, 176001 (2013)). Results discussing the interplay of slip with cross flow migration are presented by comparing Couette flow (where migration effects are generally not present) with plane Poiseulle flow (where migration effects are profound). For Couette flow, three flow regions-no slip, weak slip, and strong slip (shear banding) - are captured in the simulations. Disentanglement is clearly evidenced in a nonlinear velocity profile that exhibits shear banding, in an excess of chain ends at the slip plane, and in a nonmonotonic stress versus shear rate response. When polydispersity is introduced for entangled chains in Couette flow, slip phenomena are severely reduced and the inherent constitutive bifurcation is limited to a small region. The situation in plane Poiseulle flow is very different because the non-homogeneous nature of the flow field drives lower molecular weight chains to regions of high shear rate and high molecular weight chains to regions of low shear rate. The effect of this migration is to provide a lubricating layer which suppresses slip to higher shear rates. Accordingly, for polydisperse systems, the fundamental physics of slip in drag flow versus pressure driven flow are quite different, a fact which has evidently eluded the rheology community for the more than 80 years since the pioneering work of Mooney (J. Rheol. 2, 210 (1931)).

Wednesday 1:55 Outremont MB35

Slip at the interface between immiscible polymer melts undergoing capillary flow

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Slip at the interface between polymer melts remains poorly understood. Studies that use only rheological data to deduce the slip velocity usually involve applying a shear deformation to a stack of parallel multilayers. In order to understand slip in the context of polymer extrusion, we have investigated slip at the interface between two immiscible polymer melts undergoing pressure driven flow through a capillary die. To enable the measurement of slip velocity at the polymer/polymer interface we have adapted the Mooney method, a method usually used to study wall slip. Using the method, we measured the dependence of the interfacial slip velocity on the interfacial shear stress for cylindrical core-sheath samples of Polypropylene and Polystyrene. In agreement with prior work on multilayer sandwiches, we found two distinct power-law regimes in the relationship between the interfacial slip velocity and the interfacial shear stress. The power-law exponent changes from a value of approximately 3 at low shear stress values to approximateley 2 at high shear stresses. We then investigated the effect of varying the temperature on the slip velocity and explore the consequences of time-temperature superposition for the two polymers. Finally, we investigated the connection between slip at the interface between the two polymers and the origin of roughness at the interface.

Wednesday 2:20 Outremont MB36

Viscoelasticity of diblock single-ion conducting ionomers

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In order to serve as both electrolyte and separator in rechargeable batteries, ionomers are required to exhibit both sufficient modulus and high ionic conductivity. However, good ionic conductivity is mostly correlated with low Tg materials where rapid segmental motion of the polymer aided ion transport, decoupling of the electrical and mechanical properties of polymeric electrolytes is needed. Poly(dimethylacrylamide) as the glassy block provides sufficient modulus while the subsequent ion containing poly(ethylene oxide)-based block, synthesized by reversible addition-fragmentation chain transfer polymerization, provides a low-Tg medium for ion conduction. Small amplitude oscillatory shear is used to detect the mechanical response to assess the modulus of the glassy block and ion association behavior that acts as physical crosslinks between chains in the soft block. The delay in segmental relaxation time and terminal response time provides information about ion mobility and ion association. Samples with different ratios of the two blocks can have different morphology, and we seek an optimal composition that gives highest modulus without severe suppression of ionic conductivity and the optimal amount of ions to incorporate so that ion association aids ion transport.

Wednesday 2:45 Outremont MB37

Investigation of morphology developments in block-copolymers via mesoscale simulations

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Dissipative Particle Dynamics (DPD) is a promising method for soft matter simulations, including colloidal suspensions, polymer melts and solutions. However, this method was found to be problematic in simulating multiphase systems due to the absence of three body interactions. Many Body Dissipative Particle Dynamics (MDPD) was recently proposed to discuss the multiphase interactions mainly in liquid-vapor systems. This method uses the same thermostat as the standard DPD but the formulation of the conservative force is different. MDPD adds a density dependent term to the soft repulsions used in DPD in order to take the three-body interactions into account. Therefore, MDPD shows a strong potential to discuss dynamics of multiphase systems including structure and morphology evolution in polymer blends and co-polymers. Thus we established a systematic method to relate the simulation to real experiments for such systems by mapping the MDPD simulation parameters onto Flory-Huggins chi parameter. The accuracy of this relationship was evaluated using phase separation in small molecules, and the solubility of polymers in dilute solvent solutions via monitoring the scaling of the radius of gyration (Rg). The main objective of the present work is to study the microphase separation and morphology development under flow of co-polymeric systems using the MDPD method.

Wednesday 3:35 Outremont MB38

Physical origin of non-linearities in homopolymers and polymer nanocomposites

Erkan Senses and Pinar Akcora

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The higher order harmonic contributions to the non-linear elastic response of linear homopolymers, poly(styrene) and poly(methyl methacrylate), their blends and nanocomposites to large amplitude oscillatory shear experiments are analyzed. The elastic stresses for the particle and polymer are resolved by decomposing the total stress into its elastic and viscous components at different strain levels within a cycle of deformation. Comparison of the mathematical Fourier-Chebishev non-linear coefficients and the predictions from the non-linear deformation theory of flexible polymer networks and stiff particle networks suggest that the stretching ratio of poly(styrene) chains gives rise to the third order Fourier coefficient (G_3') for homopolymers; while the fifth harmonic (G_5') is due to interparticle interaction which represents the strength of stiff particle network.

Wednesday 4:00 Outremont MB39

Clay platelets pin interfaces in polymer blends

Milana Trifkovic, Aaron T. Hedegaard, and Christopher W. Macosko

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We investigate compatibilization of cocontinuous blends by three methods; selective localization of clay nanofillers at domain interfaces, reactive compatibilization, and the synergistic action of the two. Non-functional polyethylene (PE) and maleic anhydride grafted polyethylene (PE-g-MA) were blended with polyethylene oxide (PEO) and nanoclays with various organic modifications. Blending nanoclays with PE and PEO resulted in interfacial stabilization and suppressed coarsening similar to that achieved with reactive compatibilization (Trifkovic, et.al Macromolecules, 2012). TEM micrographs showed clay to be located in PE and at the interface between PE and PEO, which reduced the interfacial energy and consequently resulted in smaller characteristic size. The formation of a solid interface by the nanoclay particles prevented coarsening of these blends. The overall size reduction and uniformity of the blends depended on the interfacial reaction, and location and exfoliation of the clay which varied dependent on the organic modifiers of the clay.

Wednesday 4:25 Outremont MB40

Effect of particle size and shape on oscillatory and transient shear rheology of polymer nano-composites

Hojjat Mahi Hassanabadi[1], Denis Rodrigue[1], Mahdi Abbasi[2], and Manfred Wilhelm[3]

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The effect of nano-particle characteristics (size and shape) on the rheological behavior of ethylene vinyl acetate (EVA) copolymer was investigated under oscillatory (small and large amplitude shear (SAOS and LAOS)) and transient shear. Three different fillers having geometrically and chemically different structures: multiwall carbon nano-tube (tubular), clay (platelet) and calcium carbonate (spherical) were melt blended with EVA and the compositions were subjected to different shear deformations. In particular, the role of particle shape in affecting polymer-particle and particle-particle interactions and hence the linear and non-linear viscoelastic properties were highlighted. This was done by analyzing the scaling property of G' and G" in SAOS, I3/I1 and Q parameter in LAOS, as well as the amount of stress overshoot (? ?_cr and smax) in shear transient (start-up test). It was found that higher chain confinement and higher contacting capability between the particles result in stronger effects in both linear and non-linear properties. To complete the study, morphological analysis through TEM and SEM were performed. Keywords: Particle geometry, SAOS and LAOS measurements, non-linear viscoelasticity,

Wednesday 4:50 Outremont MB41

Melt rheological characteristics of PET and PET nanocomposites after solid-state polymerization

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PET/Cloisite 30B (C30B) nanocomposites of different concentrations of the organoclay were prepared using water-assisted melt-mixing. The reduction of the molecular weight of the PET matrix, caused by hydrolysis during the water-assisted extrusion, was compensated by subsequent solid-state polymerization (SSP). SSP of PET was carried out at temperatures below the melting point but above the glass transition of PET. Chemical reactions involved in the SSP are transesterification, esterification, largely controlled by the diffusion of by-products. Rheological measurements, intrinsic viscosity and titration measurements were used to analyze the obtained samples from SSP. Results of small amplitude oscillatory rheometry and inherent viscosity showed that the molecular weight of PET increased significantly after SSP. The linear molecular structure of PET was maintained, as confirmed by HNMR and CNMR spectra as well as rheological measurements. Low molecular weight PET showed nearly Newtonian behavior while with increasing molecular weight, shear-thinning behavior was observed. However, PET nanocomposites exhibited a solid-like behavior. By increasing the molecular weight during SSP, the storage modulus and complex viscosity increased in the whole frequency range for the neat PET. The complex viscosity and storage modulus of the nanocomposites at high frequencies, where the behavior of the matrix was dominant, were lower than those of the neat PET. It was also found that the extent of the SSP reaction in nanocomposites was lower than for the neat PET, due to the barrier effect of clay platelets. The Maron-Pierce model was used to evaluate the molecular weight of PET in nanocomposites before and after SSP. The complex viscosity at high frequencies was scaled with the molecular weight of PET.

Symposium NF

Non-Newtonian Flows

Organizers: Ian A. Frigaard and Vivek Sharma

Wednesday 1:30 Mont-Royal/ Hampstead NF15

Computationally challenging 3D multiscale FENE dumbbell simulations on multi-GPU systems

Alexander Rüttgers
Institute for Numerical Simulation, University of Bonn, Bonn, Germany

The computational modeling of dilute polymeric fluids usually involves an additional polymeric stress tensor in the Navier-Stokes equations and an additional system of differential equations for the stress tensor entries, compare the Oldroyd-B or the Phan-Thien Tanner (PTT) model. After discretization, these macroscopic models are often restricted in their scope of application due to numerical instabilities that appear beyond a critical Deborah or Weissenberg number (cf. high Weissenberg number problem).

One attempt to overcome this problem is multiscale modeling. This approach directly solves the kinetic equations of the microscopic system. We apply the multiscale FENE model to a 3D square-square contraction flow problem. For this purpose, we couple the stochastic Brownian configuration field method (BCF) with our fully parallelized three-dimensional Navier-Stokes solver NaSt3DGPF. The robustness of the BCF method enables the numerical simulation of high Deborah number flows for which most macroscopic methods suffer from stability issues.

In this talk, we compare the results of our simulations with that of experimental measurements from literature and obtain a very good agreement. In particular, we are able to reproduce effects such as strong vortex enhancement, streamline divergence and flow inversion for highly elastic flows.

Due to their computational complexity, our simulations require massively parallel computations. We have accelerated our implementation by using Nvidia's CUDA architecture that enables computations on graphic processing units (GPUs). Using our GPU cluster, we achieve excellent speed-up results compared to classical CPU based computing.

Wednesday 1:55 Mont-Royal/ Hampstead NF16

Different levels of approximation for the Reynolds stress tensor obtained from DNS of a FENE-P viscoelastic model in a drag reducing turbulent flow

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By analogy with the Reynolds Averaged Navier-Stokes (RANS) equations for turbulent Newtonian flows modeling turbulence of viscoelastic fluids adopting a Reynolds Average (RA) approach seems promising. There have been few attempts in the literature to derive such models, the most recent including RA conformation tensor equations. In general the Reynolds stress tensor has been modeled adopting a linear Boussinesq hypothesis, i.e. considering that this stress is proportional to the mean rate-of-strain tensor. In the present work, we investigate the representation of the Reynolds stress tensor of a viscoelastic FENE-P model in a drag reducing turbulent flow. Direct Numerical Simulation (DNS) results of a turbulent fully developed channel flow of viscoelastic fluid diluted in a Newtonian solvent are used to evaluate the Reynolds stress modeling. The highest frictional Reynolds number reached in these DNS results, is 1000, which is the order of magnitude found in some drag reduction industrial applications. We show that increasing elasticity, through increasing the Weissenberg number or increasing the fully-stretched length of the polymer molecule, deteriorates the linear Boussinesq approximation. We then propose different sets of non-linear tensorial bases that significantly improve the level of representativeness of a RA-type model. We also present a general methodology allowing to compute the scalar coefficients of such non-linear viscoelastic RA-models.

Wednesday 2:20 Mont-Royal/ Hampstead NF17

Nonlinear dynamics of turbulent drag reduction by polymers

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We address the issue of polymer-induced drag reduction in turbulent flows from the perspective of the nonlinear dynamics as well as coherent structures. Direct numerical simulations (DNS) of turbulent channel flow at different levels of drag reduction are conducted. First we show the intermittent dynamics for the Newtonian case and viscoelastic cases. At zero and low degrees of drag reduction, the flow primarily exists in a high-drag state, with occasional intervals of low drag. The high drag states, which exhibit strong turbulent motions, are named as active turbulence, while the low drag states with weaker turbulent motions are named as hibernating turbulence. At high levels of drag reduction, the situation is reversed. The trajectory spends long time periods in a low-drag state, with brief excursions to high drag states. Secondly, we show the findings of a viscoelastic extension of Karhunen-Loeve decomposition (KL decomposition). In addition to the roll and propagating modes that have been discovered in KL decomposition of Newtonian turbulence, in viscoelastic cases we observe the "sheet modes" with high total energy, which may correspond to the transition between active and hibernating states. The vanishing of propagating modes at high levels of drag reduction suggests the significant changes of dominant structures in viscoelastic turbulence. We also find that the reconstruction of flowfields from single dominant KL mode show strong correlation with the intermittent dynamics found in DNS. Our results demonstrate that the idea of active and hibernating turbulence provides a unified description of all levels of drag reduction. They also suggest that the universality of MDR with respect to polymer parameters may arise from the Newtonian origin of hibernating turbulence, which sheds light on another practical area: developing drag reduction schemes for systems in which polymer additives cannot be employed.

Wednesday 2:45 Mont-Royal/ Hampstead NF18

Polymer induced breakdown of large-scale Taylor vortex structures and the resulting drag enhancement in turbulent Taylor-Couette flows: Direct numerical simulations and mechanistic insight

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We report for the first time polymer-induced breakdown of large-scale Taylor vortex (TV) structures leading to drag enhancement in viscoelastic turbulent Taylor-Couette flows (TCF). Specifically, upon addition of trace amount (dilute solutions) of soluble high molecular weight polymer the Newtonian large-scale TVs are replaced by small-scale Taylor and Görtler vortices in the inner and outer cylinder wall regions, respectively. This flow transition is facilitated by the presence of large polymeric hoop stresses in a narrow region near the outer wall. The polymeric body force in this region changes the direction of the radial fluid motion from an outflow-dominated to an inflow-dominated regime, giving rise to strong and highly localized velocity streaks and a commensurate dramatic drag increase (DI) of up to 62%. Finally, a simple mechanism for this striking flow transition based on a self-sustaining process composed of viscoelastic Taylor-Couette (TC) and an "elastic Görtler" instability is proposed.

Wednesday 3:35 Mont-Royal/ Hampstead NF19

Rheo-ultrasonic imaging of secondary flows in a Taylor-Couette device

Marc A. Fardin, Christophe Perge, and Sebastien Manneville
Physics, Ecole Normale Superieure de Lyon, Lyon, France

The Taylor-Couette device is a geometry with two concentric cylinders, which is commonly mounted on commercial rheometers and is used extensively to study the material properties of a variety of complex fluids. When the gap between the cylinders is small the base azimuthal flow is viscometric, but if the base flow becomes unstable, secondary flows emerge and break the viscometric assumption. In particular, in a Newtonian fluid inertia generates Taylor votices. Similar secondary flows are also observed in polymer or wormlike micelles solutions due to a viscoelastic instability. In all cases, secondary flows deform the azimuthal base flow, which looses its axial invariance. We report on a new ultrasonic imaging technique that allows to follow such deformation of the main flow by measuring the time-resolved azimuthal velocity profiles all along the axis of the cylinders simultaneously to the rheological response. We show examples of the dynamics of secondary flows for several Newtonian and non-Newtonian fluids and we stress their impact on viscometry.

Wednesday 4:00 Mont-Royal/ Hampstead NF20

High Deborah number elastic instabilities around microfluidic confined cylinders

Stephen Kenney, Kade Poper, Ganesh Chapagain, and Gordon F. Christopher
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Flow of viscoelastic fluids around a confined cylinder is a hallmark fluids problem because it resembles industrial processes and is easily simulated. This flow displays multiple regimes with elastic and inertio-elastic instabilities that occur at critical Deborah (De) or Reynolds (Re) numbers. Practical limitations have restricted the experimentally explored range of De; using microfluidic channels, these limitations have been overcome, and allowed the study of high De flows. We have systematically characterized the flow around symmetrically placed, highly confined microfluidic cylinders at $0.01 < De < 1000$, using low viscosity Boger fluids. By changing fluids, flow rates and geometry, non-dimensional parameters are independently tuned, allowing a controlled and detailed study.

At low De, the nature of the flow around a confined cylinder displays inertio-elastic instabilities forming downstream of the cylinder at critical values of Re and De consistent with predictions in literature. At larger values of De attainable due to microfluidic channels, new elastic instabilities are observed that have not been previously reported. We first identify a downstream instability of temporally and spatially varying streamlines at De~50. This instability is a precursor to a new class of upstream instability at $De > 100$. During this instability, the upstream stagnation point separates from the cylinder face up to ~ 5 diameters upstream of the cylinder, and its position oscillates in a growth and collapse cycle. We characterize flow patterns and onset of both instabilities as functions of the Elasticity number and the viscoelastic Mach number, and conclude that the instability is purely elastic in nature but affected by inertia. Furthermore, we characterize the role of geometry on the onset of both instabilities. We have identified two new and unique elastic instabilities around confined cylinder flows and provide a basic description of their behavior and underlying physical mechanisms.

Wednesday 4:25 Mont-Royal/ Hampstead NF21

Flow-induced microstructure of nematic liquid crystals between eccentric rotating cylinders

Nader Noroozi and Dana Grecov
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Liquid Crystals (LCs) are anisotropic viscoelastic materials; the combination of fluid-like flow with crystal-like anisotropy makes its phases interesting as modifiers of interfacial behavior when applied as lubricants. The ability of liquid crystalline materials to form ordered boundary layers with good load-carrying capacity, and to lower the friction coefficients, wear rates and contact temperatures of sliding surfaces, thus contributing to increase the components service life and save energy has been widely demonstrated. This paper presents theory and simulation of flow-induced structures in LCs between eccentric rotating cylinders. This problem closely simulates that in a journal bearing. The objective of this study is to characterize the relationship between the flow in the annulus of eccentric cylinders and the microstructure of LCs as well as the rheological properties of LCs. In order to predict the microstructure of liquid crystalline materials, Landau de-Gennes model and Navier-Stokes equations have been solved simultaneously for start-up flow induced by rotation of the inner cylinder. Velocity profiles and pressure distributions of LC domains along with evolution of defects have been observed in time.

Wednesday 4:50 Mont-Royal/ Hampstead NF22

Rotation of an ellipsoidal particle in a viscoelastic liquid in an unconfined shear flow by numerical simulations

Gaetano D'Avino[1], Francesco Greco[2], Martien A. Hulsen[3], and Pier Luca Maffettone[1]
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The flow of non-spherical particles suspended in fluids is relevant in several applications such as injection moulding, extrusion, etc. In many processes, the suspending liquid exhibits non-Newtonian properties. The available theories dealing with dynamics of anisotropic objects in sheared viscoelastic liquids are limited to infinitely elongated particles and to asymptotically small or large Deborah numbers. Recent experiments in shear flow showed that the aspect ratio and the fluid rheology strongly affects the particle motion. A systematic study relating the particle dynamics to the geometrical and fluid properties is missing. In this work, the rotation of an ellipsoidal particle in an unconfined sheared viscoelastic liquid is investigated by 3D finite element simulations. To highlight different rheological properties, the suspending fluid is modeled by using two constitutive equations. The particle dynamics is studied by varying the aspect ratio and the Deborah number. Fluid viscoelasticity slows down the particle rotation rate as compared to a Newtonian fluid. In agreement with previous theories and recent experiments, a drift away from the Jeffery orbit and orientation towards the vorticity direction is found for low Deborah numbers. By increasing the Deborah number, a transition towards flow alignment is found. Higher aspect ratios reduce the critical Deborah number for flow alignment. The observed dynamics is qualitatively unaffected by the presence of second normal stress differences.

Symposium BM

Rheology and Processing of Bio-based Materials

Organizers: Michel Huneault and James J. Feng

Wednesday 1:30 Côte-St-Luc BM10

Red blood cell suspensions with polymer additives: Orientation, migration and margination dynamics

Kushal K. Sinha and Michael D. Graham
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In recent experimental studies, it has been shown that introducing drag reducing polymers (DRP) to blood in nano-molar concentration has many beneficial physiological effects, including the prevention of lethality from hemorrhagic shock in animals. In micro-channel experiments with suspensions of red blood cells (RBCs), DRPs have been shown to reduce cell free layer thickness and affect the orientation of the cells. The underlying mechanisms for these phenomena are not understood. In the present study, we investigate the dynamics of RBCs in Newtonian fluids and in dilute solutions of DRP in microcirculation. Cell membranes are modeled with the Yeoh strain energy function and an energy penalty for bending. Polymer molecules are modeled as bead-spring chains with finitely extensible nonlinearly elastic springs. Three dimensional simulations are performed with a Stokes flow formulation of the immersed boundary method for the RBCs, combined with Brownian dynamics for the polymer molecules. We find that the cell-free layer thickness is substantially reduced near wall with addition of polymer, while elongation of RBCs and their alignment with flow direction is significantly enhanced. The wall shear stress decreases with increase in capillary number and is reduced in presence of polymers. The wall normal migration velocity of single RBC is found to decrease by adding polymer. The combined effect of reduced migration velocity and increased alignment with flow can explain the paradoxical behavior of reduced flow resistance even with reduction in cell free layer as observed in experimental work. These predictions are in qualitative agreement with experiments.

Wednesday 1:55 Côte-St-Luc BM11

A structural parameter thixotropic model for the transient shear flow of blood

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This work has been undertaken as a continuation of our efforts to develop a sophisticated model capable of predicting accurately the time-dependent blood pressure and flow profiles throughout the entire human arterial network. In previous works we studied the effects of non-Newtonian characteristics of human blood under steady state, shear flow conditions. Under these conditions, we systematically proved that the Casson constitutive model describes best the rheology of blood, while we also developed parametric equations for the dependence of the model parameters, yield stress and model viscosity, on the physiological parameters, the hematocrit, temperature and fibrinogen concentration.

In this presentation, we offer an extension of our work to time-dependent conditions. To the best of our knowledge, this is the first attempt to model the transient flow of blood using a thixotropic structural parameter model. Our analysis shows that a modified version of the "Delaware model" [1] is capable of predicting the time dependent rheology of blood. At steady state, the model reduces to the Casson constitutive model. At low shear rates, only two additional to the Casson model parameters are needed. At moderate shear rates, an additional yield strengthening effect needs to be accounted for, indicative of the RBC rouleaux structures developed within blood. The proposed model is in good agreement with the experimental data of Bureau et al. [2], on a simple triangular step shear rate flow.

References: [1]. Mujumdar, A., A. N. Beris, and A. B. Metzner, "Transient phenomena in thixotropic systems," J. Non-Newtonian Fluid Mech. 102, 157-178, (2002). [2]. Bureau, M., J.C. Healy, D. Bourgoin, and M. Joly "Rheological hysteresis of blood at low shear rate," Biorheology 17, 191-203, (1979).

Funding: Grant Award # NSF CBET 1033296

Wednesday 2:20 Côte-St-Luc BM12

Meltability and viscoelastic behavior of mozzarella cheese with methocel as a water binder

Ramesh Subramanian
Bharti School of Engineering, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

Textural characteristics is a very important factor in determining the quality of cheese for a particular product application, consumer acceptability, and quality. Cheese is viscoelastic in nature, and water is a major component that is dispersed throughout the casein (protein) matrix. Distribution of water in Mozzarella cheese differs from most other cheese due to the microstructural differences resulting from the stretching step during its manufacture. Casein matrix in Mozzarella is oriented into fibrous aggregates forming large open channels or columns filled with water and fat droplets, and this contributes to its poor water-holding capacity. Fresh Mozzarella cheese often exudes free moisture (expressible serum) at the block and freshly cut surfaces during the early stages of maturation, making it unsuitable for shredding and melting. Use of water binders such as lecithin and carrageenan have shown to improve yield via moisture retention and texture of low-fat cheeses. Methocel (Methyl Cellulose) is a water-soluble polysaccharide gum that is used in a variety of industrial products, processed food and pharmaceuticals to increase water absorption, decrease fat absorption, inhibit syneresis (separation of liquid from a gel caused by contraction), modify viscosity, and bind water. This study examines the effect of adding a small quantity (0.2% by wt) of methocel as a water binder on the meltability and viscoelasticity of a high-moisture, skim-milk Mozzarella cheese during early stages of maturation (1, 5, 7, and 14 days after manufacture).

Wednesday 2:45 Côte-St-Luc BM13

Capturing the temporal rheological properties of a hydrating starch based snack food: Elucidating the structure-function relationships for starch using α-amylase

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Oral processing transforms a brittle snack food (e.g., potato chips) into a hydrated food bolus that has characteristics of a viscoelastic soft solid. This transformation comprises mechanical breakage and crushing, hydration by saliva, enzymatic degradation of starch by α-amylase and high shear deformation, all of which impact digestion-with implications on nutrition and health-and elicit sensory percepts that influence consumer acceptance. Thus, a key challenge when designing next generation snack foods using healthier components is to emulate the temporal rheological properties of the food bolus during oral processing while maintaining consumer acceptability. We present here our *in vitro* approach for capturing the transient rheology of a food bolus during hydration and enzymatic degradation using potato chips as a relatively simple model snack food. We show that the storage modulus of an *in vitro* bolus in physiological buffer increases over time according to first-order hydration kinetics. We have established that the moduli are critically dependent on solids content, and we have established that the oil from the chips, which disperses as individual droplets, reduces the moduli. We extend this previous work by demonstrating that α-amylase significantly reduces the elasticity of the bolus due to degradation of the potato starch; however, the bolus maintains its solid-like character, indicating that the rheology of the bolus arises not just from starch but also from plant cell material. We discuss the implications of our findings and rheological approach on oral processing and digestion of foods.

Wednesday 3:35 Côte-St-Luc BM14

Real-time monitoring of rheology in a fed-batch recycle reactor using a non-invasive rheometer

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The enzymatic liquefaction of cellulosic materials at high solids loadings is a challenging operation due to rapid rheological changes that influence flow patterns and mixing. Since fibrous biomass suspensions can reach high yield stresses even at moderate concentrations, the reaction is often performed in fed-batch mode, where part of the biomas is loaded initially and the rest is added in portions to maintain a flowable slurry at all times. A common way to operate these reactors is to load the biomass at prescribed times. From the standpoint of reducing batch times, however, it is advantageous to monitor rheological properties to assist in timing the additions. We performed fed-batch hydrolysis of cellulosic material in a fed-batch recycle reactor with continuous measurement of rheograms using the FlowScan™ non invasive rheometer. The short measurement times allowed real-time monitoring of rapid rheology changes occurring in the reactor. The effect of using two different enzyme additions policies on the evolution of rheological parameters is discussed.

Wednesday 4:00 Côte-St-Luc BM15

Numerical simulation of the flow of compressible viscoplastic biomass in a pipe

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Biomass can provide a source of renewable energy. Lignocellulosic biomass, including trees, switchgrass, and corn stover, has advantages over other bioresources, such as corn kernel and vegetable oil, because it is less coupled to food supplies and is replenished through the cultivation of fast growing agricultural residues. However, lignocellulosic biomass processing typically involves numerous steps which lead to expensive processes. One convenient way to reduce the cost of processing biomass is to increase the concentration of the insoluble solids. However, concentrated biomass is a very viscous, non-Newtonian complex fluid, which makes mixing reactants and conveying the biomass challenging. Biomass flows can be quite challenging because of a variety of problematic phenomena including large yield stresses, compressibility, heterogeneities, and instabilities. To capture all of the problematic phenomena, we need to develop models for the flow of concentrated compressible biomass in which the viscosity and yield stress depend on the pressure or the density.

We have developed a finite volume approach to simulate pressure-driven flows of compressible viscoplastic fluids. The shear stress has been represented by different models. Here we use the Bingham model, where the shear stress is a function of shear rate, yield stress, and the plastic viscosity. The yield stress of biomass depends on the concentration. In this work we report two-dimensional and axisymmetric numerical simulations to study the pressure drop of the biomass flow. The mathematical model helps to understand the connections between physical properties and flow behavior. This presentation will focus on simulation results aimed at understanding the origins of various phenomena observed in pipe flow, specifically, the nonlinear dependence of pressure drop on pipe length and the apparent stick-slip behavior. Predictions include use of experimental data for density-dependent rheological properties obtained in our laboratory.

Wednesday 4:25 Côte-St-Luc BM16

Effects of degree of sulfation and ultrasound treatment (sonication) on the rheology and microstructure of cellulose nano-crystal (CNC) aqueous suspensions

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Cellulose Nano-crystal (CNC) aqueous suspensions have been prepared with different degrees of sulfation. The rheological properties and microstructure of these CNC suspensions have been studied at different concentrations. The suspensions phase separate to liquid crystalline and isotropic domains above a first critical concentration where the fingerprint texture, characteristic of chiral nematic liquid crystals, appeared and the viscosity profile showed a three regions profile, typical of liquid crystals. The suspensions form gel above a second critical concentration where the viscosity profile showed a single shear thinning behavior over the whole range of investigated shear rates. Effects of degree of sulfation on these two critical concentrations, and the effects of ultrasound energy on the rheological properties and microstructure of these CNC aqueous suspensions were studied using polarized optical microscope combined with rheometer (optical rheometry). It was found that the viscosity of samples decreases with increasing degree of sulfation and samples with lower degree of sulfation form gels at relatively lower concentrations. Changes in the amount of applied ultrasound energy affected the suspension microstructure and the pitch size of chiral nematic domains which led to change in viscosity profile especially at low shear rates.

Wednesday 4:50 Côte-St-Luc BM17

Macroscopic vs. microscopic rheological response of nanocrystalline cellulose suspensions

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Pulp and paper industry is a major industry worldwide, producing communication papers, packaging, boxes, tissue, hygiene products, and an assortment of disposable products. Fiber for this industry comes from pulping biomass, mostly trees in modern times. Wood fibers are composites made up of spirally wound fibrils of cellulose. These fibrils consist of fully crystalline regions and amorphous less ordered regions. Effective hydrolysis of cellulosic material using sulphuric acid results in the production of colloidal suspensions of fully crystalline spindle-like particles referred to as nanocrystalline cellulose (NCC). In this paper conventional rheometry was combined with light scattering echo (LS-Echo), to study the rheological response of NCC suspensions under oscillatory shear flow deformations at both macroscopic and microscopic scales. Dynamic time sweeps were performed at various stain amplitudes corresponding to the different regions of viscoelastic response at two frequencies of 1 Hz (6.28 rad/s) and 10 Hz (62.8 rad/s). The dynamic time sweep under constant strain amplitudes showed that the storage modulus of the samples increased more rapidly with time as the amplitude of the applied strain decreased. These observations were also confirmed by the results obtained from the LS-echo. This technique was used to study the dynamics of the NCC spindles under oscillatory shear flow deformations. It was found that the particle motions were essentially reversible at strain amplitudes lower than the yield strain, as anticipated for an elastic distortion. However, beyond the yield strain the amplitude of the echo heights significantly dropped, implying irreversible changes in the particle positions, i.e., yielding. The yield strains measured by the LS-echo technique were found to correspond to the strains at which storage and loss moduli crossed over.

Thursday Morning

Symposium AP

Award Presentations

Metzner Award Presentation

Thursday 8:00 Westmount AP1

Active matter: Suspensions of self-propelled particles

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There is currently much interest in a new class of materials called Active Matter. These are materials that are continually pushed away from equilibrium at each point within the material, instead of from the exterior. Since active materials are always far from equilibrium, they are able to have material properties and assembly not restricted by equilibrium statistical mechanics. This includes enhanced fluctuations and mixing, negative intrinsic viscosity, and non-uniform concentration in confined geometries. One important class of active materials is a suspension of self-propelled particles, which are colloidal suspensions in which the colloids propel themselves through the fluid. Examples of this type are suspensions of swimming microorganisms or synthetic colloids that are engineered to use chemical reactions to move. In this talk, I will focus on two aspects of active suspensions: (1) how self-driven flow can be used to coordinate the motion of large groups and (2) how an external flow alters the dynamics in confined geometries. One mechanism by which active suspensions can produce unique responses is through coordinating their behavior using the flows they create while swimming. A number of researchers have used direct simulations or continuum theories to examine how these collective behaviors can occur due to hydrodynamic interactions. In all of these studies, the organisms are suspended in a Newtonian fluid. However, many suspensions occur in non-Newtonian environments such as saliva, mucus, or polymeric solutions added to engineer the response. We have developed a theory to include this non-Newtonian suspending fluid and used it to understand how multiple competing timescales in the system determine the response of the system. In the second part of the talk, I will discuss the results of computer simulations of swimming organisms in confined geometries and how an external flow alters the dynamics. In experiments and simulations without flow, it has been shown that swimming microorganisms accumulate near surfaces even in absence of chemical gradients or surface interactions. Using simulations, we show how this accumulation is reduced by an external flow and determine the key dimensionless group that alters the response. We also identify a dip in the swimmer concentration in the channel center for Poiseuille flow, and determine the mechanism for the dip. Finally, I will discuss the dynamics of the organisms, which impacts the beginning of biofilm formation and Taylor dispersion.

Symposium SC

Suspensions and Colloids

Organizers: Nina Shapley and Victor Breedveld

Thursday 8:40 Westmount SC42

Enhancing rotational diffusion using oscillatory shear

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Taylor dispersion – shear induced enhancement of translational diffusion – is an important phenomenon with applications ranging from pharmacology to geology. Through experiments and simulations, we show that rotational diffusion is also enhanced for anisotropic particles in oscillatory shear. This enhancement arises from variations in the particle's rotation (Jeffery orbit) and depends on the strain amplitude, rate, and particle aspect ratio in a manner that is distinct from the translational diffusion. This separate tunability of translational and rotational diffusion opens the door to new techniques for controlling positions and orientations of suspended anisotropic colloids. In addition, we also discuss the effects enhanced rotational diffusion has on suspension rheology.

Thursday 9:05 Westmount SC43

A hexatic-to-disorder transition in colloidal assembly near electrodes: Stronger flow yields less order

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Colloids are known to form two-dimensional, hexagonal closed packed (HCP) crystals near electrodes in response to electrohydrodynamic (EHD) flow. Previous work by several groups has established that the strength of the EHD flow increases as the applied AC frequency decreases, suggesting that the driving force for crystallization should increase at lower frequencies. Here we report that the HCP crystals instead undergo an order-to-disorder transition at sufficiently low frequencies, despite the increase in the attractive EHD driving force. At large frequencies (~500 Hz), monodisperse suspensions of micron-scale particles are observed to arrange into planar HCP crystals, consistent with prior work. As the frequency is decreased below approximately 250 Hz, however, the crystalline structure transitions to randomly close packed (RCP) with an orientational order parameter of significantly less than one. The transition is reversible and second order with respect to frequency, and independent measurements of the EHD aggregation rate confirm that the EHD driving force is indeed higher at the lower frequencies. We present evidence that the order-disorder transition is instead caused by an increased particle diffusivity associated with a corresponding increase in the particle height over the electrode induced at lower frequencies. The observations reported here thus represent a rare instance of an electrically tunable HCP-to-RCP transition, with broad implications for the use of time-varying frequencies to facilitate annealing of planar colloidal crystals.

Thursday 9:30 Westmount SC44

The electrorheology of suspensions containing interfacially active constituents

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We show that the addition of small quantities of nanocage sulfonated polyhedral oligomeric silsesquioxanes (s-POSS) at concentrations of 1-3 wt% to mixtures of sulfonated polystyrene in silicone oil increases the yield stress by over 200%, with the addition of s-POSS. The addition of the interfacially active s-POSS, is shown by the dielectric relaxation studies to cause a new relaxation peak in the s-POSS/s-PS/PDMS system that is absent in the s-PS/PDMS suspension. The dielectric relaxation studies indicate that the s-POSS and s-PS form a core-shell structure. This class of ER-fluids, based upon our results, with the shell layer formation due to adsorption, is sensitive to the properties of the core (s-PS) and to the adsorbed shell layer. Current theory suggests that the ER effect would largely be determined by the dielectric and conductive properties of the conductive layer of core/shell particles in ER suspensions; however, our results suggest that both the properties and concentrations of the core and the shell in response to the applied field affect the stresses of these systems within an applied electric field.

Thursday 10:25 Westmount SC45

Inertia and damping in models of jammed soft-particle suspensions

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Suspensions of soft particles exhibit a remarkable bifurcation at the random close packing volume fraction, f_c. There is a yield stress above f_c but not below, and the flow curves at various f have been shown to collapse onto a universal scaling function near this point [1]. Particle-level models take contact deformation into account to model elastic forces and treat the drag forces – in the very dense regime where long-range hydrodynamic interactions are thought to be negligible – with varying levels of sophistication: from pair-drag formulations that apply a lubrication calculation to the film at contact [2] to simple "mean drag" approaches where the mobility matrix is diagonal [3]. We show that, in simple shear, the pair-drag and mean-drag approaches give consistent results for the shear modulus, yield stress, and single-particle diffusivity as functions of f but only in the quasi-static regime. They show dramatically different behavior in the rate-dependent regime. In particular, the diffusion constant scales as the shearing rate to a non-trivial power with the power depending on the damping mechanism. Furthermore, we explore a "granular" regime where the inertia of the particles is no longer negligible and show that while the quasi static behavior is consistent with the various over damped models, the finite rate behavior shows a complex interplay between inertial and dissipative timescales.

[1] Microfluidic Rheology of Soft Colloids above and below Jamming. K. N. Nordstrom, E. Verneuil, P. E. Arratia, A. Basu, Z. Zhang, A. G. Yodh, J. P. Gollub, and D. J. Durian. Phys. Rev. Lett. 105, 175701 (2010). [2] A micromechanical model to predict the flow of soft particle glasses. Seth, J. R. and Mohan, L. and Locatelli-Champagne, C. and Cloitre, M. and Bonnecaze, R. T. Nature Materials 10 p.838 (2011). [3] Foam mechanics at the bubble scale. Durian, DJ. Phys. Rev. Lett. 75. p.4780 (1995).

Thursday 10:50 Westmount SC46

Shear induced diffusion in colloidal glasses

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The long-time, out-of cage, diffusion in concentrated suspensions is slowing down as the glass transition is approached, while inside the glassy state out-of-cage motions are practically frozen. The application of shear (steady or oscillatory) beyond a critical yield strain introduces irreversible particle rearrangements leading to shear-induced melting of the glass. Here we report on such shear-induced particle dynamics in hard sphere glasses under steady and large amplitude oscillatory shear using Brownian Dynamics simulations and experimental Light Scattering echo coupled with rheometry. The long-time shear induced diffusion is determined at different volume fractions and shear rates (in steady shear) or strain amplitudes and frequencies (in oscillatory shear). Two distinct regimes are revealed in terms of the microscopic particle dynamics. At low rates (or frequencies) shear-induced out-of-cage motions are triggered by Brownian activated diffusion, while at high rates they are related with collision induced diffusion. The diffusivity follows a linear increase with shear rate in the collision induced high rate regime, while in the low rate, Brownian activated regime, exhibits a sub-linear power law dependency. This power law exponent is found to increase towards one with volume fraction. Finally, at steady state and high shear rates a super-diffusive response is revealed, between the short-time (in-cage) and long-time (out-of-cage) motion, indicating a continuous process of cage breaking and restructuring under shear.

Thursday 11:15 Westmount SC47

Slow relaxation and dynamics in soft particle glasses

Lavanya Mohan[1], Michel Cloitre[2], and Roger Bonnecaze[1]
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Soft particle glasses like concentrated microgel suspensions exhibit slow dynamics due to their highly jammed nature. We perform experiments on microgels to determine their stress relaxation behavior on flow cessation and observe that unlike viscous liquids the stress in these materials does not vanish on flow cessation and instead there is a quick initial relaxation after which the material gets trapped with an internal stress which relaxes slowly and this stress is smaller for larger preshear stress. We propose a universal scaling for this internal stress with the initial elastic stress in the system based on results from microgels with different constituent properties. Further, we also use particle scale simulations to understand the micromechanics of this stress relaxation process after validating them by comparison to experimental data. The relaxation occurs through local facet rearrangements and the number of contacts and average compression return to the static values during the quick initial relaxation but the asymmetry in the microstructure remains as a signature of the internal stress. Radial rearrangements occur quickly but angular rearrangements are slower as they require collective motion due to the jammed nature of these materials. The effect of the internal stress in these materials can have important consequences for experiments performed on stressed samples and we illustrate this through aging experiments on microgels at zero stress and zero shear rate.

Thursday 11:40 Westmount SC48

Dispersant and thermal rheological fluid function of side-chain crystalline block co-polymer

Shigeru Yao[1], Toru Okuma[1], Satoshi Ichikawa[2], and Daisuke Tatsumi[3]
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Recently, we polymerized a block copolymer that was constructed of side-chain crystalline monomer and a solvent-compatible monomer, which we referred to as a side-chain crystalline block copolymer (SCCBC). This SCCBC has a specific melting point. We found that this SCCBC was adsorbed onto polyethylene (PE) particle by via supramolecular interaction. In addition, through this supramolecular interaction, the SCCBC acts as a good dispersant for a concentrated PE particle dispersion. In the case of the concentrated small high density PE particle dispersion system (diameter is 7.4um), that is dispersed 40wt% of PE particle in acetic acid n-butyl ester, the viscosity has decreased from 1340mpa to 0.6mPa (about 0.5% of the original value). And also the viscosity of this dispersion shows reversible temperature dependence of viscosity, that with increasing temperature, the viscosity increases to almost the original value of the dispersion without the dispersant. This phenomenon can be named as "Thermal Rheology".

Thursday 12:05 Westmount SC49

Thixotropic rheological behavior of Maya crude oil

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Heavy oil and bitumen exhibit non-Newtonian rheological behaviors at lower temperatures. Thixotropy is one such behavior. Thixotropy affects the efficiency and length scale of mixing during blending operations, and flow behaviors in pipes and pipelines following flow disruption where it affects the pressure required to reinitiate flow. In the present work, thixotropic behaviors of Maya crude oil are explored systematically using a stress-controlled rheometer. Maya crude oil is shown to be a shear thinning fluid below 313 K. The thixotropic behaviors are identified and explored using transient stress techniques (hysteresis loops, step-wise change in shear rate, start-up experiments). The magnitude of the thixotropy effect is larger at lower temperatures. Relationships are identified between rest times and other thixotropic parameters such as hysteresis loop area and stress decay in start-up experiments. Stress growth, which occurrs as a result of a step-down in shear rate, is shown to correlate with temperature. The results also provide a benchmark data set for validation of rheological models for heavy oil that are immerging in the literature. Keywords: Heavy oil, thixotropy, viscosity, shear history, rest time.

Symposium GS

Gels and Self-assembled Systems

Organizers: Jai Pathak and Matthew E. Helgeson

Thursday 8:40 Verdun/Lachine GS19

Microrheological characterization of cell-mediated hydrogel degradation

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There is a growing interest and major benefit of hydrogel matrices that can be remodeled by a cell during migration in applications such as wound healing, tissue engineering and stem cell culture. In order to effectively design these scaffolds an in depth knowledge of how a cell senses and remodels the pericellular region, region directly around the cell, is required. Despite this, microenvironmental changes during the degradation of a synthetic hydrogel scaffold remain poorly understood. To characterize synthetic scaffold microenvironments, we have combined passive microrheological measurements, multiple particle tracking microrheology (MPT), with three-dimensional cell encapsulation to measure the dynamic environment cells create prior to and during migration. MPT measurements directly relate the Brownian motion of probe particles embedded into a fluid to rheological properties, such as creep compliance, diffusivity and viscosity. This technique combines rheological measurements with optical techniques, enabling visualization of the microenvironment and quantification of dynamic material properties during cell mediated degradation, remodeling and migration. We measure the evolving microstructure of a photopolymerizable matrix metalloproteinase (MMP) degradable poly(ethylene glycol) (PEG) norbornene gel during controlled enzymatic and human mesenchymal stem cell (hMSC) mediated degradation. MPT measurements precisely characterize the gel-sol transition, microenvironment heterogeneity and hydrogel microstructure during these dynamic processes. The versatility of this hydrogel system enables an in depth, systematic study of how cell motility is affected by chemical cues and physical cues, such as inhibition of MMP secretion and myosin II and porosity of the network, respectively. Combining MPT with 3D cell encapsulation enables the characterization of the time scale and spatial properties of the evolving scaffold during cell motility.

Thursday 9:05 Verdun/Lachine GS20

Control over the structure of conjugated polymers through kinetics of self-assembly

Pablo de la Iglesia, Gregory Newbloom, and Danilo C. Pozzo

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Rheological, small angle neutron scattering (SANS), and dielectric measurements are used to characterize the gelation of poly(3-alkyl-thiophene) (P3AT) and poly(9,9 dioctyl fluorene) (PFO) in organic solvents. The effect of supersaturation over the system's structure and properties is quantified. Supersaturation is controlled by using a range of temperatures and solvent quality. Solvent quality is modified by mixing two miscible organic solvents: dodecane (poor solvent) and o-dichlorobenzene (good solvent). The mechanical, electrical, and structural properties of the gels are characterized under different conditions. Rheological studies reveal a strong dependency between the level of supersaturation of the system and the gelation kinetics. Fits using the Avrami crystallization theory reveal a change in the dimensionality of the networks as the driving force for gelation is varied. SANS experiments also give valuable insight into the conformation of the polymer assemblies over several length scales. The scattering profiles reveal a dependency between the size of the network aggregates and the supersaturation of the system, without significantly changing the building blocks. The system's evolving conductivity is also probed during gelation. The electrical behavior of the systems shows that structural conformation of these networks is a key parameter in varying the charge transport along organogels. This study demonstrates the possibility of controlling network structures in conjugated polymers by changing the driving forces that are used for aggregation, making possible to optimize the structure and properties of organogels for specific applications.

Thursday 9:30 Verdun/Lachine GS21

Predicting tack response of crosslinked and uncrosslinked gels using fractional constitutive equations

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Pressure Sensitive Adhesives (PSAs) are widely used in industrial applications and daily life. A commonly-used test to determine adhesive performance is the tack test. The kinematics of the test are identical to a 'reverse squeeze flow' in a filament stretching device with a very small initial gap. Under these imposed kinematics, a lubrication analysis is appropriate, and most of the adhesive strength comes from the peak force generated in this initial lubrication regime. It is therefore important from a design standpoint to be able to quantitatively predict the evolution in the total tensile force generated in a tack experiment. PSAs are commonly made from chemically and physically cross-linked gels that have

multi-scale microstructures and exhibit power-law responses in canonical rheological experiments such as Small Amplitude Oscillatory Shear (SAOS). Fractional calculus models have been proven to be especially well suited for modeling the rheological response of power-law materials. In this work, we use the fractional Kelvin-Voigt model (FKVM) to characterize the linear viscoelastic response of a commercially available flurosilicone gel. We then couple the FKVM with the lubrication solution obtained upon solving the squeeze flow problem. Using this coupled model we show how we can predict a priori the tensile stress growth for low to moderate strains during a tack experiment. Particularly, we capture the measured power-law scalings with time and and show how it is directly related to the SAOS response. We next demonstrate how the nonlinear strain-hardening response of the gels at large strains can be captured using the Gent constitutive model for rubber-like materials. Finally we extend the analysis to uncrosslinked materials such as Xanthan gum using a fractional Maxwell equation and predict the power-laws seen in squeeze flows under constant velocity and constant strain-rate conditions.

Thursday 10:25 Verdun/Lachine GS22

Impact of dispersed nanoparticulate material on the gelation of thermoreversible block copolymer solutions

Lynn Walker, Vicki A. Cheng, and Melissa M. Dao

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Self-assembled block copolymer templates are used to control the nanoscale structure of materials that would not otherwise order in solution. In this work, we have developed a technique to use close-packed cubic and hexagonally-packed cylindrical mesophases of a thermoreversible block copolymer (PEO-PPO-PEO) to impart spatial order on dispersed nanoparticles and globular proteins. The thermoreversible transition from fluid phase to a soft solid is a distinct increase in the modulus of several orders of magnitude over a narrow temperature range. The frequency dependence of the rheology through the transition is characterized to determine the nature of the transition and the impact of system variables (composition of dispersed phase, block copolymer type and ramp rate). This is modeled in the context of gelation to better understand the mechanical state of the soft materials. The impact of shear on structure through the transition is also characterized rheologically and structurally.

Thursday 10:50 Verdun/Lachine GS23

Formation of interconnected morphologies of symmetrical block copolymer/nanorod comoposites under cylindrical confinement: A coarse-grained molecular dynamics study

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Our recent experiment and simulation on confined self-assembly of block copolymer (BCP)/nanoparticle (NP) composites in electrospun nanofiber have proven to be a useful guidance for fabrication of the composite materials with ordered nanostructures. Specifically, we have examined how nanoparticle presence can influence the formation of very different asymmetrical BCP morphologies under cylindrical confinement when compared with that of pure asymmetrical BCP, both qualitatively and quantitatively. Using the same coarse-grained molecular dynamics tool, we have further extended our study to self-assembly of nanorods with BCP under cylindrical confinement. Unlike nanoparticles, nanorods can readily be interconnected with each other, and also induce asymmetrical BCP morphologies at much lower loading that nanoparticles do. Such interconnected nanorods, when incorporated within nanofibers, have great potential to provide highly conductive pathways for energy applications, such as battery electrodes and separators. Symmetric BCP under cylindrical confinement with nanorod aspect ratio of 1, 5, and 10 are examined with three different types of nanorod-BCP attraction: a) neutral nanorod, b) A (wall-attractive phase)-attractive nanorods, and c) B (wall-repulsive phase)-attractive nanorods. As one may have expected, much less loading of longer nanorods are required to observe formation of radially and axially interconnected nanorods within the cylinder. The interconnected nanorods often, but not always, induce asymmetrical BCP morphology as well. From this trend, we were able to extract a dimensionless parameter, D/N, or the polymer domain diameter over the nanorod aspect ratio, to be correlated to the onset of nanorod interconnectivity and formation of asymmetrical BCP morphology. By developing a phase diagram with respect to D/N, one can predict the formation of desired BCP morphology and nanorod connectivity and placement within cylindrical confinement.

Thursday 11:15 Verdun/Lachine GS24

Rheological expression of clay self-exfoliation in a polymer nanocomposite

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Dynamic mechanical spectroscopy and small angle x-ray scattering (SAXS) were used to monitor the structural development of a clay/polymer nanocomposite during self-exfoliation at varying temperature levels. Upon mixing organo-clay powder aggregates into end-functionalized polybutadiene, the aggregates break up into individual clay particles (stacks of clay sheets) and, finally, separate into individual clay sheets (which consist of three layers: an aluminum rich center interposed between two layers composed of silicon, hydrogen, and oxygen) to form a nanocomposite of randomly oriented clay sheets in a polymeric matrix. This very effective "self-exfoliation" mechanism was discovered in 2004 but its origin is still not definitively known. The exceptionality of this mechanism lies in the observation that it occurs rapidly and without requiring shear or sonication. As the clay exfoliation proceeds and the clay surface accessible to the polymer increases, polymer molecules and clay connect into a sample-spanning network, a physical gel, with increasing modulus and decreasing relaxation times. Thus, small amplitude oscillatory shear (SAOS) is a sensitive probe for the evolving structure and is chosen here for exploring the exfoliation dynamics. With SAOS, a maximum rate of exfoliation was found at intermediate temperatures. SAXS enabled direct observation of the increasing spacing between clay sheets. Results from SAXS agreed with results from SAOS in that the clay sheet spacing rapidly increased. The results were analyzed with regard to several previously proposed mechanisms of exfoliation and some inconsistencies were found. Alternative exfoliation mechanisms are therefore hypothesized to fully explain the SAOS and SAXS data.

Thursday 11:40 Verdun/Lachine GS25

A continuum mechanical model for instability of discoidal high-density liproproteins

Mohsen Maleki and Eliot Fried

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Lipoprotein particles are responsible for packaging and transport of cholesterol in the body. In reverse cholesterol transport (RCT), high-density lipoprotein (HDL) particles scavenge cholesterol and deliver it to the liver for excretion. A comprehensive study of the biophysical basis for the vasculoprotective functionalities of HDL particles is crucial for developing effective tools to control atherosclerosis. During RCT, an HDL particle undergoes various shape transitions, varying from nascent discoidal to mature spheroidal, accompanied by changes in the conformation of its apolipoprotein building block apoA-I. A discoidal HDL particle consists of a lipid bilayer bound by an apoA-I chain. Consistent with experimental observations, molecular dynamics (MD) simulations predict intermediate nonplanar, twisted, saddle-like conformations for discoidal HDL particles. We present a continuum mechanical model for a discoidal HDL. In accord with models of biomembranes, the lipid bilayer is treated as two-dimensional fluid film with surface tension and Canham-Helfrich bending energy density. The apoA-I chain is modeled as an inextensible twist-free elastic filament with bending resistance. Using the second-variation condition, the linear stability of a discoidal HDL is explored. Based on the existing values of the salient physical parameters, we obtain a stability diagram. The results reveal that in the first planar and transverse unstable modes, a discoidal HDL adopts planar elliptic and nonplanar saddle-like surfaces. These observations are consistent with experiment measurements and MD simulations.

Thursday 12:05 Verdun/Lachine GS26

Microstructural evolution of a polymer-like micellar solution during shear start-up and cessation

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Surfactant polymer-like micelles (PLM) exhibit shear banding (SB) over a wide range of shear rates in their steady state flow curve. Of great practical and basic scientific interest is the transient non-linear rheological behavior occurring at the start-up of shear flow leading to SB. Prior investigations have elucidated many aspects of the onset of shear banding. However, to date, there is no explicit quantitative information on the state of alignment and orientation of PLMs during transient flow. To address this, we developed a new time-resolved scanning narrow-aperture flow small angle neutron scattering instrument that allows us to probe microstructural changes with time resolutions on the order of tens of millisecond. We present the first time-resolved SANS measurements in the velocity-gradient (1-2) plane of the microstructure of a model, shear-banding PLM solution (CpCl:NaSal, 2:1 molar ratio with 0.5 M NaCl in D2O) during flow start-up and cessation. We identify four stages of flow start up: an initial elastic response with minor micelle alignment for time-scales shorter than the breakage time, a homogeneous alignment throughout the gap that persists for approximately three average relaxation times, followed by a splitting into a highly aligned band and a nearly isotropic band, which reaches steady behavior after approximately two times the reptation time. Flow cessation is also non-trivial, exhibiting an initial fast relaxation, believed to be due to an initial reconformation of the micelles, followed by a slower relaxation of the aligned state, before an isotropic quiescent state is reached. These results provide new insights into the physical mechanisms underlying shear banding and other transient phenomena in related viscoelastic fluids, as well as providing critical tests of constitutive models for polymer-like micelles.

Symposium MB

Polymer Melts and Blends

Organizers: Savvas G. Hatzikiriakos and Michael Mackay

Thursday 8:40 Outremont MB42

Silica/poly (2-vinyl pyridine) nanocomposites: Segmental dynamics of polymers and the nanoparticle network

Shushan Gong[1], Joseph F. Moll[2], Quan Chen[1], Sanat K. Kumar[3], and Ralph H. Colby[1]

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The addition of nanoparticles can tremendously change some physical properties of polymers, enabling many applications, such as automotive coatings (mechanical property), electronic devices (electrical property), and packaging (gas barrier property). In recent studies, three filler-polymer interaction mechanisms have been proposed to explain those physical changes; agglomeration, nanoparticle network, and interfacial bound polymer layer. Here, we used transmission electron microscopy (TEM), dielectric relaxation spectroscopy (DRS), and rheology to study this interaction in our silica/poly (2-vinyl pyridine) nanocomposite system. Nanocomposites are prepared by solvent casting, with pyridine added to charge-stabilize silica nanoparticles in solution and thus help to disperse the particles. TEM is used to probe the silica nanoparticles'

dispersion state, while DRS and rheology are used to study the segmental dynamics and entanglement of polymer chains. The role of bound polymer layer in the polymer-particle network will be quantitatively discussed.

Thursday 9:05 Outremont MB43

Rheological properties of polypropylene incorporating nanocrystalline cellulose

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In this work, rheology was used as a complementary characterization tool to evaluate nanocrystalline cellulose (NCC) dispersion in polypropylene (PP). Rheological measurements including linear and non-linear viscoelastic tests were performed on PP/NCC samples. Small amplitude oscillatory (SAOS) tests showed substantial increase in complex viscosity and loss and storage moduli of PP samples with a high level of NCC dispersion. However, both linear and non-linear behavior of PP did not change for samples with poor NCC dispersion. The effect of NCC concentration was also investigated for samples with high level of NCC dispersion. Below the rheological percolation, improvement in rheological properties was attributed to the high specific area created by NCC dispersion. On the other hand, rheological properties were controlled by the presence of a 3-D network of NCC nanoparticles above the percolation threshold.

Thursday 9:30 Outremont MB44

Role of small chains in interfacial slip of linear polymer melts

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We have characterized the interfacial slip of monodisperse and bidisperse linear polybutadiene samples sandwiched between coated-glass and silicon-wafer in steady-state planar Couette flow using tracer particle velocimetry and confocal microscopy. We examined several narrow-distributed polybutadiene samples (PI < 1.11) with molecular weights in the range of 3 to 107 kg mol^{-1} (all above the entanglement molecular weight of polybutadiene M_e ~ 1.8 kg mol^{-1}) as well as bidisperse samples of different compositions. Experiments were carried out at shear rates over the range of ~ 0.1 - 10 s^{-1} and slip velocity, slip length and critical shear rate for the onset of strong slip were determined. Results showed that small chains play an important role in the interfacial slip and flow dynamics of linear polymers. While none of monodisperse samples exhibited perceptible interfacial slip, significant slip was observed for bidisperse samples containing small chains. This was attributed to their reduced interfacial coefficient of friction which is likely a complicated function of the nature of entanglement and chain adsorption at the interface. Furthermore, a small deviation from linearity in the velocity profile of all samples containing 107k chains was observed violating the commonly-assumed homogenous shear profile in planar Couette flow.

Thursday 10:25 Outremont MB45

Analysis of helical instability in film blowing process

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In film blowing process, the draw resonance and helical motion of bubbles are typical instabilities. The draw resonance, one of the Hopf bifurcations, as in the other extensional deformation processes, is definitely characterized by the periodic oscillation of state variables such as bubble radius and thickness beyond critical onsets. Unlike other extensional deformation processes, however, forming a film bubble with large blow-up ratio may lead to helical motion, which rotates around the steady-state bubble axis with a constant period and considerable eccentricity. In this study, film blowing process experiments have been conducted using polyethylene resins (LDPE, LLDPE, HDPE) with different extensional features to establish stability windows and to investigate the effect of process conditions on the helical motion. The experimentally observed results qualitatively agreed with marginal curves demarcating stable state from helical and draw resonance instabilities, which were predicted by the simple film blowing model with the combination of the concept of buckling. In the helical instability regime, the experimental results demonstrated that rotational periods of helical motion became shorter and eccentricity representing the extent of deviation from the bubble axis became larger as the bubble radius (i.e. high BUR) increased. However, this tendency of helical motion decreased with increasing draw ratio due to the increased flow-directional force.

Thursday 10:50 Outremont MB46

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

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Polypropylene (PP) has a rather weak melt strength and, when foamed, this often results in fracture of thin parts, especially through bubble coalescence and rupture. This can be partially overcome via the increased strain-hardening behavior brought about by using long chain branched PP (LPP). This not only improves the resistance to deformation of thin parts during processing, but it also tends to prevent bubble coalescence in the bubble growth process. Therefore, it is important to optimize the rheological properties of the PP resins in order to deliver good foam products, with well-controlled cell type, size and density. In this work the influence of long chain branching on the rheology, the foaming

behavior, the morphology, and the mechanical properties of the micro-layered PP/PP foams is investigated. Two different types of LPPs are used and named as LPP-1 and LPP-2. The nucleating agent used was talc micro-particles. LPP-2 shows noticeable changes with the talc content in shear rheological properties between 1.0 and 1.5 wt% while LPP-1 shows no significant changes with particle content. Although both LPPs show strong strain hardening behavior with Trouton ratios well in excess of 3 at all extensional rates, regardless of talc content, LPP-2 is more strain-hardening. 16 and 32 alternating foam/film layered structures are fabricated with both materials, and while the strain-hardening of LPP-2 leads to the well-defined layers and non-coalesced bubble structure, the relatively weak strain-hardening of LPP-1 causes bubble collapse and layer rupture. Similarly, the cell density and mechanical properties of the LPP-2 layered film foams increase with increasing number of layers, whereas those of LPP-1 decrease.

Thursday 11:15 Outremont MB47

Die drool theory

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When molten plastic is extruded from a die, it sometimes collects on the open face of the die. Known as die drool, this phenomenon costs plastics manufacturers by requiring die cleaning. This has been attributed to many causes, but none of these has led to an equation for the drool rate. In this work we provide an exact analytical solution for the drool rate, and we base this solution on a postulate of a cohesive slip layer near the die walls. We thus attribute die drool to cohesive failure within the fluid at an internal surface where the fluid slips on itself. We adimensionalize the drool rate with the production rate, and call this the build up ratio, BR. We provide an exact analytical solution for BR when the cohesive slip layer either slips at the die wall, or when it does not. We examine two important extrusion geometries: slit (which we then extend to pipe) and tube flow. We identify two new experiments: one to measure BR as a function of pressure drop, and another, as a function of the die aspect ratio, and we then use our new theory to design droolometers.

Thursday 11:40 Outremont MB48

On negative pressures reported in modeling of rotating polymer melt processing machinery

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Meaningless negative pressures are frequently reported in the scientific literature obtained from flow simulations (usually fully 3D), involving twin screw extruders and other types of rotating polymer melt processing machinery, sometimes even lower than - 500 kPa. Some authors simply report such pressures without commenting on their significance. Others simply state that the determination of negative pressures is of no consequence and only the pressure gradients really matter. Some other authors associate the negative pressures with the no-melt regions of starve-fed extruders, and they usually locate the melt/air interface along the lines where the pressure drops below zero. However, from simulations of lubricated journal bearings, it has been known for a long time that negative pressures are determined as a result of single fluid modeling in expansion flow regions and they are associated with cavitation phenomena, when the pressure drops below the vapor pressure. There appears to be a dichotomy between those modeling twin screw extruders and those modeling lubricated journal bearings, with the former failing to acknowledge that single fluid modeling in unsatisfactory for modeling of expansion flow regions in rotating machinery. Raising the base pressure level may remove the negative pressure values, but this is no universal cure for twin screw extruder modeling, because these machines are usually operated at low pressures, with good possibility of pressure dropping below the vapor pressure of trapped gases and additives included in molten polymers. This cast doubts on the validity and accuracy of numerous publications and their usefulness in scale-up procedures. Improved modeling is called for, with consideration of the negative pressures determined from single fluid simulations.

Thursday 12:05 Outremont MB49

Compressional flow accelerates interfacial reactions between nylon-6 and polyethylene-graft-maleic anhydride

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Layered polyethylene/nylon-6 materials are commonly employed in food packaging for their remarkable oxygen and water barrier properties. However, adhesion between these incompatible polymers is crucial for mechanical and barrier integrity. Previous literature has shown that addition of small amounts of polyethylene-graft-maleic anhydride (PE-g-MA) improves adhesion by reacting with the terminal amine on nylon-6, creating a graft copolymer in situ. This process is known as reactive compatibilization, and has been employed for a wide variety of polymer systems to improve properties such as impact strength and toughness. The amount of copolymer on the interface strongly influences adhesion and mechanical properties. This work examines the effects of processing and compressional flow on interfacial reaction kinetics between nylon-6 and PE-g-MA/HDPE blends. Samples were prepared with multilayer coextrusion and compression molding, with varying degrees of compressional flow. Adhesion and copolymer conversion were evaluated using an asymmetric dual cantilever beam (crack propagation) method. X-ray photoelectron spectroscopy was utilized to corroborate conversion data. Results show a dramatic increase in reaction rate with compressional flow. Possible mechanisms for the reaction rate increase will be discussed.

Symposium NF

Non-Newtonian Flows

Organizers: Ian A. Frigaard and Vivek Sharma

Thursday 8:40 Mont-Royal/ Hampstead NF23

Dilute rigid dumbbell suspensions in large-amplitude oscillatory shear flow: Shear stress response

R. Byron Bird[1], A. Jeffrey Giacomin[2], Chuanchom Aumnate[2], and Andrew M. Schmalzer[2]
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We evaluate the simplest relevant molecular model, a dilute suspension of rigid dumbbells, in large-amplitude oscillatory shear flow. We solve for the shear stress response, and specifically, we derive explicit expressions for the first and third harmonics. We thus connect the properties of the rigid dumbbells with the shear stress response, producing new structure-property relations for the interpretation of large-amplitude oscillatory shear flow measurements. We compare our results with the corotational Maxwell model, the simplest relevant continuum model for large-amplitude oscillatory shear flow.

Thursday 9:05 Mont-Royal/ Hampstead NF24

Coarse-grain tunable dissipative particle dynamics. Part 2: Droplet dynamics in micro- and nano-emulsions

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Coarse grained (CG) simulation methods, such as CG molecular dynamics and Stokesian dynamics, are normally used to gain a better understanding of mesoscopic phenomena. Hoogerbrugge and Koelman proposed a new simulation method called Dissipative Particle Dynamics (DPD) in 1992, which has a variety of applications, including Newtonian fluids, colloidal suspensions, emulsions, and so on. The interest in microscale technologies is rapidly developing in the process industry. This has already led to the development of interesting microfluidic devices and applications. Due to the multiscale phenomena in droplet dynamics from single droplets to highly concentrated emulsions (HCE) on one hand and complexity of the problem on the other hand, there is a need for a mesoscale simulation technique to capture the right underlying physics in these systems. This makes DPD a suitable candidate, since it is capable of capturing microscopic phenomena and provide comparison to macroscopic simulations and experiments, within a reasonable calculation time compared to Molecular Dynamics (MD). We present a new DPD simulation method, whose coarse-grained level is tunable and intends to capture the physics of droplet dynamics. In particular we focus on the interplay between droplet size and the stress level in shear flows for three different combinations: Newtonian droplet in Newtonian matrix, non-Newtonian droplet in Newtonian matrix, and non-Newtonian droplet in non-Newtonian matrix. The geometrical changes in these three cases will be compared to macroscopic models and experimental results and the validity of this mesoscopic simulation will be discussed. In addition, the dependency of surface tension to droplet size in the case of Newtonian droplets in Newtonian matrix is shown and the effect of this term on the dynamics of nanoscopic droplets is discussed. For the case of non-Newtonian droplets, their dynamics is studied for polymer chains with different molecular weight and chain characteristics.

Thursday 9:30 Mont-Royal/ Hampstead NF25

The effect of nanoparticle colloidal dispersions rheology on liquid transfer during gravure printing

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Roll-to-roll patterning of small-scale features on a rapidly moving web is an industrially important process with a broad range of commercial applications both old and new. In gravure coating, an engraved roller with a regular array of shallow cavities/cells is used to pick up fluid from a reservoir and print onto a flexible substrate. In this talk we will present a combined experimental and numerical investigation into the effect that complex fluid rheology can have on the dynamics of liquid transfer from an idealized gravure cell to a flat rigid substrate. The focus of this talk will be the effect of shear thickening and shear thinning on the ink transfer process in gravure coating. The shear thickening systems used in the study are colloidal dispersions of silica nanoparticles in both PPG and aqueous PEO solutions. For the experiments, a simplified process was developed which imposes an extensional flow using a modified filament stretching rheometer in which one of the endplates is replaced by a plate containing a single truncated conical gravure cell. The deformation and stretching of the resulting liquid bridges, the motion of the contact line within the gravure cell and the total amount of fluid removed from the gravure cell will be presented as a function of the imposed stretch rate, the fluid rheology, the geometry of the gravure cell, the gravure cell configuration and the wettability of both the top plate and the gravure cell. A series of numerical simulations designed to match and extend the experimental studies will also be presented. To achieve discrete shear thickening behavior in the simulations, a simple generalized Newtonian constitutive models was constructed from Carreau-like equations. We will show that excellent agreement between the experiments and simulation was obtained. The performance of shear thickening and shear thinning nanoparticle dispersions will be compared directly to both Newtonian fluids and viscoelastic fluids studied previously.

Thursday 10:25 Mont-Royal/ Hampstead NF26

High-Deborah-number flows in microfluidic analogues of porous media

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In this work, we present numerical results for high-Deborah-number flows around a confined cylinder and through arrays of cylinders using the Oldroyd-B and Phan-Thien-Tanner (PTT) models. The numerical results were obtained using the log-conformation technique [1], in combination with a high-resolution finite volume method [2]. A wide range of flow conditions is simulated, ranging from quasi-Newtonian flows at low Deborah numbers (De), up to unsteady flow conditions at high De, under low Reynolds number conditions.

Numerical simulations were obtained up to De = 100, and a rich sequence of flow dynamic regimes was observed and mapped. Different arrangements of the cylinders in the porous media analogues were considered, and the instability was found to be significantly influenced by the topology of the arrays of cylinders. The use of these microfluidic devices as efficient micro-mixers is also discussed.

References: [1] R. Fattal and R. Kupferman, J. Non-Newt. Fluid Mech., 123 (2004) 281. [2] A. Afonso, P.J. Oliveira, F.T. Pinho and M.A. Alves, J. Non-Newt. Fluid Mech., 157 (2009) 55.

Thursday 10:50 Mont-Royal/ Hampstead NF27

Simulation of macromolecules immersed in stretching flow by dissipative particle dynamics; interpretation of response modes by proper orthogonal decomposition

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We employ Dissipative Particle Dynamics (DPD) to create a stretching flow in a domain with periodic boundary conditions. The flow features a stagnation point flow at the center of the simulation box. Test bodies, such as macromolecules, cells or vesicles, are initially placed at the stagnation point, and time records of their kinematics are recorded. Post processing is carried out with Polynomial Orthogonal Decomposition (POD), a tool commonly employed in the analysis of simulated turbulence, and adapted for particle systems (L. Grinberg, Proper orthogonal decomposition of atomistic flow simulations, Journal of Computational Physics 231 (2012), 5542). The decomposition separates the basic modes of deformation of the test body from the thermal fluctuations. The method will be illustrated with the modes of an inextensible filament over the whole range of bending resistance.

Thursday 11:15 Mont-Royal/ Hampstead NF28

Numerical simulation of extension rate in a co-rotating twin screw mixer

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Mixing is integral to food processing in incorporating ingredients, introducing air, and forming the desired structure. Previous research group work with Newtonian corn syrup has shown the importance of extensional flow in bubble size distribution and bubble break-up. This has significant impact on finished texture in baked products. Here a model power-law fluid was used with experimental values obtained from a 2% aqueous CMC (Carboxymethylcellulose) solution. The geometry chosen was the nine-paddle mixing section of a Readco continuous mixer. A fluid inflow rate of 55.31 cc/s and a mixer speed of 100 rpm were used. The 360° simulation was executed using Polyflow (ANSYS, Inc.). Rate of deformation tensor values were exported and extension rate was calculated using the second and third invariants. Extension rates were then mapped across several xy planes to see the influence of increasing axial distance from the mixer entrance. Extension rate peaks were seen at the upper and lower tips of the vertical left-hand paddles. Beyond the initial plane closest to the mixer entrance, similar maximum extension rate values were seen. Peak values were also seen near the mixer center. Areas with high shear, between the two paddle sets and between paddle tips and the barrel wall, showed maximum shear rate values. The Manas-Zloczower mixing index (λ) is often used to evaluate dispersive mixing efficiency, incorporating both rotational and elongational flow. This parameter was compared with extension rate across the mixer to see the correlation between the mixing information provided by each. Efficient dispersive mixing is predicted at λ=0.7. Peak extension rate values were seen not only at λ=0.7 but across the range from 0.4 to 0.75. Above this point, increasing elongational flow did not produce more stretching. It was found that more stretching was caused by a combination of rotational and elongational flow.

Thursday 11:40 Mont-Royal/ Hampstead NF29

Locomotion of helical bodies in viscoelastic fluids

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Many microorganisms swim by rotating one or many helical flagella, often propelling themselves through fluids that exhibit both viscous and elastic responses to deformations. In an effort to better understand the complex interaction between the fluid and body in such systems, we have studied numerically the force-free swimming of a rotating helix in a viscoelastic (Oldroyd-B) fluid. The introduction of viscoelasticity can either enhance or retard the swimming speed depending on the body geometry and the properties of the fluid (through a dimensionless Deborah number). The numerical results show how small-amplitude theoretical calculations connect smoothly to large-amplitude experimental measurements.

Thursday 12:05 Mont-Royal/ Hampstead NF30

Dynamics of a bubble raft under oscillatory compression

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We study the kinetics and dynamics of a bubble raft of slightly polydisperse bubbles subject to oscillatory compression between two parallel plates. High resolution video image is used to track the bubbles. The foam displays both elastic and plastic behaviors under stress. The bubble rearrangements are spatially correlated, an indication that local plastic events induce fragile zones of higher fluidity around its neighborhood. Investigations of the granular temperature of the bubbles between the hot (oscillating boundary) and the cold (stationary boundary) plates shows a sigmoidal gradient reminiscent of heat flow in solids. We discuss the meaning of the granular thermal conductivity of the system and its connection to fluidity.

Symposium BM

Rheology and Processing of Bio-based Materials

Organizers: Michel Huneault and James J. Feng

Thursday 8:40 Côte-St-Luc BM18

Apparent yield stress measurements of cellulose nanofiber suspensions

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Cellulose nanofibers (CNF) are processed at low solids contents (< 4 wt%) in water. Even at low solids content, CNF/water suspensions tend to have shear-thinning behavior and yield stress due to the structures that seem to form at rest. In CNF suspensions, the measurement method may influence the results because of wall slippage. Researchers are using vane geometries to minimize wall slippage effect. Through literature, some researchers have suggested some oscillatory techniques using standard geometries (parallel-plates and cone & plate geometries) to follow the yield effect on elasticity. In this work, we compare yielding and flow of CNF suspensions obtained by steady-state shear and oscillatory rheological measurements. Parallel-plate and vane geometries were utilized. In vane geometry, steady-shear studies were run in stress-controlled and rated-controlled modes. In parallel-plate geometry, tests were done in both steady-shear and oscillatory modes including “shear stress ramp”, “stress-growth”, “moduli cross-over”, and “storage modulus-strain product maximum”. The suspensions are also characterized in terms of stress growth and relaxation experiments. For suspensions lower than 3% solids, the yield stress measured different procedures are within 20%, but for high solids suspensions, differences between the methods can be as large as 100%. The difference in the results are likely due to wall-slippage: the results of steady-shear studies in parallel-plate geometry were lower than those of vane geometry or oscillatory mode. Therefore, the use vane geometry or oscillatory mode in parallel-plate geometry for high solids CNF. suspensions is suggested. The apparent yield stress increases with solids in a similar manner as compared to others.

Thursday 9:05 Côte-St-Luc BM19

The rheology of paper coatings that contain cellulose nanofibers

Findley Richmond, Albert Co, and Douglas W. Bousfield
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Cellulose Nanofibers (CNF) has the potential to be produced at low cost on site of a paper company. Some preliminary results demonstrate some potential strength improvements of these coatings, but an in-depth study is needed to overcome some of the rheological challenges of using CNF. CNF was produced at the University of Maine Process Development center using a bleached softwood kraft pulp. The CNF is concentrated to 10.5% solids through filtration and evaporation methods. Two studies were conducted in terms of addition CNF to a formulation: 1) the latex binder content is held constant with increasing amount of CNF and 2) latex levels are reduced in proportion of the CNF addition or starch addition. In all cases, the total solids of the mixtures were kept at 60% solid content. The mixtures were characterized in terms of their rheological properties with a controlled stress rheometer using parallel plate geometries in constant shear and oscillatory tests. The steady shear viscosity and the complex viscosity of the mixtures that contain CNF increase a significant amount, even when the concentration is 2 part of CNF for 100 parts of pigment (pph). This increase is larger than the increase seen with starch addition. The coatings are highly shear thinning, with power law factor of around 0.1. CNF is able to form a type of network structure that gives rise to high viscosities at low shear rates and an apparent yield stress; this is similar to what others have found for other biomass slurries. The complex viscosities are found to be over two orders of magnitude larger than the steady shear viscosities at the equivalent shear rate/frequency. This breakdown of Cox-Mertz relationship is likely due to a slip layer that forms in steady shear, giving rise to the measurement of a low viscosity. Typical coating equipment may have to be modified to handle coatings that contain significant amounts of CNF.

Thursday 9:30 Côte-St-Luc BM20

Modeling and simulation for effective solids handling of flexible fibers

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Flexible fibrous particles are widely encountered in nature and industry, e.g., plant stover, glass fiber, and paper pulp. Previous studies indicate that the deformability of the fibers has a significant impact on the properties of the bulk materials and the fiber suspensions. Here, the shear flows of flexible fibers are simulated using the Discrete Element Method (DEM) to systematically explore the effect of particle flexibility on the flow behavior and constitutive laws. In the simulations, a fiber is formed by connecting a number of spheres in a straight line using deformable and elastic bonds. The forces/moments induced by the bond deformation resist the relative normal, tangential, bending, and torsional movements between two bonded spheres. The bond stiffness determines the difficulty of particle deformation, and the bond damping accounts for the energy dissipation in the particle vibration process. The simulation results show that the elastically-bonded fiber particles have smaller coefficient of restitution compared to the rigidly connected particles. In addition, the coefficient of restitution decreases as the bond stiffness decreases and the bond damping coefficient increases. As a result, smaller stresses are obtained for the granular flows of the fibers with lower bond stiffness and larger bond damping coefficient. For the flexible fibers, besides the kinetic energy, the potential energy is also generated due to bond deformation. It is found that during shear flows at a specified shear rate, the average potential energy per fiber increases as the bond stiffness decreases and the bond damping coefficient decreases.

Thursday 10:25 Côte-St-Luc BM21

Application of poly(lactic acid) stereocomplex in modification of PLA rheological properties

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Poly(lactic acid) (PLA) is a fast growing bio-based and biodegradable polymer that has raised lots of interest recently. Despite good mechanical, optical and barrier properties, rheological properties of PLA are relatively poor and inadequate for some melt processing techniques. Due to the presence of a chiral carbon atom, lactic acid has two enantiomeric forms called L-lactic acid and D-lactic acid. This can lead to an interesting phenomenon where L- and D-rich PLA chains called PLLA and PDLA respectively, co-crystallize and form a crystal structure known as stereocomplex. PLA stereocomplex is distinguished from PLLA or PDLA homocrystals by a 50 C higher melting point, which is a considerable advantage since it lets to preserve the stereocomplex crystals in molten PLA and alter the rheological properties. Many reports exist on PLA stereocomplex formation; however, a few are dedicated to rheological investigation of this process. Therefore, PLA stereocomplexation process was studied from a rheological point of view due to sensitivity of viscoelastic properties to structural changes during stereocomplex formation. Furthermore, the role of stereocomplex as a rheological properties modifier of PLA was investigated. PDLA was melt blended in low concentrations with PLLA to produce stereocomplex. Amorphous samples were prepared and crystallization was carried out in a rheometer at high temperatures to simulate melt processing conditions. Stereocomplexation was explored over time by measuring rheological parameters in small deformation oscillatory shear mode at a low frequency using parallel plate geometry. Moreover, after the completion of crystallization, final crystalline structure was probed over a wide range of frequencies to investigate the rheological modification role of PDLA on PLLA major component. Differences in rheological characteristics of asymmetric PLLA/PDLA blends compared to neat PLLA were associated to the structural changes happened due to the formation of stereocomplex.

Thursday 10:50 Côte-St-Luc BM22

Shear-induced isothermal crystallization kinetics of linear and LCB-PLA: Impact of shear and molecular structure

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Shear-induced crystallization in semi-crystalline polymers commonly occurs in industrial processing such as extrusion and injection molding. This phenomenon prominently affects the properties of final products. Polylactide (PLA) is a bio-based semi-crystalline polymer and a sustainable alternative to petrochemical-derived products. In this work, the isothermal crystallization kinetics of linear and long-chain branched (LCB)-PLA with different degree of branching (DB) were investigated as a function of shear rate, shearing time, and crystallization temperature. PLA with different degree of LCB were produced by the incorporation of various concentrations of a multi-functional chain extender. LCB-PLAs exhibited significantly increased melt viscosity, elasticity, and melt relaxation time spectrum. The impact of shear flow and molecular structure on the crystallization kinetics was investigated. Time sweep tests were conducted at crystallization temperature Tc (130 to 140 °C), to monitor the characteristic material functions such as shear modulus (G'), and complex viscosity (η*). To examine the effect of shear rate and shearing time, the system was exposed to a constant shear rate varying from 0.1 to 5 s^{-1} for a period of time ranging from 0.1 to 10 min prior to starting the time sweep test. The results indicated that, in addition to Tc, shear rate and shearing time profoundly affect the crystallization kinetics. The induction time of crystallization, t_0, substantially decreased with both increasing shear rate and shearing time. For T_c, shear rate,

and shearing time constant, t_0 of the crystallization process was influenced by the molecular structure and DB. LCB-PLA was found to be more sensitive to shear flow than linear PLA. The long branched chains in LCB-PLA increased the nucleation rate, leading to accelerated crystallization kinetics. In addition to molecular topology, the DB content was also found to impact the shear-induced crystallization of the PLA melt.

Thursday 11:15 Côte-St-Luc BM23

A rheological study of the crystallization behaviour of PLA-reinforced crystalline nanocellulose bio-nanocomposites

Andrea M. Arias[1], Marie-Claude Heuzey[1], and Michel A. Huneault[2]
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In this study, the crystallization behavior of compounded polylactide and polylactide-based crystalline nanocellulose (CNC) bio-nanocomposites was investigated by means of isothermal experiments under steady and oscillatory shear. Test were carried out at temperatures between 110 and 140 °C. In order to better understand the effect of the reinforcement on the crystallization phenomena, this investigation was accomplished in two main steps. First, the matrix crystallization was thoroughly explored and afterwards the reinforcement role in the morphology evolution and crystallization kinetics was examined. The rheological results, carried out in parallel plate flow geometry, were correlated to SEM observations of selected samples at different stages of the sigmoidal curves. Experimental issues associated to the study of such systems are pointed out, and key parameters ensuring reproducible and accurate measurements are discussed. A complete understanding of the crystallization in nano-reinforced systems remains a challenge.

Thursday 11:40 Côte-St-Luc BM24

Plasticized chitosan/metallocene polyethylene blends: Effect of formulation on properties

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Chitosan is a biopolymer obtained through the deacetylation of chitin. It is of great interest for food packaging because of its natural origin, biodegradability, non-toxicity and mostly its antibacterial activity. This project aims at developing chitosan-based films through a melt process route and film extrusion. Since chitosan cannot be melted, its plasticisation is a promising technique for its melt processing, alone or with a thermoplastic polymer. Plasticized chitosan typically comprises water, acetic acid and glycerol. The acetic acid solution is used in the plasticized formulation to disorganize the ordered structure of chitosan and to allow glycerol to plasticize it further. In this work, various formulations were investigated based on acetic acid content in aqueous solution (0 to 5 % v/v), acetic acid/chitosan powder ratio (60/40 to 83/27 wt/wt) and chitosan powder/glycerol ratio (100/0 to 33/67 wt/wt). Plasticized chitosan was prepared in an internal mixer at 80 °C, and in a second step the plasticized chitosan was blended with a metallocene polyethylene mPE at a 50/50 (wt/wt) ratio in the internal mixer at 120 °C. Subsequently the blends were compression molded for characterization of rheological and mechanical properties. The samples were also characterized in terms of morphology and antibacterial properties. In terms of formulation, the acetic acid/chitosan ratio had the most significant effect on the rheological properties. SEM images showed that chitosan is swollen by the acetic acid solution and it results in a better dispersion of the chitosan particules in mPE in the presence of glycerol. As expected, the rheological properties were strongly sensitive to the blend morphology and confirmed the important roles of acetic acid and glycerol on the chitosan structure. Since an excess of glycerol or acetic acid deteriorate mechanical properties, the plasticized formulation needs to be optimized. Finally, all chitosan/mPE blend formulations present an antibacterial activity as opposed to neat mPE.

Thursday 12:05 Côte-St-Luc BM25

Rheological characterization of canola oil based bio-lubricants

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The general trend towards the use of high performance lubricants and environmentally friendly products supports the design of new industrial lubricants. Bio-oils, as promising growing substitutes for mineral oils, need more research to deal with new and inherited problems. Studying lubricants involves the implementation of both their micro and macroscopic aspects. This research is an effort to study industrial bio lubricants and to develop a more comprehensive approach. Different commercial canola oil based lubricants were studied using different rheological tests. For validation and comparison, engine oil, silicone oil and mineral hydraulic oil were tested. Liquid crystals are anisotropic viscoelastic materials; the combination of fluid-like flow with crystal-like anisotropy makes their phases interesting as modifiers of interfacial behavior when applied as lubricants or additives to lubricants. Therefore the effect of two liquid crystals additives on the bio- lubricant behavior was investigated. A thorough rheological characterization was performed for all the bio-lubricants and bio-lubricants added by liquid crystals using a conventional rotary rheometer. They exhibited constant viscosity at both moderate and high shear rates and shear thinning at low shear rates and temperatures below 30 oC. Frequency sweep tests revealed a significant viscoelasticity of the bio-lubricant which developed over time. Time dependence, structure recovery, gap size effect, surfactant behavior, and geometry's material influence were all investigated. The rheological characterization of different bio-lubricants revealed some important and new features associated with them.

Poster Session

Symposium PO

Poster Session

Organizers: Christopher C. White and Patrick T. Underhill

Wednesday 5:30 Salons Fontaine C-H PO1

Interpreting LAOStrain and LAOStress from the perspective of model-based framework rheology

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Towards the task of joining understanding and predictability of complex material behavior we propose a different philosophy for the interpretation of LAOS results. The methodology consists on choosing a constitutive model whose parameters are clearly and physically interpreted and using it as a framework to understand material behavior. We call this methodology Model-Based Framework Rheology (MBFR). A model can be roughly seen as a combination of basis functions and coefficients or parameters. The philosophy consists on taking the advantage of a our experience and knowledge with respect to a certain model parameter and generalize its concept to a more complex situation by relaxing the usual restriction this parameter has in the model where it was conceived and defined. The resulting analysis is born with a physical interpretation and is ready to be implemented in a different problem. The difficulty, and the strength, of this philosophy comes from finding a model framework with a reasonable degree of complexity. If the basis functions form a too simple set, then the parameters will carry all the complexity of the material. In this case it seems that is not reasonable to expect that the model will perform adequately in different conditions. On the other side of the problem, if one defines an enormous number of functions, there are lots of coefficients to be determined and it is hard to attribute a physical interpretation to these coefficients, what is not desirable also. However, an appropriate choice of the model framework provides a rich interpretation of the results and a reasonable predictiveness of the material behavior in other conditions are obtained. We propose this approach as a complement, rather than a substitution, of the previous methodologies employed in the literature. In fact we will find, whenever it is possible, how to connect one approach from the other.

Wednesday 5:30 Salons Fontaine C-H PO2

Numerical simulation of the non-isothermal re-start problem of waxy crude oils

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An important challenge of the oil production in reservoirs located in deep and ultra-deep water concerns the low temperature environment. Below the Gelation Temperature these waxy crude oils form gelled structures that alter significantly the rheological properties of the material when compared with these properties at the reservoir temperature. Non-newtonian features such as elasticity, plasticity, viscous effects, and time-dependency become present at low temperatures. The re-start of production after a shut down is an important problem faced by the oil industry. In this case the material is exposed for a long time to this environment and a cooling process takes place. As a consequence, a long portion of the tube is blocked by the gelled oil. Since in this scenario the material develops a yield stress, the pressure necessary to re-start the flow can be much higher than the one necessary to operate in normal conditions. Since the rheological properties are strongly dependent on temperature, this problem needs to consider the non-isothermal effects. The present work solves numerically the velocity, pressure, and temperature field, by considering viscosity and yield stress functions of the temperature. The Wax Appearance Temperature is used to active the non-Newtonian characters of the rheological property while an Ahrrenius type of dependency is used to compute the viscosity function for temperatures above the WAT, where the fluid is still Newtonian. In the present work, the fluid is modeled as an apparent yield stress fluid with a thixotropic behavior where the current stress level is considered the breaking agent of microstructure. A family of flow curves, depending on the current temperature and cooling rate are considered the locus of attractor points that generate the driving potential for microstructure changes. The pressure drop necessary to re-start the flow is determined for different flow/material conditions.

Wednesday 5:30 Salons Fontaine C-H PO3

Kinetic theory description and advanced simulation of evolving microstructures

Francisco Chinesta[1], Emmanuelle Abisset-Chavanne[2], and Amine Ammar[3]
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Rich and evolving microstructures can be described in a direct manner by considering all their details at the microscopic scale. However, such a description involves many computational difficulties because the extremely large amount of information that it requires. Coarser descriptions are preferred in many cases. An appealing scale of description is the one of kinetic theory, that is a nice compromise between the finest one, and the

coarsest one, the macroscopic one, in which parts and processes are described. Kinetic theory approaches require the definition and introduction of conformational coordinates able to describe the main aspects of such rich microstructures. Then, a balance equation is derived, within the framework of Fokker-Planck descriptions, that because the existence of such conformational coordinates becomes multidimensional (highly multidimensional in many cases). The solution of such models is a tricky issue in many cases, but thanks to the separated representations involved Proper Generalized Decompositions, the curse of dimensionality can be efficiently circumvented. In this presentation we explore different possibilities of kinetic theory descriptions of micro and nano-structured complex fluids.

Wednesday 5:30 Salons Fontaine C-H PO4

Different levels of approximation for the Reynolds stress tensor obtained from DNS of a FENE-P viscoelastic model in a drag reducing turbulent flow

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By analogy with the Reynolds Averaged Navier-Stokes (RANS) equations for turbulent Newtonian flows modeling turbulence of viscoelastic fluids adopting a Reynolds Average (RA) approach seems promising. There have been few attempts in the literature to derive such models, the most recent including RA conformation tensor equations. In general the Reynolds stress tensor has been modeled adopting a linear Boussinesq hypothesis, i.e. considering that this stress is proportional to the mean rate-of-strain tensor. In the present work, we investigate the representation of the Reynolds stress tensor of a viscoelastic FENE-P model in a drag reducing turbulent flow. Direct Numerical Simulation (DNS) results of a turbulent fully developed channel flow of viscoelastic fluid diluted in a Newtonian solvent are used to evaluate the Reynolds stress modeling. The highest frictional Reynolds number reached in these DNS results, is 1000, which is the order of magnitude found in some drag reduction industrial applications. We show that increasing elasticity, through increasing the Weissenberg number or increasing the fully-stretched length of the polymer molecule, deteriorates the linear Boussinesq approximation. We then propose different sets of non-linear tensorial bases that significantly improve the level of representativeness of a RA-type model. We also present a general methodology allowing to compute the scalar coefficients of such non-linear viscoelastic RA-models.

Wednesday 5:30 Salons Fontaine C-H PO5

Interface displacement in viscoelastic coextrusion: Numerical simulation

Benoit Debbaut
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In the present contribution we intend to propose a model for the simulation of interface displacement in viscoelastic coextrusion in a circular tube. The role of elasticity is examined, with a special emphasis on the second normal stress difference.

Wednesday 5:30 Salons Fontaine C-H PO7

Prediction of air bubble dispersion in a viscous fluid in a twin-screw continuous mixer using FEM simulations of dispersive mixing

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Bubble break-up was studied during mixing of a viscous Newtonian fluid in a co-rotating twin screw continuous mixer using experimental observations and finite element method (FEM) simulation of dispersive mixing. Bubble break-up was greatest with two paddle element configurations that had no stagger and a reverse stagger respectively while a third configuration with a forward element stagger showed the least break-up. The decrease in bubble break-up was found to be due to the decrease in the elongation flow density and an increase in local forward flow in the forward angle stagger configuration. Maximum stable bubble diameters and effective shear rate for break-up calculated at different locations in the mixer using the fundamental capillary number theory for drop and bubble break-up correlated well with the measured local mean bubble sizes and the mean local shear rates calculated using FEM simulations of the flow.

Wednesday 5:30 Salons Fontaine C-H PO8

Modelling the jetting of dilute polymer solutions in drop-on-demand inkjet printing

Claire McIlroy, Oliver G. Harlen, and Neil F. Morrison
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Inkjet printing has developed as a crucial technology for the accurate spatial deposition of solutions. In drop-on-demand printing individual ink drops are ejected through a nozzle. The shape of a drop upon exit is that of a nearly spherical bead attached to a long ligament. Subsequently, the ligament may catch up and merge with the main drop or breakup into satellite drops. The addition of small amounts of polymer to a solution has a significant effect on this breakup process. In particular, high molecular weight polymers can inhibit the formation of these unwanted satellite drops, but print speed may be compromised. We have developed a simplified jetting model that predicts the printability of polymeric fluids. A dilute polymer solution is modelled as a suspension of FENE dumbbells with parameters chosen to fit Zimm theory. By solving this jetting model numerically, we can determine how the maximum jettable polymer concentration varies with molecular weight. For molecules with finite extensibility L, there exists three regimes defined by the jet Weissenberg number. The jetting behaviour of each regime depends upon a critical factor that limits print speed; Wi < 1/2 is restricted by zero shear viscosity, ½ < Wi < L by viscoelasticity and Wi > L by high strain rate extensional viscosity. We compare the predictions of our model with published experimental data for two different inkjet systems: a micropipette system and an industrial inkjet print head. The jetting model gives quantitative agreement with the experimental data for jetting under micropipette conditions. For the latter case, we compare the predictions of our model with full numerical simulations. We discuss how the nozzle geometry used in industrial printing can stretch out polymer molecules inside the nozzle before ejection and thus further restrict the maximum jettable polymer concentration. In some cases, the polymer may undergo central scission due to high strain rates at the nozzle exit.

Wednesday 5:30 Salons Fontaine C-H PO9

CFD simulations of electrohydrodynamic jets of viscoelastic fluids

Marcos A. d'Avila[1] and Nicolao C. Lima[2]
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Electrohydrodynamic deals basically with the effects of an electric field on continuum media. A fluid under the effect of an electric field tends to deform due to an electric force that acts on it. The electrospinning process consists on the thinning of a polymeric jet at the end of a nozzle by the effects of electrostatic forces and, for that reason, it involves a high number of parameters. In this context, in the present work a solver was implemented on the CFD package OpenFOAM based on the leaky dielectric model in order to describe the thinning of a viscoelastic jet at the end of a nozzle. The validation of the code was made comparing the results obtained by the simulations with experimental ones for Newtonian fluids. The Giesekus constitutive equation was used to describe the viscoelastic behavior of the fluid. The results showed to be physically consistent and the model has shown to be promising for the study of electrohydrodynamic jets.

Wednesday 5:30 Salons Fontaine C-H PO10

Properties of polydisperse polymer melts subject to connfinement and flow as determined by dynamic Monte Carlo simulations

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The behavior of confined polymer melts plays an important role in many processing techniques and industrial applications. When subjected to high degrees of confinement, polymer chains orient parallel to the hard surface or interface present. This orientation subsequently affects the optical and mechanical properties of the polymer melt. In order to study confined polymer melts, a modified version of Tadeusz Pakula's Cooperative Motion Algorithm is implemented. Monodisperse and polydisperse linear homopolymers are studied between hard neutral walls on a face centered cubic (FCC) lattice. This method introduces a new way of mapping polydispersity onto a lattice based model that resembles various probability distributions allowing for the study of polydisperse polymer melts. The use of this algorithm is consistent with the known experimental facts and provides additional insight into the effects of confinement and polydispersity. Confinement reduces the Rouse time of polymer melts and while maintaining the same weight-average molecular weight, with varying degrees of polydispersity, a further reduction of the Rouse time occurs. When the polydisperse polymer melts are subject to either parabolic or shear flow their general behavior is similar to the monodisperse melts. However, at higher flow and shear rates, there is an induced migration of chains of different lengths. This induced migration broadens out the viscosity curve, serves as a method for stabilizing slip, and in some cases leads to an emergence of an infinite-shear viscosity. These simulations demonstrate the mechanisms that polydisperse polymer melts can undergo to maintain their bulk properties when subjected to high degrees of confinement, or when subject to flow, on a molecular scale that has not been previously observed.

Wednesday 5:30 Salons Fontaine C-H PO11

A study on an algorithm determining discrete relaxation spectrum

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Determination of relaxation spectrum suffers from ill-posedness problem. Hence it is impossible to obtain a unique solution by only the minimization of the sum of square error (SSE) without any constraint. However, at least for continuous spectrum, acceptable algorithms perform the minimization of SSE under appropriate constraints such as the penalty for the curvature of the spectrum. Thus, most well-known algorithms for continuous spectrum predict almost the same spectrum if the error in the data is sufficiently small.

However, in the case of discrete spectrum, there are additional degrees of freedom. Thus a number of researchers have doubted that a unique discrete spectrum is exists, even in a weak concept of uniqueness. We think that addition of more constraints on discrete spectrum may provide a systematic method to reduce the arbitrariness of discrete spectrum. As an example, we propose a constraint that a discrete spectrum should have the same shape with continuous versions obtained from acceptable algorithm. We tried to find an optimized discrete spectrum whose relaxation intensities are located on the scaled curve of the continuous spectrum obtained from fixed-point iteration algorithm. We determine the number of relaxation times at which more relaxation time does not give rise to significant decrease of SSE. For a given number of relaxation times N, we divide the interval of relaxation times into N subintervals. By use of Monte Carlo method, we seek N relaxation times at each corresponding subintervals with maintaining the relaxation intensities lies on the scaled curve of continuous spectrum.

Wednesday 5:30 Salons Fontaine C-H PO12

Stochastic motion of a pair of Brownian particles in non-adsorbing polymer solutions

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The pair interaction of colloids in polymer solutions plays an important role in many processes such as protein crystallization, molecular crowding, self-assembly of colloidal particles, and food processing. However, the relevant dynamics and transport phenomena in the colloid-polymer mixtures are not well understood. Here we present a stochastic model that describes the correlated random motion of a pair of spherical colloids in non-adsorbing polymer solutions. The pair interaction is affected by the thermal fluctuation, three-dimensional hydrodynamic interactions in inhomogeneous medium, and the entropic force owing to the polymer depletion effect. The mobility tensor is computed by the simplified two-layer model using the boundary integral method, which accounts for the momentum transport in the low viscosity layer around the colloids. The coupling of Brownian force is determined based on the computed mobility and the fluctuation-dissipation theory. Overall the attractive entropy force causes a reduction of cross-correlation and an increase of autocorrelation of the colloids. The result is relevant to the experimental analysis using optical tweezers, and represents an essential step for the ongoing dynamic simulation of many-particle behaviors in colloid-polymer mixtures.

Wednesday 5:30 Salons Fontaine C-H PO13

Rheology of linear and branched polylactides

Sahar Nouri, Charles Dubois, and Pierre G. Lafleur
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Polylactide has been the focus of many researches in recent years. Contrary to its many advantages such as good mechanical properties and compostability, there are some deficiencies associated to PLA such as slow crystallization and poor processability. Low melt strength of commercial grades of PLA as a result of their linear structure is a challenge, especially in applications requiring high melt elasticity such as film blowing process. Reactive modification of linear PLA and direct branched polymer synthesis are the two methods used to produce branched PLA. However, the first approach is limited due to the possibility of crosslinking and gel formation and lack of a real control over the final structure, while in the second method there is a higher control over the final structure of the product, no possibility of crosslinking, and flexibility in designing different molecular architectures. It is necessary to understand the relationship between the branched structure and rheological properties of PLA for melt processing applications. In this work, star shaped, comb like and hyper branched PLA were prepared by using initiators and a comonomer. Rheological properties of branched PLAs were compared to a commercial linear one. In shear mode, linear viscoelastic properties were studied; linear PLA showed a well-defined Newtonian plateau over a wide range of angular frequency while for the branched structures the transition from the Newtonian plateau to the power-law region occurred at lower frequencies and they revealed more intensified shear-thinning behavior. Based on the shear data, relaxation spectra were calculated, showing that peaks appear at higher relation times for the branched samples. Measuring extensional viscosity by an ARES showed that although the elongational viscosity of some branches were lower than the linear one but a significant strain hardening was observed for all the branched PLA while the linear material respected the linear viscoelastic behavior over a large strain range.

Wednesday 5:30 Salons Fontaine C-H PO15

Nonequilibrium work relations for dilute polymer solutions

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In this work, we present a general framework based on the Jarzynski equality that allows for the determination of equilibrium and nonequilibrium free energy landscapes of dilute polymer solutions in flow. The rheology of polymer solutions strongly depends on their equilibrium and nonequilibrium steady state properties. Using Brownian dynamics simulation in conjunction with experimental analyses, we apply our framework to individual polymer stretching trajectories in tethered uniform, planar extensional, and shear flows. In addition, we show that equilibrium properties such as polymer relaxation time and chain elasticity can be determined from a wide array of fundamental steady-state properties. Overall, connecting equilibrium and nonequilibrium properties of dilute polymer solutions provides a new platform to study the dynamics of flowing soft matter systems.

Wednesday 5:30 Salons Fontaine C-H PO16

SAXS/WAXS studies of flow-induced crystallization of poly(1-butene) in uniaxial extensional flow

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We report studies of flow-induced crystallization of poly(1-butene) in uniaxial extensional flow. Flow was produced using an SER extensional flow fixture housed in a custom built convection oven designed to provide x-ray access for in situ studies of polymer structure using synchrotron x-ray scattering techniques. Samples were loaded into the SER fixture, heated well into the melt, and then cooled to a temperature at which quiescent crystallization would be prohibitively slow. A short interval of uniaxial extensional flow was then applied, after which simultaneous wide- and small-angle x-ray scattering (SAXS and WAXS) patterns were collected to study the phase transformation kinetics and morphology of the subsequent accelerated crystallization. The degree of crystallite orientation was generally found to decrease over the course of the

crystallization. WAXS measurements yielded systematically higher degrees of crystallite orientation than SAXS. Both SAXS and WAXS gave generally consistent results for the extent of crystallization, although the SAXS invariant showed a decrease at long times that is not mirrored in the WAXS data. The impact of both deformation rate and total applied strain on the crystallization process were examined.

Wednesday 5:30 Salons Fontaine C-H PO17

Effect of chelating agent on the rheology and interfacial properties of ethoxylated surfactants and polymer systems used in chemical EOR

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In this study, the interaction between chelating agents, ethoxylated surfactants and polymers is investigated for enhancement of oil recovery in carbonate reservoirs. Surfactants and polymers (SP) are used in the enhanced oil recovery to increase the sweep efficiency by increasing the viscosity of the water and decreasing the interfacial tension between water and oil. Brine salinity has great impact on the stability of polymer, and chelating agent was introduced to minimize this effect. Different SP formulations were evaluated under different conditions of temperature and salinity. Effect of different types of surfactants and polymer systems on the rheology and thermal stability was assessed in the presence of chelating agents. The optimum conditions of salinity and temperature were determined for the given SP system. The rheology of the different SP formulations was measured to examine the influence of the saline environment on viscosity in presence and absence of chelating agents. SP systems that show the highest thermal stability and lead to the highest improvement in viscosity and the lowest values of interfacial tension was selected for further evaluation.

Wednesday 5:30 Salons Fontaine C-H PO18

Effect of electrolytes on interface induced disassembly of a self-assembled polyelectrolyte/surfactant nanoparticle complex

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In this study, we present static and dynamic interfacial properties of self-assembled polyelectrolyte complex nanoparticles containing entrapped surfactant molecules at a fluid-fluid interface in the presence and absence of different salts. Surface tension measurements correlated with microrheology studies were used to monitor the adsorption of these surfactant-like nanoparticles. Surface tension vs. time measurements of an aqueous solution of these polyelectrolyte complex nanoparticles (PCNs) show a concentration dependent biphasic adsorption to the air/water interface while interfacial microrheology data show a concentration dependent initial increase in the surface viscosity (up to 10-7 N m/s), followed by a sharp decrease (10-9 Nm/s). In the absence of salts, the PEI/SDS nanopaticles undergo a two-stage adsorption to the air/water interface. Based on these observations we propose that the PCNs at fluid/fluid interfaces exist in two states: initial accumulation of PCNs at the air/water interface as nanoparticles, followed by interface induced disassembly of the accumulated PCNs into their components. The lack of change in particle size, charge and viscosity of the bulk aqueous solution of PCNs with time indicates that this disintegration of the self-assembled PCNs is an interfacial phenomenon. Further, with addition of salts, a single stage adsorption was noted for PEI/SDS nanoparticles at the interface, even for relatively low SDS concentration. This suggests that the presence of electrolytes can enhance the surface activity properties of PEI/SDS nanoparticle system and reduce the CMC of SDS. Such systems can be used for applications requiring directed delivery and triggered release of entrapped surfactants or macromolecules at fluid/fluid interfaces.

Wednesday 5:30 Salons Fontaine C-H PO19

Effect of nanoparticle and copolymer domain geometries on the rheological properties of block copolymer nanocomposites

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Block copolymers nanocomposites are materials which may exhibit a rich variety of microstructures, depending on the molecular structure of the copolymer and on the nature and shape of the nanoparticles. When in the ordered state, the blocks are usually arranged in lamellar, cylindrical or spherical nanometer-sized domains. The addition of nanoparticle may stabilize or alter the copolymer morphology. The rheological properties of such materials are very sensitive to the morphology and to the shape and degree of dispersion of the nanoparticles. When subjected to shear, and especially extension, some domains and particles usually align with the flow, producing highly anisotropic samples. The rheological properties of such aligned materials will also be anisotropic. The interactions between the nanoparticles and the copolymers either may help or inhibit the alignment of block domains, and they may also affect the kinetics of order-order transformations. In this study we prepared nanocomposites of SEBS block copolymers containing different nanoparticles (nanoclays, carbon nanotubes and silica nanoparticles) by solution and / or melt mixing and their shear and elongational rheological properties were evaluated. The morphology of the samples was studied by small angle x-ray scattering (SAXS) and microscopy techniques. It was possible to see that the presence of nanoparticles with different geometries greatly affects the morphology and rheological properties of the materials.

Wednesday 5:30 Salons Fontaine C-H PO20

The importance of chemical structure in the extensional rheology of entangled linear polymers

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According to the tube model a polymer melt can be course-grained into three independent parameters: a tube diameter (a), the number of entanglements per chain (Z), and the equilibration time of one entanglement (τ_e). The tube model predicts that all linear polymers with the same Z have identical linear viscoelastic responses when the modulus is scaled by the corresponding plateau modulus and the frequency is scaled by τ_e. The tube model can be extended further to imply that different polymers (i.e. polymers with different chemical structures) exhibit identical normalized nonlinear rheological responses if they have the same value of Z and nonlinear parameters such as the maximum stretch ratio, λ_{max}. The goal of this study is to test the hypothesis that linear polymers with the same number of entanglements per chain give identical responses in the linear and nonlinear regimes irrespective of chemical structure. We examine the linear and nonlinear rheological responses of two monodisperse linear amorphous polymers with high glass transition temperatures in both shear and extensional flows. The two polymers examined are 290k MW linear polystyrene and 270k MW linear PMMA with Z=22. The extensional rheological experiments for PMMA are performed on an updated filament stretching rheometer, whose components and working principles will be presented in detail.

Wednesday 5:30 Salons Fontaine C-H PO21

Extensional rheology of entangled polystyrene solutions suggests importance of nematic interactions

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Local correlations in the orientation of neighboring molecules have been shown to exist both experimentally and theoretically for polymer melts, blends and networks. Such nematic interactions alter the stress-optic coefficient, but predict no change in the overall stress in long time scales in the linear viscoelastic regime. The impact of nematic effects on the extensional stress-strain response of concentrated polymer solutions has not been experimentally investigated. In this work, we consider the influence of several solvents on the linear and nonlinear rheological responses of concentrated polymer solutions in extensional flow. We prepared three polystyrene (PS) solutions with identical concentrations of the same PS sample (with the molecular weight M = 545k), but diluted with three different solvents, oligomeric styrene (OS) with M = 1k, 2k, and 4k. The three solutions have exactly the same physical tube model parameters when compared in the same, normalized time scale. Although the three solutions behave identically in small amplitude oscillatory shear flow, their behavior is markedly different in extensional flow covering large strains. The solution in OS 1k solvent is significantly more strain hardening than the solution in OS 4k under similar conditions. The experimental observations presented here directly demonstrate that the tube model and its governing parameters are insufficient to describe the nonlinear extensional behavior of entangled polymer solutions. We propose a hypothesis that the nematic interactions among the polymers and between polymer and solvent are in part responsible for the nonlinear rheological response of concentrated polymer solutions in strong extensional flow.

Wednesday 5:30 Salons Fontaine C-H PO22

Uniaxial extension of entangled polymer melts and solutions at fast rates

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Transient nonlinear responses of entangled polymers to startup deformation indicate a transition from the initial elastic deformation to irreversible deformation (flow) [1-3]. This yielding behavior varies with the applied rate: at a higher rate the entanglement network can be strained to a higher degree before its breakdown. In this work, we subject entangled melts such as polystyrene to startup uniaxial extension at even higher rates, i.e., close to the second crossover in the SAOS diagram. The objective is to explore the origin of the non-elastic contributions to the mechanical stress.

[1] S. Q. Wang, S. Ravindranath, Y. Wang and P. Boukany, J. Chem. Phys. 127, 064903 (2007). [2] Y. Y. Wang and S. Q. Wang, J. Rheol. 53, 1389 (2009). [3] S. Q. Wang, S. Ravindranath and P. E. Boukany, Macromolecules 44, 183 (2011).

Wednesday 5:30 Salons Fontaine C-H PO23

Shear-induced structures and flow instabilities

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We study the Taylor-Couette flow of a dilute micellar system known to generate shear-induced structures. We show that flow instabilities must be taken into account since both the Reynolds number and the Weissenberg number may be large. Before nucleation of shear-induced structures, the flow can be inertially unstable, but once shear-induced structures are nucleated the kinematics of the flow become chaotic, in a pattern reminiscent of the inertio-elastic turbulence known in dilute polymer solutions. We outline a general framework for the interplay between flow instabilities and flow-induced structures.

Wednesday 5:30 Salons Fontaine C-H PO24

Pressure-driven oscillatory flows of wormlike micellar mixtures

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Recent experimental results have been reported on a wormlike micellar mixture, CPyCl/NaSal in solvent, subjected to oscillatory forcings including pressure-drive oscillatory tube flow (L. Casanellas. et al. Rheol Acta, 2012). Resonance and inhomogeneities were observed in the resultant velocity profiles including an observation of shear-banded profiles. The authors followed up with a theoretical analysis using an upper convected Maxwell (UCM) model with and without Newtonian solvent. The quasilinear model is unable to capture the nonlinearities involved. A more relevant model for wormlike micellar solutions is the nonlinear Vasquez-Cook-McKinley (VCM) model which takes into account the breakage and reforming of the worms. The VCM model has been analyzed in constant pressure driven channel flow (M. Cromer et al., JNNFM, 2011) and in oscillatory shear flow in concentric cylinders (L. Zhou et al. 2010). In this poster numerical simulations of the oscillatory pressure-driven tube flow of the VCM model are presented and the results are compared with those of the experiments.

Wednesday 5:30 Salons Fontaine C-H PO25

Effect of carbon-based nanofillers on the rheological and electrical properties of polymer nanocomposites

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Nanocarbon materials have unique physical and chemical properties and are critical ingredients in emerging materials systems. In this study, carbon-based nanofillers, such as carbon nanotubes (CNTs) as 1-D nanostructure, graphene oxide (GO) sheets as 2-D and graphite nanoplatelets (GNPs) as 3-D, were introduced to compare the effect of nanofillers on the rheological and electrical properties of polystyrene (PS) nanocomposites. PS nanocomposites were prepared through the latex technology utilizing freeze-drying the suspension system comprised of monodisperse PS sub-micron particle and nanofiller. CNT and GNP were used without chemical modification in order not to deteriorate their intrinsic properties. GO was synthesized by using the modified Hummers' method from a commercial graphite. The PS/CNT nanocomposites showed enhanced rheological and electrical properties after physical dispersion with surfactant. The PS/GO nanocomposites also showed enhanced properties in spite of the decrease of electrical conductivity by strong acid treatment. However, the PS/GNP nanocomposites did not show such substantial enhancement because GNP is an aggregate of graphene layers bonded by van der Waals force between the layers.

Wednesday 5:30 Salons Fontaine C-H PO26

Prediction of viscosity behavior of n-alkanes under ambient and high pressure and temperature conditions

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Understanding of the relationship between structure and properties of hydrocarbons is a vital step in the process of improving fuels and lubricants performance. The rheological properties of short (C10-16) and intermediate (C20-40) alkanes are of particular interest as they form main constituents of fuel and lubricant, respectively. Although the environmental conditions faced by fuels and lubes in the engine can be quite different, depending on the application, both fuels and lubes can experience very high pressures and temperatures. In this work we compute viscosity of short alkanes at high temperature-high pressure condition, and viscosity-temperature relation for intermediate alkanes.

In the first part, we performed Equilibrium MD simulations to calculate the shear viscosity of n-C10 and n-C16 under ambient (298 K, 1 bar) and high temperature-high pressure (423 K, 2000 bar) conditions. We compared the results from two force fields (FFs): an all-atom (AA) and a computationally efficient united atom (UA). A quantitative agreement on the viscosity within 9% of experimental values is observed with the AA FF, while the UA FF underpredicts the viscosity values by 20-40%.

In the second part, we performed Non-Equilibrium MD simulations using UA FF to compute viscosity at two temperatures (323 and 373 K). The purpose was to obtain the viscosity-temperature relation for two different isomers of C16 and C30 alkanes. Viscosities were fitted to the Walther equation, which stipulates the double log of viscosity to be a linear function of the log of temperature. Even though UA FF underpredicts viscosity value by 30-40%, the prediction of viscosity-temperature relation is within 5% of the experimental values.

Overall, We conclude that NEMD protocol with UA force field is good to predict viscosity-temperature relations, whereas AA force field is required to make a good prediction of viscosity values. The AA representation is crucial under extreme conditions where hydrogen-hydrogen contacts are important.

Wednesday 5:30 Salons Fontaine C-H PO27

The evolving rheology of polyurethane foam during expansion

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Gas that is responsible for blowing polyurethane into foam is produced from a reaction between polyisocyanate and water, forming carbamic acid, which then decomposes to form an amine and CO_2. Polymerization occurs via a competing reaction of the polyisocyanate and polyol to form cross-linked polyurethane. As the foam expands, the rheology changes dramatically due to the increasing viscosity and elasticity of the continuous, polymerizing phase and the increase in the volume fraction of the discrete, gas phase. By studying a system formulated without water, we showed with IR spectrophotometry that the kinetics of polymerization is affected only somewhat by the presence of water, and, therefore, that this model system can approximate the continuous phase. Testing was performed with a TA Instruments ARG2 rheometer on the dry polyurethane system in order to quantify the effects of cure and temperature on the continuous phase rheology. Rheology measurements of the complete foaming system were carried out to understand the effect of gas fraction on the flow of the foam and verify whether or not the effects of the dispersed and continuous phases can be decoupled in a viscosity model. Separate experiments were conducted to determine dependence of density (gas fraction) on time and temperature, as well as to quantify the bubble sizes. Finally, the density measurements were also related to the foam rheology.

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

Wednesday 5:30 Salons Fontaine C-H PO28

Shear rheometry characterization of healing behavior displayed by a thermoreversible physically associating polymer gel subjected to shear-induced fracture

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Thermoreversible gels are solvent-filled three dimensional networks of polymer chains interconnected by physical (transient) crosslinks that are highly temperature sensitive. At room temperature, the gels studied here mechanically behave as soft viscoelastic solids. During shear inception experiments at relatively high shear rates, the crosslinks within the gel's structure are disrupted, and the gels display a corresponding overshoot in the measured stress response due to the cohesive fracture of the gel (Erk & Shull, Langmuir, 28, 4472-4478 (2012)). When the fractured gel is heated above a critical temperature (33-36C) and then cooled to room temperature, the physically crosslinked network is re-formed and the gel recovers its original elasticity. Interestingly, partial to full recovery of the fractured gel can also be achieved by room temperature aging at zero shear rate. In this study, the fracture and healing behavior of a model acrylic triblock copolymer gel has been characterized by shear rheometry at different aging times and temperatures. The extent of healing is quantified by re-fracturing an aged gel after a set aging time and comparing the original value of the stress overshoot peak with the post-aging value. By studying the fracture-healing response of this model material at different aging temperatures, the observed healing kinetics can be related with simple mathematical models to the gel's characteristic relaxation behavior and temperature sensitivity.

Wednesday 5:30 Salons Fontaine C-H PO29

Morphological and rheological properties of immiscible polymer blends based on virgin and recycled polyethylene and polypropylene

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Despite several compatibilization studies published in the literature for virgin polyethylene/polypropylene (PE/PP), very few studies with limited success are available in the case of blends of recycled origin. As expected, low mechanical performance of recycled PE/PP blends is not only caused by incompatibility between both phases, but negative influence of other parameters like contamination and polymer degradation are mostly linked to the thermo-mechanical history of the materials. All these parameters are interfering with blend compatibilization. To find out more about the effect of these parameters, small amplitude oscillatory shear (SAOS) tests were performed on PE/PP blends from both recycled and virgin origins with similar co-continuous morphologies. According to rheological results, the recycled and virgin blends show completely different viscoelastic behaviors. For example, a solid-like response at low frequencies was only observed for the recycled blends. The most probable explanation for this observation can be related to the presence of contaminants in recycled blends, especially nano-size fillers which have a tendency to accumulate at the PE/PP interface. The presence of these nano-particles was determined via transmission electron micrography (TEM) and their composition was approximated as metal oxides (pigments, fillers, etc.) via energy dispersive spectroscopy (EDS).

Wednesday 5:30 Salons Fontaine C-H PO30

A rheo-optical study of monodisperse H-polyisoprenes to delineate the nature of “strain hardening” in uniaxial extension

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One leading nonlinear response of entangled polymers with long chain branching (LCB) is "strain hardening" upon startup uniaxial extension [Laun and Munstedt (1978); Wagner et al. (2002)]. True strain hardening involves stress responses that exceed the rubber elasticity limit due to non-Gaussian stretching in the finite extensibility limit [Liu et al. (2013b)]. Our recent study [Liu et al. (2013a)] showed a first example of when such real strain hardening is possible in simple shear of LCB polystyrene solutions. In this work we use in situ birefringence to examine the uniaxial extension of model monodisperse H-polyisoprene melts and determine whether or not the so called "strain hardening" involves non-Gaussian stretching, i.e., violates the stress-optical rule.

Laun, H. M. and H. Munstedt, "Elongational behavior of a low-density polyethylene melt" Rheol. Acta 17, 415-425 (1978). Liu, G., S. Cheng, H. Lee, H. Ma, H. Xu, T. Chang, R. P. Quirk and S. Q. Wang, "Strain Hardening in Startup Shear of Long-Chain Branched Polymer Solutions," Phys. Rev. Lett. 111, 068302 (2013a). Liu, G., H. Sun, S. Rangou, K. Ntetsikas, A. Avgeropoulos and S. Q. Wang, "Studying the origin of "strain hardening": Basic difference between extension and shear," J. Rheol. 57, 89-104 (2013b). Wagner, M., H. Bastian, A. Bernnat, S. Kurzbeck and C. Chai, "Determination of elongational viscosity of polymer melts by RME and Rheotens experiments," Rheol. Acta 41, 316-325 (2002).

Wednesday 5:30 Salons Fontaine C-H PO31

Spatiotemporal structure evolution and metastable states in shear banding wormlike micelles probed using LAOS and small angle neutron scattering

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Polymer-like micelles (or wormlike micelles, WLMs) are models for understanding polymer physics as well as of technological interest across a broad range of applications ranging from enhanced oil & gas recovery to consumer products. WLMs exhibit a flow instability known as shear banding, which leads to an inhomogeneous flow and an apparent plateau in the shear stress as a function of shear rate. Models of the phenomenon are based on a non-monotonic stress constitutive relationship suggesting the existence of metastable states (M. E. Cates and S. M. Fielding. Adv. Phys. 2006, 55:7-8, 799-879). Experimental evidence for these metastable states is limited and usually inferred from transient shear rate ramp experiments. Here we demonstrate the ability of LAOS to probe the metastable states of a model shear banding WLM (6 wt% CPCl/NaSal (2:1) with 0.5 M NaCl in D2O). Experimental evidence for these metastable states is gained from shear stress and microstructure measurements made using combinations of rheometry, small angle neutron scattering (SANS) and small angle light scattering (SALS) techniques. A state-of-the-art SANS shear cell sample environment designed to probe the microstructure in the velocity-velocity gradient plane of shear (A. K. Gurnon, et al. J. Vis. Exp., in-press.) provides quantification of the shearing microstructure in terms of two parameters: an angle of orientation and an alignment factor. Predictions of the dynamic stress using the stress-SANS rule are compared to the measured shear stress of the WLM undergoing start-up and LAOS flow. For the first time, we successfully define the time-evolution of the local microstructure and corresponding stress for shear conditions corresponding to shear banding and metastable states. Complementary rheo-SALS experiments show butterfly patterns characteristic of shear-induced de-mixing. Quantitative measurements of spatiotemporal structural evolution and rheology are used to test constitutive models and learn more about the rich behavior of WLM solutions.

Wednesday 5:30 Salons Fontaine C-H PO32

Effective blending of ultrahigh molecular weight polyethylene with high density polyethylene achieved via solid-state shear pulverization

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In recent years, attempts have been made to improve the processability of ultrahigh molecular weight polyethylene (UHMWPE) by blending it with lower molecular weight (MW) high density polyethylene (HDPE) or polypropylene. These blends have the potential to result in improved impact properties and crack resistance of the lower MW polymers. Because of the enormous viscosity mismatch between components, efforts to prepare these blends via conventional melt processes have generally led to little or no dispersion, making these processes unsuitable for achieving well mixed blends. Scientific interest in these blends is associated with the study of flow-induced crystallization; in these cases blends are prepared by solution mixing, which provides effective blending but utilizes copious amounts of solvent, making this process unsuitable for scaling to industrial levels. We demonstrate our ability to achieve effective mixing of UHMWPE and HDPE via solid-state shear pulverization (SSSP), by taking advantage of its exceptional utility in achieving intimate mixing free from kinetic limitations. We present a novel method of effectively blending up to 50 wt% UHMWPE with HDPE via SSSP. Using oscillatory shear rheology, differential scanning calorimetry (DSC), and tensile testing, we analyze the effect of UHMWPE on properties of blends prepared via SSSP. Rheology and DSC data indicate that the degree of mixing between UHMWPE and HDPE domains can be increased dramatically with subsequent passes of SSSP and single screw extrusion. For blends with up to 50 wt% UHMWPE we observe only slight increases in magnitude of complex viscosity ($|\eta^*|$) at high

frequencies but major increases in |η*| with increasing UHMWPE content at low frequencies. Blends prepared via SSSP show dramatic increases in impact strength; e.g., for a 50/50 wt% UHMWPE/HDPE blend, impact strength increases by ~600 % (relative to the parent neat HDPE) after a second SSSP pass. Studies on uniaxial extensional rheology are currently underway.

Wednesday 5:30 Salons Fontaine C-H PO33

Surface transitions of macromolecules under flow

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Understanding how macromolecules with complex architecture, containing branches, blocks, co-monomers, charge, and combinations of these, is at the heart of macromolecular separations, characterization, and manufacturing. Within the nSoft consortium, a NIST-led industrial consortium composed of soft materials manufacturers, we have developed a measurement protocol for molecular surface transitions using a combination of neutron reflectivity, quartz crystal microbalance, and rheo-Small Angle Neutron Scattering. Here, we present data from protein adsorbtion/desorbtion studies under flow conditions that highlights the role of surface interactions on the stability of biofilms during flow/fill processing and transportation. We also present data extending these measurements to emerging molecules using in engineering composites and commodity plastics. Using precise measures of molecular conformation as a function of flow rate, solvent quality, and temperature, we are able to map the transitions that dictate the efficacy of leading chromatography techniques such as Temperature Gradient Interaction Chromatography (TGIC).

Wednesday 5:30 Salons Fontaine C-H PO34

Decrease in viscosity of polyisoprene solutions on addition of multi-walled carbon nanotubes

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The addition of small amounts of carbon nanotubes to a polymer matrix can result in large changes in the mechanical properties of the polymer. In this work, the rheological behavior of suspensions of multi-walled carbon nanotubes (MWCNTs) in solutions of polyisoprene (PIP) is studied experimentally. PIP is dissolved in chloroform, then MWCNTs are dispersed uniformly in the PIP solutions using an ultrasonic bath sonicator. Sonication times of many hours are required to obtain stable dispersions. We find that the viscosity of the MWCNT/PIP composite is a factor or 10 lower than that of a solution of pure PIP at the same polymer concentration, and independent of shear rate over the range studied. The viscosity decreases further as the concentration of MWCNTs increases. Small-amplitude oscillatory shear measurements show that the loss modulus of the composite is approximately proportional to ?1 at low frequencies, as predicted by the Maxwell model, while the storage modulus is too small to be measured. The observed decrease in viscosity is very unusual, and we discuss a possible mechanism.

Wednesday 5:30 Salons Fontaine C-H PO35

The influence of hydrophobic interactions on the aggregation of long semi-flexible molecules with end patches

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We used Dissipative Particle Dynamics (DPD), an explicit solvent technique to perform mesoscale simulations, to understand the effect that repulsive interactions have on aggregates' morphologies of long molecules with end-patches, such as proteins and polymers. Simulations at the mesoscale level allow us to study large complex systems that are inaccessible nowadays for atomistic simulations.

In this work, we studied long-thin and semi-flexible chains with end-patches in both sides. These included three kinds of 'beads' to represent the central section of the molecule, the end patches and the solvent. A systematic study of the effect of repulsive interactions at different concentrations was performed. We analyze systems of 10 molecules with a total number of 3 million beads per simulation.

We followed aggregation dynamics and categorized seven sub-classes, as a function of the aggregation anchor points, *i.e.* end-to-end, side by side, *etc.* We observed that small changes in repulsive interactions between the central section of the molecule and the end-patches tend to increase the frequency of 'side by side' aggregation. Similarly, small changes in the interaction parameters between the solvent and any section of the long semi-flexible molecules tend to decrease the aggregation rate.

Financial support for this research was provided by COLCIENCIAS (grant number 110152128526), the Universidad Nacional de Colombia (research grant number 15371). Computational resources for this research were provided by the Research Computing and Cyberinfrastructure unit of Penn State. *This work was supported in part through instrumentation funded by the National Science Foundation through grant OCI-0821527.*

Wednesday 5:30 Salons Fontaine C-H PO36

Start-up of steady uniaxial extension of $(ABA)_n$ multiblock copolymer systems

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Thermoplastic elastomers, such as glassy-rubbery-glassy ABA triblock copolymers, can exhibit appropriate mechanical properties for various practical applications. However, trapped entanglements and finite extensibility of the rubbery midblocks typically limit the range of deformations achievable for such materials, and longer block lengths often lead to inaccessible order-disorder temperatures, a key parameter for processing.

An auspicious solution to these problems is multiblock copolymers. Recent literature has shown that mechanical behavior, especially in steady uniaxial extension, can be greatly enhanced in $(ABA)_n$ multiblock copolymer systems over their ABA triblock counterparts [1]. Additionally, the architecture of multiblocks lends itself to accessible order-disorder temperatures [2]. In this study, we investigated the effects of polymer architecture on the start-up of steady uniaxial extension of poly(DL-lactide-*b*-ε-decalactone-*b*-DL-lactide)$_n$ multiblock copolymer systems. We varied both block lengths and volume fractions to systematically decouple their effects on extensional behavior. Various plasticizers were blended with the multiblocks with the goal to dramatically increase strain at break. Finally, we attempted to predict uniaxial extension with such models as the Edward-Vilgis model and compared to experimental data.

[1] Y. Matsumiya, H. Watanabe, A. Takano, and Y. Takahashi, "Uniaxial Extensional Behavior of $(SIS)_p$-Type Multiblock Copolymer Systems: Structural Origin of High Extensibility," Macromolecules **46**, 2681-2695 (2013). [2] L. Wu, E. W. Cochran, T. P. Lodge, and F. S. Bates, "Consequences of Block Number on the Order-Disorder Transition and Viscoelastic Properties of Linear $(AB)_n$ Multiblock Copolymers," Macromolecules **37**, 3360-3368 (2004).

Wednesday 5:30 Salons Fontaine C-H PO37

Control over the structure of conjugated polymers through kinetics of self-assembly

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Rheological, small angle neutron scattering (SANS), and dielectric measurements are used to characterize the gelation of poly(3-alkyl-thiophene) (P3AT) and poly(9,9 dioctyl fluorene) (PFO) in organic solvents. The effect of supersaturation over the system's structure and properties is quantified. Supersaturation is controlled by using a range of temperatures and solvent quality. Solvent quality is modified by mixing two miscible organic solvents: dodecane (poor solvent) and o-dichlorobenzene (good solvent). The mechanical, electrical, and structural properties of the gels are characterized under different conditions. Rheological studies reveal a strong dependency between the level of supersaturation of the system and the gelation kinetics. Fits using the Avrami crystallization theory reveal a change in the dimensionality of the networks as the driving force for gelation is varied. SANS experiments also give valuable insight into the conformation of the polymer assemblies over several length scales. The scattering profiles reveal a dependency between the size of the network aggregates and the supersaturation of the system, without significantly changing the building blocks. The system's evolving conductivity is also probed during gelation. The electrical behavior of the systems shows that structural conformation of these networks is a key parameter in varying the charge transport along organogels. This study demonstrates the possibility of controlling network structures in conjugated polymers by changing the driving forces that are used for aggregation, making possible to optimize the structure and properties of organogels for specific applications.

Wednesday 5:30 Salons Fontaine C-H PO38

Break up of macroscopic multilayer polymeric films by nucleation and growth of holes induced by inhomogeneity

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Polymeric films has found wide applications in different industrial and scientific fields. There are reasons which can trigger instabilities in these systems and lead them to break up in particular applications or processes. In this research, Break up of macroscopic, 3layer polymeric film under high temperature, in which situation all layers are in melt state, was studied. However it is well known that macroscopic films having thickness of a few micrometers are meta stable or stable, but break up of multilayer system by nucleation and growth of holes was observed. Nucleation process was investigated to be due to the inhomogeneities present in system. These inhomogeneities include of presence of microscopic ash particles which are common in non-clean room film forming conditions, containing of air bubbles or un-smooth surface of formed films. In this study nucleation initiated by air bubbles and ash particles in three layer systems is experimentally observed, moreover it was seen that in three layer system with combination of Polystyrene/Poly amide/ Polystyrene, stratified respectively on glass substrate, both of upper layers get involved in instabilities and they break up. Dewetting of macroscopic multilayer system was identical to dewetting scenario of monolayer and bilayer thin films. with exception that poly amide film dewets in a way that always is surrendered by medium of polystyrene and never touches air interface, in the other hand this behavior itself cause the upper layer to be more unstable and dewet simultaneously with Poly amide layer. Like thin films dewetting, random hexagonal shapes forms as dewetting pattern but in three layer case these patterns have additional feature which is the formation of final droplets having core-shell structure (poly amide encompassed by Poly styrene) and macroscopically are in fried-egg shape. By observation of these patterns, hope can be arise that by controlled dewetting in complex systems we can reach complex morphologies and patterns by the least possible cost

Wednesday 5:30 Salons Fontaine C-H PO39

Rheological properties of chitosan-based solutions for electrospraying and electrospinning processes

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The dynamic rheological properties of chitosan-based solutions were studied using small amplitude oscillatory shear (SAOS). The effect of chitosan concentration, acetic acid and the presence of a co-spinning agent (polyethylene oxide, PEO, molecular weight: 600kDa) was investigated. Chitosan/acetic acid solutions with a low molecular weight chitosan presented a Newtonian behavior regardless of the chitosan or acetic acid content, whilst at high molecular weight, solutions presented a shear-thinning behavior that increased with both polymer concentration and acetic acid content. In general, chitosan molecular weight had a higher impact on the shear-thinning behavior than chitosan concentration. An increase in the viscosity of chitosan solutions with acetic acid content was observed due to a hydrodynamic volume expansion of the chitosan chains as their amino groups became fully protonated. On the other hand, both PEO and chitosan/PEO solutions presented a non-Newtonian behavior. In addition, these blends presented a decrease in viscosity as the PEO content increased. In all solutions, the viscous response governed over the elastic one in the frequency range analyzed. Results from rheological measurements were correlated with processing in both electrospraying and electrospinning processes. Electrospraying could be obtained from chitosan/acetic acid solutions at low viscosity values (<1 Pa.s), while electrospinning required the addition of PEO to chitosan solutions to allow enough chain entanglements. In this case, fibers were obtained from solutions with higher viscosity values (>1 Pa.s).

Wednesday 5:30 Salons Fontaine C-H PO40

Non-hydrodynamic interactions due to block-copolymer dry-brushes affecting the coalescence rate of viscous polymeric drops

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The effect of the interfacial diffusivity of block-copolymers (BC) on the binary flow-induced coalescence of polymeric drops was investigated via boundary integral simulations, assuming Stokes flow and that the BCs act as insoluble surfactants [1]. The need to introduce and additional attractive force to match the simulations with the experimental drainage times, measured in a computer controlled four-roll mill by Leal and co-workers [2], led us to speculated that the entropic attraction between the facing drop interfaces, having the BCs in a dry-brush regime, was the main cause of this enhanced attractive force [1]. To test this hypothesis, here, we present simulations results of the effect on coalescence of this entropic attractive force, which was previously calculated via self-consistent mean field theory as a function of the distance between the drop interfaces and incorporated as a disjoining pressure in the boundary integral code.

[1] Vannozzi C "Coalescence of surfactant covered drops in extensional flows-Effects of the interfacial diffusivity" Phys. Fluids, 2012. [2] Yoon Y, Hsu A, Leal L. G. "Experimental investigation of the effects of copolymer surfactants on flow-induced coalescence of drops" Phys. Fluids 2007.

Wednesday 5:30 Salons Fontaine C-H PO41

A bio-inspired model of mechanical energy harvesting based on flexoelectric membranes

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Membrane flexoelectricity is an electromechanical coupling process that describes membrane electrical polarization due to bending and membrane bending under electric fields. In this paper we propose, formulate and characterize a mechanical energy harvesting system consisting of a deformable soft flexoelectric thin membrane subjected to harmonic forcing from contacting bulk fluids. The key elements of the energy harvester are formulated and characterized, including (i) mechanical-to-electrical energy conversion efficiency, (ii) the electromechanical shape equation connecting fluid forces-membrane curvature-electric displacement, and (iii) the electric power generation and efficiency. The energy conversion efficiency is cast as a ratio of flexoelectric coupling to the product of electric and bending elasticity. The device is described by a second order curvature dynamics coupled to the electric displacement equation and as such results in mechanical power absorption with a resonant peak whose amplitude decreases with bending viscosity. The electric power generation is proportional to the conversion factor and the power efficiency decreases with frequency. Under high bending viscosity, the power efficiency increases with the conversion factor and under low viscosities it decreases with the conversion factor. The presented theoretical results contribute to the on-going experimental efforts to develop mechanical energy harvesting from fluid flow energy through solid-fluid interactions and electromechanical transduction.

Wednesday 5:30 Salons Fontaine C-H PO42

Novel optical & microfluidic microrheometry techniques for biological complex fluids characterization

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The need for characterizing the rheological response of biological complex fluids such as proteins is increasing rapidly. This is in part due to the rapid development of protein based formulations for biotherapeutic applications. In fact it is estimated that by 2014 seven of the top ten drugs will be protein based products. Developing formulations with these biological complex fluids comes with its own set of challenges as complex specific and non-specific interactions can lead to self-association, irreversible aggregate formation. These in turn lead to issues in formulation storage stability, high viscosity and associated issues in manufacturing and injectability. Understanding and establishing the structure-property relationships in such systems and understanding interactions in complex biopharmaceutical formulations is therefore key to designing stable new therapeutic solutions and novel drug delivery mechanisms. Characterizing the rheological response in these systems is however highly challenging- available sample volumes are usually very small, the systems are weakly structured, interfacial effects are important and the samples can be quite heterogeneous with a number of different contributions to the overall rheological response. In this talk we will illustrate new developments on two fronts-(1) Microfluidic based techniques for rapid low volume viscosity measurements and (2) Dynamic Light Scattering based optical microrheology for advanced rheological characterization of the viscoelasticity and dynamics in these systems. These new developments tend to overcome some of the key measurement challenges for these systems and maybe amenable for high throughput approaches. Measurements and insights from a protein system-Bovine Serum Albumin (BSA) in addition to a number of different polymeric systems (Polyethylene Oxide, Polyacralamide/Polyacralate) will be presented. The study on the BSA system will in addition present insights into the aggregation based evolution of the viscoelastic response.

Wednesday 5:30 Salons Fontaine C-H PO44

Measuring interfacial viscoelastic properties of emulsifiers and proteins

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KSV NIMA creates value for its customers by providing advanced, innovative instruments for thin film fabrication and characterization. KSV NIMA Langmuir and Langmuir-Blodgett deposition troughs are the leading instruments for fabrication of organized monolayers and multilayer molecular structures at interfaces.

Interfacial rheology concerns the unique two- dimensional systems formed between two immiscible phases like liquid and gas or liquid and liquid. The stability of an interface depends on its viscoelastic properties, and is critical in many industries where foams, emulsions and dispersions are used. The KSV NIMA Interfacial Shear Rheometer (KSV NIMA ISR) uses a floating magnetic probe to detect the viscoelasticity of an interface. The method is highly sensitive and has been proven suitable for many different viscoelastic interfaces. The method extends the interfacial rheology measurements from not only studying absorption of macromolecules but also to study Langmuir monolayers of surface active compounds.

Here we present results on measuring the viscoelastic properties of emulsifiers and the adsorption and network formation of protein solutions to interfaces. We also demonstrate how the precise control of surface pressure during the measurement makes it possible to model natural systems like cell membranes enabling viscoelastic change measurements at the membrane level.

Wednesday 5:30 Salons Fontaine C-H PO45

Rheological control of composite hydrogels via pH tuning of mussel-inspired coordinate crosslinks

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Mussels are a family of resilient bivalves which exist in a wide variety of environments across the globe. Among the unique properties of the mussel is the ability of its byssus threads to self-heal after plastic deformation, even when severed from the live mussel. The stiff proteinaceous mussel fibers contain a significant fraction of dopamine and histidine functional groups, both of which form complexes with different transition metal ions. We present a study on hydrogels composed of functionalized 4-arm poly(ethylene glycol) as a simplified synthetic mimic of the mussel thread proteins. We show that a simple Arrhenius-type scaling law describes the mechanical response of these gels under various conditions, and that we can control the structure and response of the gels via pH tuning. Finally, we show the full spectrum of property combinations that can be achieved through composite gels of various permutations of functional group and transition metal.

Wednesday 5:30 Salons Fontaine C-H PO46

Yield stress in globular protein solutions: Insights from rheology and small-angle scattering experiments

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The rheology of protein solutions including an understanding of how protein clustering affects solution viscosity is important to solve challenges in concentrated bio-therapeutic formulations. We studied solutions of Bovine Serum Albumin (BSA, isoelectric point pI=4.95) in surfactant-free Phosphate Buffered Saline at pH=7.4, and a monoclonal antibody ("mAb", IgG1, pI=8.6) in its formulation buffer (20 mM Histidine/Histidine Hydrochloride at pH=6.0 with a sugar and surfactant). The latter solution was incubated at 40 ^{o}C for about a month to promote aggregation. The start-up of steady shear in both solutions was measured at room temperature and showed a signature of shear yielding. In 0.2 µm filtered mAb solutions the yield stress disappears. In BSA the yield stress is not always eliminated because proteins form a viscoelastic film at the air/water (A/W) interface, but monotonic dependence of the low shear rate viscosity on concentration is restored, as observed in a study with another mAb.[1] The yield stress is mostly due to protein adsorption at the A/W interface in surfactant-free BSA, whereas aggregates are responsible for yielding in surfactant-laden mAb. We have performed small-angle neutron scattering (SANS) and discerned a correlation between the yield stress and the scattering at low wavevector (q): the low q upturn in the BSA solutions persists after filtering, but it is eliminated after filtration in mAb solutions. Protein adsorption at A/W interfaces accounts for the low q upturn in SANS and the apparent yield stress of BSA. SANS shows that a reaction-limited aggregation creates aggregates of fractal dimension 2.3 that are responsible for the yield stress in aggregated mAb. The measured fractal dimension here compares well with other literature reports.[2,3]

[1] J. A. Pathak et al., Biophys. J., 2013, 104, 913-923. [2] J. Feder et al., Phys. Rev. Lett., 1984, 53, 1403-1406. [3] P. Arosio et al., J. Phys. Chem. B, 2012, 116, 7066-7075.

Research funded by MedImmune.

Wednesday 5:30 Salons Fontaine C-H PO47

Biomechanics of vitreous gel: A rheological study

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The vitreous gel is one of the major components in the human ocular globe. Despite its involvement in several pathologic and non-pathologic processes, the vitreous humor remains a very mysterious part of the eye. Several ocular diseases such as retinal tear,tractional retinal detachment, retinal edema, choroidal detachment, vitreous hemorrhage, and glaucoma can arise as a result of vitreous-related complications, which occur mostly due to the vitreous humor's macromolecular organization and viscoelastic properties. What has been missing in the current clinical application is the fundamental understanding of the link between the macromolecular organization and viscoelastic properties of the vitreous gel and its related pathologies, therapeutic treatments, surgeries. This study emphasizes methods to characterize biomechanics of vitreous gel and to correlate the molecular structure, component interactions, and viscoelastic properties of the vitreous humor to vitreous-related pathologies and surgeries. Freshly harvested porcine eyes were dissected and the vitreous was cut directly onto the rheometer plate. A stressed-controlled shear rheometer was used to obtain the rheological properties. We modeled the creep deformation of the vitreous gel using the two-element retardation spectrum model. By associating each element of the model to an individual biopolymeric system in the vitreous gel, a distinct response to the applied stress was observed from each component. We hypothesized that the first viscoelastic response with the short time scale is associated with the collagen structure, while the second viscoelastic response with longer time scale is related to the microfibrils and hyaluronan network. We also observed the same time scales in the failure analyses and oscillation experiments. Our results show that both collagen structure and hyaluronan network contribute to overall viscoelasticity of vitreous gel and therefore, both biopolymer systems must be accounted for in the process of liquefaction.

Wednesday 5:30 Salons Fontaine C-H PO48

Rheological characterization of thickening agents for dysphagia management

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On average, ten million Americans are evaluated every year for swallowing difficulties. Dysphagia is the medical term for difficulty in swallowing. Untreated dysphagia can lead to pulmonary aspiration and ultimately aspiration pneumonia due to presence of foreign material in the lungs. Thickened fluids are used to manage dysphagia. These thickening agents increase the stability of suspensions and create a weak gel structure. In this study, a series of thickening agents in varying concentrations were measured with a rotational rheometer, the Anton Paar MCR. An array of rheological techniques, including LAOS, was utilized to probe the visco-elastic response of these materials at various temperatures in the life cycle of the product.

Wednesday 5:30 Salons Fontaine C-H PO49

Hydrodynamic synchronization in rotating optical landscapes

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Hydrodynamic synchronization provides a general mechanism for the spontaneous emergence of coherent beating states in independently driven mesoscopic oscillators. A complete physical picture of those phenomena is of definite importance to the understanding of biological cooperative motions of cilia and flagella. Moreover, it can potentially suggest novel routes to exploit synchronization in technological applications of soft matter. We demonstrate that driving colloidal particles in rotating energy landscapes results in a strong tendency towards synchronization, favoring states where all beads rotate in phase. The resulting dynamics can be described in terms of activated jumps with transition rates that are strongly affected by hydrodynamics leading to an increased probability and lifetime of the synchronous states. Using holographic optical tweezers we quantitatively verify our predictions in a variety of spatial configurations of rotors [1].

[1] N. Koumakis and R. Di Leonardo, Phys. Rev. Lett. 110, 174103.

Wednesday 5:30 Salons Fontaine C-H PO50

The medium amplitude oscillatory shear (MAOS) of semi-dilute colloid dispersions - third harmonic of the suspension stress

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We study the response of semi-dilute colloidal dispersions under Medium Amplitude Oscillatory Shear (MAOS). Using an excluded annulus model of the hard-core repulsion and hydrodynamic interactions among the particles, we determine the third harmonic of the stress response of a colloidal dispersion in the pair limit while varying the relative strength of hydrodynamic forces. Importantly, the influence of hydrodynamic forces, both in magnitude and in character, on the MAOS of semi-dilute dispersions is made explicit through comparison of such nonlinear rheological properties as a function of the ratio of the hard-core to hydrodynamic radius. We show through comparison with experiments that hydrodynamic forces have a considerable effect on the microstructure and rheology of dispersions undergoing MAOS. The nonlinear, oscillatory rheology of semi-dilute suspensions is a sensitive probe of the influence of non-conservative, hydrodynamic, forces.

Wednesday 5:30 Salons Fontaine C-H PO51

Microrheology of interfacial shells formed during liquid-liquid mixing

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The flow properties of formulated products greatly determine how they are processed, packaged, and used. We are often concerned about combining multiple ingredients, each with their own distinct rheology, into a flowable composite. Ideal blending rarely occurs. Instead, mixing often generates localized structures (shells) around droplets that are much thicker than any ingredient. In the case of surfactant hydration, water can act as a rheological modifier by triggering the formation of liquid crystalline phases that inhibit mixing; this transformation is one to avoid. On the other hand, structural formation is sometimes the goal; for instance, oppositely charged surfactants and polymers can be mixed to create dispersed, rubbery complexes. In both cases, the rheology of interfacial microstructure needs to be controlled but is difficult to measure since the shells cannot be isolated. This presents how microrheology can measure the mechanical properties within localized shell structures formed as surfactants contact water or aqueous polymers. Relevant interfacial microstructures are measured to be 10^3 more viscous than the separated original ingredients.

Wednesday 5:30 Salons Fontaine C-H PO52

The rheology of graphene oxide vorticity banding

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Graphene has been the subject of an immense amount of research over the past decade as it offers outstanding mechanical and electrical properties. Graphene oxide is a form of graphene with charged oxygen-based functional groups that allow easy processing in the aqueous phase. The advantageous properties of graphene oxide are often exploited in solution and thus it is extremely beneficial to understand and furthermore control the rheology of the material in water. The rheology of graphene oxide in aqueous solution has been investigated. Graphene oxide in aqueous solution has been found to have a relative viscosity on the order of ~10,000 at low concentrations (~0.1 mg/mL). Furthermore, it was observed that graphene oxide can be induced into vorticity banding flow with the introduction of salts into solution. Although vorticity banding has been reported in a wide array of different materials, this is the first reported observation of vorticity banding in graphene oxide solutions.

Keywords: Graphene oxide, pseudoplastic, vorticity banding, percolated network

Wednesday 5:30 Salons Fontaine C-H PO53

The rheology of carbon black stabilized Pickering emulsions

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Emulsions offer stable, discrete droplets of one phase in a second, immiscible phase. This meta-stable system is often stabilized through the use of ampipathic surfactant molecules, which lowers the intefacial tension between the two phases. Pickering emulsions offer emulsification

through the use of particles rather than surfactant molecules. Emulsification with particles at the interface leads to different interfacial rheology than what is observed with surfactant molecules. Modified carbon black molecules, which are typically hydrophobic, have been used to stabilize oil-in-water emulsions. The fractal nature of carbon black molecules leads to interesting rheological behavior, which is reported as a result of this study.

Wednesday 5:30 Salons Fontaine C-H PO54

Spatial cooperativity in dense sheared suspensions

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The rheology of complex fluids is of paramount importance for many applications, and has consequently received much attention. For polymers, their flow behavior is by now well understood and can be accurately predicted with the help of constitutive models. Such models have also been proposed for other complex fluids but it was shown that the viscosity of materials such as emulsions or particle suspensions can be very different if the material is sufficiently confined. The key experimental observation is that if a local viscosity is calculated from the ratio of a local stress and strain rate, the former can be below the bulk viscosity by more than an order of magnitude. The physical interpretation proposed is that in these jammed systems there are collective effects that allow for local rearrangements even is the stress is smaller than the one necessary to create a macroscopic flow. This has been quantified in the so-called 'fluidity' model, that describes deviations from the bulk rheology in terms of a spatially varying local viscosity. The model then introduces a characteristic length scale for the spatial variation of the viscosity.

We study suspensions of hard, non-Brownian, particles in a density matched solvent and dry granular materials. MRI measurements in a Couette cell allow us to obtain the local viscosity. These measurements show pronounced non-local effects that are well described by the fluidity model. However they also provide us with the reason for the spatial variation of the viscosity in this system: the system develops an inhomogeneous density of particles.These heterogeneities can be measured directly with the MRI, which allows us to show that the origin of the non-locality of the viscosity can be understood quantitatively in these granular systems. The characteristic length scale in the fluidity model can then also be interpreted as the length scale of the heterogeneity in volume fraction, in our case the entire gap of the Couette cell: hundreds of particles.

Wednesday 5:30 Salons Fontaine C-H PO55

Electric effects on Newtonian and viscoelastic droplets

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In the present work, a solver on the open CFD software OpenFOAM was implemented, based on the leaky dielectric model, in order to study the effects of an electric field in conducting droplets. These simulations were performed considering both Newtonian and viscoelastic fluids. The Giesekus constitutive equation was used to describe the viscoelastic behavior. The results of the deformation of a conducting droplet were compared to analytical results, for Newtonian fluids, and with theoretical results, for viscoelastic ones.It was observed that the most important parameter that influences the deformation of the drop, indeed, is the electric field. Other parameters, such as the conductivity, permittivity and elasticity, also play a role on the deformation magnitude. Due to the applied electric field, it was observed that the droplet deforms on a stable spheroidal form. For viscoelastic fluids the deformation was reduced with the increase of the relaxation time. Also, it was observed, as in some experimental results, the formation of four vortexes inside and outside the droplet.

Wednesday 5:30 Salons Fontaine C-H PO56

Long flexible fiber orientation simulation in squeeze flow

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The mechanical properties of fiber reinforced polymers are highly dependent on fiber orientation. There are many models for fiber orientation calculations available in the literature, however, most of them address the short and rigid fibers and the models which are developed for long flexible fibers are usually implemented in a simple shear flow case. The last stage of LFT (Long Fiber Thermoplastics) preparation is press molding. In this process the flow inside the mold could be characterized as squeeze flow and its parameters are crucial for fiber orientation. Simulating a long flexible fiber in a squeeze flow is a challenge since the center mass of a fiber may not be on the fiber, flow field gradient is not constant in space and time and the force is acting on the fiber from multiple directions unlike in the simple shear flow case. Furthermore the results will depend on fibers initial location in the mold. Long flexible fiber was simulated in a rheometric squeeze flow using a model with elements from the “Bead-Chain” model which treats the fiber as a collection of beads and the “Rod-Chain” model which unites several beads into rods to reduce calculations. In the literature these models are found to be implemented mostly in the simple shear flow case. The velocity field of a squeeze flow is calculated using analytical solution which also helps to reduce calculations.

Wednesday 5:30 Salons Fontaine C-H PO57

Motion of gas bubbles in a viscoplastic material

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One of the most troublesome problems in the petroleum industry is annular gas migration. Gas invasion occurs when pressure is lower in the annulus than at the formation face during drilling or well completion procedures. The gas might migrate to a lower pressure zone, or possibly to the surface. The objective of our research is to determine stagnant conditions and terminal velocity for gas bubbles occurring in a viscoplastic material, in order to establish under which conditions gas migration might occur. We use Carbopol dispersions to simulate the properties of cement slurries. The bubble velocity is measured both directly, using a stopwatch, and through analysis of movies using a Matlab program. Results were obtained for a wide range of injected air volumes and flow rates. Curious phenomena were also observed and correlated with the rheological properties of the material.

Wednesday 5:30 Salons Fontaine C-H PO58

Assessment of sedimentation stability of dispersions via multiple light scattering and rheology

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The stability of organic peroxide dispersions consisting of different levels of rheology modifiers was studied via Multiple Light Scattering using a Turbiscan? instrument in order to develop a more efficacious dispersion formulation. Turbiscan? analyzer measures the stability index and kinetics of destabilization based on light scattering of migrating particles in the dispersion. To compare the Turbiscan Stability Index (TSI) measurements with classical macroscopic rheology measurements, we used strain rheometry to measure yield stress and viscoelastic parameters. Statistical modeling was applied to the data obtained using Turbiscan and traditional rheology. Predictive models built upon TSI data confirm and quantify the capabilities of a stabilizer in the various dispersion formulations. Results also demonstrated that stability index values are in good agreement with findings from oscillatory rheology techniques.

Wednesday 5:30 Salons Fontaine C-H PO59

Particle pressure and normal stress differences in red blood cell and capsule suspensions

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It is well known that a suspension of non-Brownian particles in a Newtonian fluid exhibits non-Newtonian characteristics in the form of normal stress differences and particle pressure, which are the results of hydrodynamic interactions among the suspended particles. Of particular interest is the particle pressure, which is believed to drive the particle migration in a sheared suspension, and, hence, is a key ingredient in macroscopic models of suspensions, such as the suspension balance model. Experiments and computer simulations of rigid spheres have shown that the particle pressure is positive (compressive), meaning that the dispersed phase would spread under shear. In contrast, a negative (tensile) particle pressure implies a tendency of the particle to move closer. In this work, we report particle pressure and normal stress differences obtained from three-dimensional computer simulations of semi-dense suspension of extremely deformable particles (non-Brownian, inertia-less), namely, the red blood cells and capsules, which are viscous drops enclosed by elastic membranes. The striking result is that the particle pressure for such suspensions is found to be negative, as opposed to positive pressure found for rigid particle suspensions. The magnitude of the particle pressure increases with increasing volume fraction of the cells and increasing cell deformability. Similarly, unlike rigid particle suspensions, for which several experiments and computer simulations have shown that the first normal stress difference is negative, here we find it to be positive for deformable cell suspension, similar to polymer suspensions. These results are explained by analyzing the elastic force developed in the cell membrane due to flow-induced deformation. The positive first normal stress difference, as well as the negative particle pressure for blood cells implies that these particles would naturally form clusters leading to cell aggregation.

Wednesday 5:30 Salons Fontaine C-H PO60

Interfacial rheology and microstructure of carbon nanotubes at the air-water interface

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Interface-driven assembly of particles has been demonstrated by a number of authors [1, 2]. The corresponding physics is intriguing, but fairly well documented for micron-size particles with a moderate aspect ratio (<10) [3, 4]. Carbon nanotubes (CNTs) are rolled cylinders of graphene sheets with an aspect ratio exceeding 100, for which their interfacial behavior remains largely unexplored. In the present work, we investigated the interfacial assembly and rheology of both functionalized and non-functionalized CNTs at the air-water interface. Our findings indicate that CNTs with appropriate wettability adsorb strongly at the air-water interface, leading to an increase in surface pressure. To understand the evolution of the interfacial structure under compression, the CNT-decorated interface was studied both optically (*in situ*) and with electron microscopy (after performing Langmuir-Schaefer deposition). Preliminary data on the interfacial shear rheology were measured using a double-

wall du Nouy ring (DDR) setup. The findings may have implications on the development of more stable emulsions and the production of CNT thin films with controllable packing density and orientational ordering.

References: [1] Pieranski, P., Two-dimensional interfacial colloidal crystals. Phys. Rev. Lett., 45(7), 569-572 (1980). [2] Bowden, N. *et al.*, Self-assembly of mesoscale objects into ordered two-dimensional arrays. Science, 276(5310), 233-235 (1997). [3] Basavaraj, M.G. *et al.*, Packing, flipping, and buckling transitions in compressed monolayers of ellipsoidal latex particles. Langmuir, 22(15), 6605-6612 (2006). [4] Lewandowski, E.P. *et al.*, Orientation and self-assembly of cylindrical particles by anisotropic capillary interactions. Langmuir, 26(19), 15142-15154 (2010).

This work is supported by NSF CAREER award (#1253613).

Wednesday 5:30 Salons Fontaine C-H PO61

Role of inertia and dissipation mechanism on diffusion and avalanches in soft-particle suspensions

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When suspended soft particles like micro-emulsions or gas bubbles in a wet foam are confined at particle volume fraction above the random-close-packing density, they develop a proper zero frequency storage modulus and a finite yield stress when driven at vanishing rate. At vanishing rate, the modulus and yield stress should be controlled by the energetics of deformation of the particles and dynamical effects such as hydrodynamics should be irrelevant. At finite rate, the role of microscopic dynamics should become important. In particular, one may observe significant differences in the case where the particles have inertia – as in the case of micro-emulsions – or when the particles are essentially massless -- as in the case of air bubbles in a foam. We study the rheology, diffusion, and power spectrum of stress fluctuations in several variants of Durian's bubble model that include particle inertia as a parameter. We show that in the inertial case the system responds essentially identically to Lennard-Jones glasses. In particular, it shows a rate dependence of the single-particle diffusion co-efficient that scales like strain rate to the power of 1/2. This result is essentially independent of particle volume fraction. As the inertia is decreased, the response crosses over to something closer to strain rate to the power of 2/3. We also discuss differences in the spectrum of stress fluctuations.

Wednesday 5:30 Salons Fontaine C-H PO62

Fundamental rheological studies of cellulose nano-fibril water suspensions

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Presently, aluminum and synthetic plastics are widely used for food packaging, partly because they have excellent barrier properties. However, with increasing environmental concerns, renewable and biodegradable materials are being sought as substitutes. Cellulose nano-fibril (CNF), which is produced by disintegrating wood fibres, can be deposited on conventional papers as thin barrier coatings. CNF is stiff and biodegradable, and has low weight and high specific surface area. Aqueous solutions of these high-aspect-ratio nano-fibrils form strong, stiff gels in which an entangled network is strengthened by inter-fibrillar hydrogen bonds. Using CNF gels in industrial production requires knowledge of its viscoelastic and barrier properties. In this work, the viscoelastic properties of CNF water suspensions were investigated using mechanical rheometry. The results show that different CNF concentration regimes have different rheological behavior. Increasing the concentration, from 0.05 %w to 0.5 %w, changes the gel-like CNF solution with frequency dependent storage (G') and loss modulus (G"), to solid-like suspension with G' and G" almost independent of frequency. The study of shear-dependent viscosity for dilute CNF suspensions and our measurement of intrinsic viscosity will also be presented.

Wednesday 5:30 Salons Fontaine C-H PO63

Shear rheology of functionalized silica nanoparticle dispersions

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The external surfaces of 4 nm diameter silica nanoparticles were functionalized with octyl groups, anthracene attached to pentyl chains, and trimethylsilane groups. These nanoparticles were characterized by infra-red spectroscopy, transmission electron microscopy, thermogravimetric and elemental analysis. The average number of functional groups per particle and their thermal stability were determined. Rheological measurements were carried out on 10 wt. % nanoparticle dispersions in toluene and decane at 25 ^{o}C and 80 ^{o}C over shear rate rang from 0.001 to 200 s^{-1} in a concentric cylinder under steady shear condition. The objective was to simulate the behavior of asphaltenes - a nano-aggregated fraction in crude oils. Two cycles of low to high shear were applied to the samples. The second cycle results were used to describe behaviors, to eliminate possible effects linked to differing shear histories. All three functionalized silica nanoparticle dispersions in toluene and decane exhibit reversible shear-thinning behaviors. The dispersions possess comparable relative viscosities in both solvents that at fixed shear rate are orders of magnitude greater than unfunctionalized silica particle suspension in water, asphaltenes in solvents and non-interacting hard spheres, at low shear rate, but approach these baselines at high shear rate. The decrease in relative viscosity of the functionalized particle suspensions vis-à-vis the other suspensions is attributed to the breakup of functionalized-nanoparticle aggregates or networks at high shear. However, the strength of the networks is too great both at 25 ^{o}C and at 80 ^{o}C for these nanoparticles to serve as models for asphaltene behavior. The detailed experimental results and a preliminary assessment of the differences in the rheological behavior of the three different functionalized silica nanoparticles are discussed.

Wednesday 5:30 Salons Fontaine C-H PO64

Nonlinear microrheology of attractive colloidal dispersions

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We study the nonlinear microrheology of attractive colloidal suspensions. In nonlinear microrheology a Brownian probe is driven by an external force through a complex fluid, and its motion is studied to infer material properties of the suspending fluid. Most work focuses on suspensions of spheres interacting via hard-sphere repulsion, in the presence or absence of hydrodynamic interactions, with the microviscosity determined by application of Stokes' drag law. But in many materials attractive interactions between particles exist, and previous studies have shown that for weak flows, attractions give rise to changes in viscosity. The probe's motion through the suspension distorts the configuration of particles; the extent of this distortion is given by the Peclet number, $Pe = F^{ext}/(kT/a)$, which gives the strength of probe forcing compared to thermal forces. In a suspension of attractive hard-spheres, an additional parameter arises: $A = F^{p}/(kT/a)$, which gives the strength of attractions relative to thermal fluctuations. The relative importance of these contributions to particle motion, and hence viscous response, evolves with the degree of displacement from equilibrium. When the force on the probe is weak, the dipolar disturbance to the microstructure is muted by attractive forces. For strong external forcing, a boundary layer forms near contact where advection, diffusion, and attractions balance; attractions increase the concentration of particles inside the boundary layer relative to hard-sphere suspensions. The low-Pe plateau in the microviscosity increases with attraction strength. The suspension force-thins with increasing Pe to a Newtonian plateau which, for moderate attractions, is independent of the attraction strength. Comparison to analogous results for low-Pe macroscopic shear shows good agreement.

Wednesday 5:30 Salons Fontaine C-H PO65

Three dimensional cluster distributions in processed multi-wall carbon nanotube composites

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We report the 3D structure of carbon nanotube networks in glassy polymers via confocal microscopy and image analysis to analyze the interplay between structure, properties and processing. We discover that the CNTs networks consist of ramified clusters whose size and frequency scale with cluster mass with characteristic exponents that are typical of percolating systems. The scaling relationships hold over a range of concentrations and processing operations (squeezing, shearing, annealing) even though these operations vary the electrical conductivity. In the particular case of annealing experiments, we observe that the phenomena of conductivity recovery is associated with residual flow, providing a partial explanation for this intriguing effect. Our results suggest that the power law scaling of cluster mass with size and frequency may be an important principle governing MWCNT structure in processed composites. Further, they suggest that subtle effects in MWCNT structure may play a significant role in composite electrical conductivity.

Wednesday 5:30 Salons Fontaine C-H PO66

Structure and rheology of aging colloidal gels by dynamic simulation

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We study via dynamic simulation the structural evolution and rheology of a weak colloidal gel formed by the space-spanning aggregation of reversibly bound particles suspended a Newtonian solvent. By breaking inter-particle bonds, Brownian forces are able to rearrange the freshly formed gel over long times, with structural and rheological consequences. By analysis of long-duration dynamic simulations of 750,000 particles, we are able to sample a macroscopically representative range of structural length scales characteristic of such gels. Analyzing the evolving structure and particle dynamics, we characterize the heterogeneous particle transport and its effect on linear-response viscoelastic moduli. The resultant structural rearrangement is compared to predictions from coarsening theories.

Wednesday 5:30 Salons Fontaine C-H PO67

Shear-induced structure and migration of colloidal particles in concentrated polymer solutions

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Suspensions with a viscoelastic continuous phase can exhibit interesting and unexpected microstructural features. One of these is the formation of small, vorticity-aligned particle clusters in simple shear, which has occasionally been observed in the past [DeGroot et al. (J. Coll. Interf. Sci., 1994); Pasquino et al. (Rheol. Acta, 2010)], without fully uncovering the underlying mechanism. We used rheo-SALS to probe the dynamics of this phenomenon for a suspension of colloidal silica particles in shear-thinning entangled polymer solutions. It was found that shear rates in the shear-thinning regime resulted in particle aggregation and orientation of aggregates along the vorticity axis. In contrast, application of strain in the Newtonian, low-shear regime did not yield clusters, and even led to restoration of a uniform particle distribution in an already ordered, pre-sheared suspension. Comparison of the SALS patterns with simultaneously measured viscosity data provided insight into the microstructural

evolution in these suspensions under shear, revealing the decoupled dynamics of aggregation and flow orientation. Additional experiments with a Boger fluid showed that these effects were predominantly caused by shear-thinning.

In addition to the simple shear flow experiments, these dilute colloidal suspensions were also subjected to channel flow through rectangular glass capillaries. Concentration profiles were determined via confocal microscopy. Depending on shear rate, cross-channel migration of particles was observed in different directions: toward the center of the channel at low shear rates and toward the walls at high shear rates.

Controlling and optimizing the migration, aggregation and alignment of colloidal particles in concentrated polymer solutions is highly relevant for the processing of "mixed matrix membranes", which combine a continuous polymer phase with embedded inorganic particulates that enhance the membrane properties.

Wednesday 5:30 Salons Fontaine C-H PO68

Electrosterically-stabilized nanocrystals of cellulose: Effect of salt and pH

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Electrosterically-stabilized nanocrystals of cellulose (ENCC) are novel nanoparticles that consist of cellulose crystals protruded at each end with amorphous chains, giving more stability to the particles in aqueous suspensions. These nanoparticles are produced in a two-step oxidation procedure. The first step is based on periodate oxidation of wood pulp followed by chloride oxidation. This procedure results in highly charged nanoparticles which contain 6.6 mmol of carboxylate groups per gram of cellulose. Ubbelohde viscometry was performed to determine the intrinsic viscosity of suspensions at various pH (3.5 and 8.5) and salt content (from 0 to 200 mM). Fedors model has been used to plot the viscosimetry data. The obtained values were 102 mL/g and 178 mL/g for the intrinsic viscosity of ENCC in their protonated (pH = 3.5) and deprotonated forms (pH = 8.5), respectively. This difference is attributed to the effect of electrostatic repulsion, which also increases with pH due to the deprotonation of carboxylate groups into their sodium form. The addition of salt shows a decrease in the reduced viscosity due to the screening of electrostatic charges in the cellulose suspensions.

Wednesday 5:30 Salons Fontaine C-H PO69

Natural convection of a Bingham fluid in a vertical channel

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Vertical ducts filled with yield stress fluids and with differentially heated walls are found in the drilling and cementing of oil wells, as well as potentially in other construction geometries and geophysical contexts. In these settings it is of interest to determine whether or not the thermal heating effects are sufficient to promote fluid motion and eventually instability. As an archetypical flow we consider a vertical plane channel between two differentially heated walls. In addition to the constant temperature difference there is a stabilizing vertical gradient in the imposed temperature. This configuration was studied by Bergholz [1], in the case of Newtonian fluids.

The base flow is governed by 2 dimensionless parameters: a stratification parameter and a Bingham number. Above a critical Bingham number we find that there is no motion, regardless of the stratification parameter. We study the rich structure of solutions found below this critical Bingham number. For most of the dimensionless parameter space we find solutions with 2 or 3 unyielded plugs, and mainly we have explored the behaviour of these solutions. Of academic interest is the fact that for sufficiently large stratification parameter and small Bingham number it appears we can find infinitely many unyielded plug regions - a peculiarity for a steady flow in a finite domain. We present a complete picture of the different flows in the parameter space governed by Bingham number and stratification parameter.

References: [1] R. F. Bergholz, J. Fluid Mech. (1978), 84, pp. 743-768.

Wednesday 5:30 Salons Fontaine C-H PO70

Role of microstructure and manufacturing in transport properties of highly porous ceramics

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Porous and permeable ceramic scaffolds are useful to many applications ranging from catalyst supports, filtering molten metal alloys, and high temperature insulation. Magnesium oxide ceramics manufactured by a number of routes are studied here as an alternative for traditional battery separators. In additional to more common slip casting approaches, ceramic foams with porosities over 90% can be created by drying and sintering particle stabilized oil-water emulsions. Additional porosity may improve ionic transport through the ceramic while maintaining the mechanical rigidity of the underlying ceramic. Processing parameters such as emulsion mixing speed, particle concentration, and drying time are related to final properties such as porosity, permeability, and mechanical strength. In addition to bulk properties, the microstructure is critical in determining transport properties through the ceramic. The impact of the hydroxylation of magnesium oxide to brucite and the resulting changes in the final microstructure through the sintering process are important in understanding the permeability of the ceramic. We will discuss in detail the hydrolysis of the magnesium oxide and resultant gelation of magnesium oxide suspensions. Finally we will show preliminary results of these materials in a molten salt battery.

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

Wednesday 5:30 Salons Fontaine C-H PO71

Frozen-in patterns in yield stress fluid

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Stable multi-layer flows can be achieved at high Reynolds numbers by using a yield stress fluids in a lubricating outer layer. These flows have been demonstrated to be linearly and nonlinearly stable as well as observable experimentally and computationally; see Frigaard (2001), Moyers-Gonzalez et al. (2004), Huen et al. (2007), Hormozi et al. (2011a) and Hormozi et al. (2011b). We present results of experimental, computational and theoretical studies targeted at extending the visco-plastic lubrication concept to patterned extrusion products and to the transport of encapsulated fluid droplets. In the experimental and computational parts, we show that by controlling the flow rates and rheology of different fluid streams it appears possible to engineer wavy walled tubes/channels, inserts and to produce droplets of varying shapes and sizes. In all cases the yield stress of the fluids "freezes in" the interface shape between simultaneously pumped streams of two fluids. A distinction between this method and other droplet forming techniques is that length-scales are governed by the inlet conditions and the fluid Rheological properties, rather than by capillary phenomena. This opens up possibilities for application in industries that do not operate on the micro-scale, as in most large scale industrial processing (e.g., oil, food, personal care and drug industries). We also present the result of an asymptotic solution that gives the relation between the size of encapsulated droplet and the state of stress in the flow.

References: I.A. Frigaard, J. Non-Newt. Fluid Mech., 100, (2001) 4976. M. Moyers-Gonzalez, I.A. Frigaard & C. Nouar, J. Fluid Mech.,506, (2004) 117-146. C.K. Huen, I.A. Frigaard & D.M. Martinez, J. Non-Newt. Fluid Mech., 142, (2007) 150-161. S. Hormozi, K. Wielage-Burchard & I.A. Frigaard, J. Fluid Mech.,673, (2011) 432-467. S. Hormozi, K. Wielage-Burchard & I.A. Frigaard, J. Non-Newt. Fluid .Mech.,166, (2011) 262-278.

Wednesday 5:30 Salons Fontaine C-H PO72

Transport and dispersion of solid particles along a fracture

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In hydraulic fracturing, specially engineered suspensions are pumped at high pressure and rate into the reservoir, causing a propagating fracture to open. When the pressure is released the fracture is supported by the grains of solid proppant that are left behind. Recent trends in the oil industry have included the use of cyclic pumping of a proppant slurry interspersed with clear frac fluid, which is found to increase the subsequent productivity. It is therefore of interest to understand how slugs of proppant pumped in a cyclic fashion can disperse in the pipe on the way and finally in the fracture. We present a model to describe dispersion of solid particles (proppant) along the fracture in a laminar flow of shear thinning yield stress fluids. We consider two-phase governing equations, assuming that solid and fluid phases can be described as two phases of incompressible continua. We adopt the standard Hele-Shaw type scales and multi-timescale approaches to derive a 1D advection/diffusion model along the streamlines for transport and dispersion of the mean solid particle concentration. We show the effects of lift, drag and centrifugal forces on the dispersion dynamics of the particles along the fracture.

Wednesday 5:30 Salons Fontaine C-H PO73

Thixotropic-viscoelastic rheological fingerprints in strain-control and stress-control LAOS

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In this work we explore the rheological trends of thixotropic viscoelastic constitutive models, focusing on the fundamental characteristics of the kinetic rate equation. We begin with a minimalist constitutive model that contains only five material parameters, which we show to be the minimum required to capture all fundamental thixotropic and viscoelastic phenomena. We examine the distinct rheological material function signatures produced when kinetic structure breakdown is dictated either by stress or by strain rate. Constitutive model behavior is characterized using asymptotic nonlinearities in large amplitude oscillatory shear (LAOS). We explore the differences between model responses to controlled strain oscillations (LAOStrain) and controlled stress oscillations (LAOStress). In addition, we explore the effects of a sixth model parameter (the most common addition to simple models in the literature), introduced to govern the order of the kinetic rate equation. Finally, we compare these model signatures to the experimental signature of a real thixotropic material, demonstrating how these model rheological fingerprints serve to aid and enhance constitutive model selection.

Wednesday 5:30 Salons Fontaine C-H PO74

Effect of interfacial rheology on film drainage from contact lenses

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The drainage of thin films is an important phenomenon commonly observed on the front our eyes each time we blink. The human tear film is coated with an insoluble layer of lipids (Meibum), which is expected to play a role in stabilizing the tear film against rapid thinning and rupture. Using interfacial rheology measurements, Meibum has been shown to be highly viscoelastic. To better understand the role of the surface viscoelasticity in tear film stability, we investigate the gravity-driven drainage of thin films on a contact lens. An aqueous film laden with a viscoelastic lipid monolayer is entrained on a contact lens substrate using a modified Langmuir trough. An interferometer is then used to capture the drainage dynamics of these films. Our results suggest that the drainage dynamics of both these systems can be understood using a relatively simple hydrodynamic model. Additionally, we observe that Meibum is particularly effective in slowing the rate of film drainage.

Wednesday 5:30 Salons Fontaine C-H PO75

Developments in asphalt testing with rotational rheometers

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The development of rotational rheometer tests for the characterization of asphalt and the prediction of its longevity is an active area of research in the field of rheology. Standard tests like Original Binder, Rolled Thin Film Oven, and Pressure Aged Vessel testing have contributed greatly to setting specifications for asphalt used in paving roads. However, they have shortcomings and need additional refinement. The Multiple Stress Creep and Recovery (MSCR) test has shown itself to be a useful predictor for rutting when used in conjunction with Original Binder. Modifications to the procedure and data analysis that should improve the robustness of the test will be discussed in this poster. Four developmental tests will also be discussed: First, the Linear Amplitude Sweep test, with its use of the Viscoelastic Continuum Damage model; 2nd, Large Amplitude Oscillatory Strain (LAOS); 3rd, Low temperature testing to correlate with Bending Beam Rheometer testing; 4th, concentric cylinder testing of asphalt containing crumb rubber. With these tests, we hope to have better characterization of asphalt binders, make better predictions regarding pavement performance, and increase the use of rotational rheometers for asphalt testing.

Wednesday 5:30 Salons Fontaine C-H PO76

"Paint without priming; spackle without cracking" – a unique rheometer configuration used to study the newest in paint nanotechnology

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Spackling compounds used for repairing damages in wood, plaster, or drywall have traditionally been composed of low density, inorganic fillers which crack, flake, or shrink after application. As these physical changes of the spackling result in an uneven repair surface, sanding and/or priming must first occur before painting over a spackled area. New technologies in wall repair and painting have introduced spackling compounds composed of advanced acrylic resins and fillers which self-prime, shorten drying times, and provide strength to eliminate shrinkage or cracking of the repair. The Immobilization Cell for Anton Paar rheometers, including porous measuring geometries, has been used to measure the effects of drying on strength and rigidity of these new compounds under varying temperature conditions. With this measuring configuration, film formation during drying has also been studied to investigate self-priming performance of the advanced acrylic resins. The rheological properties of these new materials have been compared to that of conventional spackling compounds to show the advancements in paint technology with overcoming challenges associated with paint preparation and to substantiate marketing claims for the new spackling compounds.

Wednesday 5:30 Salons Fontaine C-H PO77

Tribo-rheology accessory for controlled stress rheometers

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When designing new and novel materials, a thorough characterization of material properties is critical at each stage of manufacturing, processing, and end use conditions. Of these, an understanding of the impact of frictional effects and long term usage on the wear on the material properties can be beneficial for improving overall product longevity. Such information is pertinent to a wide spectrum of applications including prosthetic devices, personal care creams and lotions, automotive components, and greases. The traditional approach to investigating frictional effects involves the use of a tribometer equipped with normal force and either linear or rotational displacement rate control. In this poster we introduce and discuss the application of a tribo-rheometry accessory for performing tribological measurements on commercially available DHR rheometers. The accessory exploits the superior normal force control afforded by the DHR's FRT normal transducer and the torque sensitivity of the magnetic bearing combined with excellent displacement resolution. A number of different configurations for the tribo-rheology accessory are presented and the versatility of the platform for measuring the coefficient of friction is demonstrated.

Wednesday 5:30 Salons Fontaine C-H PO78

Rheo-SANS and flow-SANS for simultaneous probing of rheology and flow-induced microstructure at Oak Ridge National Laboratory

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Characterizing the relationship between microstructure and rheology allows fundamental understanding of the properties of materials and facilitates rational formulation and processing of complex fluids and soft materials in industrial applications. Direct insight into the flow-induced structures responsible for rheological behavior can be gained through simultaneous rheology and small-angle neutron scattering (SANS) experiments, or rheo-SANS. Currently, rheo-SANS measurements can be performed in the United States only at the National Institute of Standards and Technology (NIST), while specialized instrumentation for characterizing polymer melts has recently been established at Los Alamos National Laboratory. This poster will describe the rheo-SANS facilities that are currently being developed at Oak Ridge National Laboratory (ORNL) for integration with SANS beam lines at the High Flux Isotope Reactor and the Spallation Neutron Source. The unique advantages of the neutron sources at ORNL for establishing capabilities that are complementary to existing rheo-SANS facilities will be outlined. The ORNL neutron facilities are part of the Department of Energy national scientific user facility program, and will soon be accepting proposals for beam time with the rheo-SANS sample environment. In addition, we will describe associated flow-SANS and neutron reflectometry techniques available at ORNL that allow microstructural characterization in channel flow. Our aim is to inform the global rheology community of the availability of these techniques at ORNL, and to engage potential users regarding the optimization of these instruments to benefit their research programs in soft matter and rheology.

Wednesday 5:30 Salons Fontaine C-H PO79

Determination of dynamic viscoelastic functions from creep test

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Dynamic test is an useful method to measure the linear viscoelastic properties of viscoelastic materials. However, there is an obstacle to measure these properties in a wide range of frequency. As for the molten state of viscoelastic material, time-temperature superposition can be breakthrough for the limitation of measurements. However, time-temperature superposition is hard to be applied to polymer solutions, because of phase separation and evaporation of solvents. According to linear viscoelastic theory, static and dynamic data are inter-convertible. Creep test gives reliable data in long time region. Thus, creep test is expected to be a method to overcome the limitation of dynamic test of polymer solutions. However, it is impossible to convert the creep compliance to dynamic viscoelastic functions directly by a numerical integration. So the creep-recovery test can be an alternative way, although it demands to consider the influence of residual torque and a lot of experiments. In this study, we will suggest a method for determining dynamic moduli for low frequency region by numerical Laplace transform of creep compliance $J(s)$ and conversion of s to frequency by use of complex analysis.

Wednesday 5:30 Salons Fontaine C-H PO80

Accuracy of micro-particle image velocimetry applied to blood micro flows for velocity profile measurements

Katie L. Pitts[1] and Marianne Fenech[2]
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The accuracy of micro-particle image velocimetry (µPIV) is evaluated for blood as a working fluid in channels on the order of 150 µm. µPIV is capable of measuring the velocity profile in small channels, such as those on the scale of the microcirculation. The velocity profile is used to establish the shear rate at the wall, which governs the uptake of oxygen and nutrients in the body. The velocity profile shape parameters can be calculated from the velocity profile, which can be used for evaluating the rheology of the blood. Two methods of µPIV are compared and the accuracy of these measurements is established through comparisons with theory and literature values. The data processing of the velocity profile data is optimized. Once accuracy is established, µPIV is applied to relevant biomedical and rheological investigations with blood, such as sodium alginate as a viscosity modifier in the blood for cases of hemorrhagic shock or increased perfusion.

Wednesday 5:30 Salons Fontaine C-H PO81

Improving the image quality of rheo-optical measurements

Philippe Sierro, Fritz Soergel, and Jint Nijman
Thermo Scientific, Karlsruhe, Germany

The combination of rheometry with light microscopy (rheo-optics) allows, on the one hand, to study the change of a material's structure and properties under shear in rotational measurements. The recorded microscopic images reveal the induced structural changes like orientation, deformation, coalescence, aggregation or disaggregation. On the other hand, stress/strain or temperature dependent changes, like crystallization, can be investigated with non-destructive oscillatory measurements.

In order to extent the useable measurement range of the rheometer for rheo-optical measurements to (much) higher shear-rates and to improve the image quality for low contrast emulsion samples, several modifications have been made to the optical system of the RheoScope module.

We will present measurement results with sharp images for shear-rates up to 44000 1/s as well as images of a low-contrast emulsion with enhanced quality and contrast.

Wednesday 5:30 Salons Fontaine C-H PO82

Using simultaneous rheometry and FT-IR spectroscopy for studying the morphology of emulsions under shear

Kiyoji Sugimoto[1], Manfred Feustel[2], Fritz Soergel[3], and Jint Nijman[3]
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In numerous different applications, for example in the food, pharmaceutical, health care and cosmetics industry, emulsions are widely used. Emulsions typically consist of at least two liquid phases, surfactant agents and stabilizers and exhibit complex rheological properties, making it difficult to understand flow phenomena on a microscopic level.

Emulsion can be studied under shearing deformation using a light microscope in combination with a shearing device or a rheometer but there are insurmountable technical limitations to this technique. For example when the dispersed droplets are too small or when the refractive indices of the two liquid phases are too similar.

In such cases, the combination of rheometry and simultaneous, in-situ FT-IR spectroscopy under shearing deformation offers a versatile tool for efficient and comprehensive emulsion research and stability testing. This hyphenated method setup proofs to be an useful tool in understanding the microscopic state of droplets in concentrated emulsions. We will present measurement results which show the dynamics of molecular organization of an emulsion under shear.

Wednesday 5:30 Salons Fontaine C-H PO83

Investigation of flow instabilities in coaxial measuring systems using a dual motor rheometer

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Rotational rheometry has made several advances since the introduction of the first practical concentric cylinder rotational rheometer by Maurice Couette in 1890. In the Couette method, the measuring bob is stationary while the outer cup rotates. More commonly, coaxial system based measurements are conducted using the Searle method, wherein the measuring bob is set in motion while the outer cup is stationary. In this study, different low viscosity fluids were measured in coaxial measuring systems on a rheometer that allows the use of different control modes such as Single Motor Transducer (SMT), Combined Motor Transducer (CMT), and Counter-Rotation. The design of this rheometer is such that both Couette and Searle methods can be accomplished on the same instrument. The impact of control modes on flow instabilities and onset of fluid inertia was studied.

Wednesday 5:30 Salons Fontaine C-H PO84

Effects of rheology on tribology

Frederik Wolf
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Tribology is the science of interacting surfaces in relative motion wherein friction, lubrication, and wear are studied. The behavior of lubricated tribological systems is strongly influenced by the rheological properties of the lubricants and solids used. The rheological properties depend on the internal structure of the fluids, which can change due to applied stresses or temperature. As such, these properties affect tribological properties, transition into hydrodynamics, and static friction. Information about stability, rheological properties, and tribological behavior was gained by utilizing a highly accurate rheometer. This study involved investigations on rheological effects, especially visco-elastic properties, and their impact on the tribological properties, with special emphasis on shear-sensitive visco-elastic fluids. Discussed are the associated rheological and tribological measuring techniques, their applicability and transferability, and their synergies.

Wednesday 5:30 Salons Fontaine C-H PO85

Mechanical and morphological characterization tools for thin polymer membranes at fuel cell operating conditions

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While proton exchange membrane (PEM) fuel cells have been the focus of development in the past, anion exchange membranes (AEM) have the potential to dramatically lower the cost of fuel cells by utilizing non-noble catalysts and a variety of fuel sources. As part of a broader effort to develop novel, thin and robust anion exchange membranes, creating a test fixture for mechanical characterization at relevant fuel cell operating conditions is being explored. New polymers are synthesized in small quantities and are typically on the order of 10-100 microns thick to increase ion transport. Standard tensile tests or dynamic mechanical analysis does not allow for adequate testing of these small sample sizes. Hence, a modification of the Sentmanat Extensional Rheometer (SER) to perform tensile and dynamic modulus testing on thin membranes is presented. Since the as-designed L-shaped pins do not secure thin polymer films at lower temperatures, a screw down clamp replaces the pins, allowing for mechanical characterization of small amounts of polymer. In a parallel effort, a humidity delivery system is being developed for the TA Instruments ARES-G2 rheometer to allow for testing at a range of temperatures (20-100°C) and relative humidity conditions (0-100% RH)

relevant to an operating fuel cell. The novel testing apparatus is benchmarked with low density polyethylene and Nafion. New anion exchange membranes are also compared. Additionally, the morphology change under extensional strain of polyethylene-b-poly(vinylbenzyl trimethyl ammonium) has been explored using small angle x-ray scattering (SAXS).

Wednesday 5:30 Salons Fontaine C-H PO86

New touch-screen, small-footprint, benchtop, rotational rheometers for visual, real-time, graphical monitoring of viscosity and yield tests

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A new, touch-screen, small-footprint, bench-top, rotational rheometer allows real-time, graphical monitoring of viscosity and yield tests. This permits operators to directly view the data, immediately observing non-Newtonian viscosity behavior or yield points, for example. An additional advantage is the ease of manual, multi-step program entry without software. Program and data files may be directly saved onto easily-portable, USB “flash drives” or “memory sticks”. Various rheological math models are built-in. Comparisons may be made between data sets obtained with identical tests. Operation of the touch-screen functions will be discussed. Data from rheological analysis of various materials will be presented, including both rotational viscometric and yield stress measurements. Automated operation with Windows®-based software will be discussed and representative data presented, as well.

Wednesday 5:30 Salons Fontaine C-H PO87

Estimation of error and bracketing of the value of the zero-shear-rate viscosity

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The zero-shear-rate viscosity η_0 can be of critical importance in determining and correlating the influence of material or thermodynamic variables on rheological behavior. Unfortunately, η_0 can be impractical or impossible to measure directly for neat polymers of high molecular weight, or for many structured materials. Thus extrapolation methods are used. However, any estimation of η_0 and its confidence interval requires that each point results from an independent observation, which is rarely, if ever, the case. Out of curiosity, $|\eta^*|(\omega)$ was measured using the following sequence: calibrate, load a fresh sample, hold 10 min, select a frequency at random and record $|\eta^*|$. The resulting estimates of η_0 and its error were then compared with those using the same frequencies run in sequence and with a single loading (i.e., a frequency sweep) to answer the question of the location of the η_0 based on independent observations in the prediction band found by using a frequency sweep.

Wednesday 5:30 Salons Fontaine C-H PO88

Process control via in-line viscosity measurement with non-Newtonian fluids: A new innovative method

Olivier Réglat
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Modern transformation processes require good efficient and reliable in-line controls in order to minimize operating costs and maximize quality. In this context, viscosity is one of the major parameters to take into account. For non-Newtonian fluids, a viscosity value just by itself means nothing if it is not referred to specific corresponding flow conditions. The VISCOLINE, a process pipe rheometer, offers an innovative measurement technique based on mixing principles. The VISCOLINE is composed of a pair of low pressure drop static mixers specially designed to be distinct and obey to Metzner and Otto concept applied to pipes. The average shear rate through each static mixer is associated with a power consumption of the fluid to define the viscosity function. The instrument provides, on a continuous base, a shear thinning and a consistency indexes, as well as viscosity. An accurate flow rate measurement is obtained with the Optimass 7010T, a monopipe Coriolis mass meter. This is the ideal combination with the VISCOLINE for non-Newtonian applications. Three successful applications will be presented in this poster. At a yogurt factory, results are the reduction of yogurt texture fluctuations, and optimisation of the protein consumption. In this case, the VISCOLINE was designed to control a smoothing valve on the white mass after maturation. At a brewery, the detection of the specific point for the transition from yeast to beer during the pumping process is optimized. In this case, a sanitary 2-inch VISCOLINE and a solenoid valve were installed on the main line, just below the main transfer pump. Solenoid valve is controlled using the viscosity reading in real-time. Also, in the oil industry, the increase of the efficiency of drilling operation by measuring viscosity at six different flow conditions corresponding to specific steps in the process of drilling, to lubricate the bit, to bring the debris back to the ground and insure the well will not collapse at the end of the drilling operation.

Wednesday 5:30 Salons Fontaine C-H PO89

Rheology as a tool to assess the release of alpha-lipoic acid from emulsions

Vera B. Isaac, Jemima D. Moraes, Bruna G. Chiari, and Marcos A. Corrêa
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The availability of an active substance through the skin depends basically on two consecutive steps: the release of this substance by the vehicle and its subsequent permeation through the skin. Hence, studies on the specific properties of vehicles, such as their rheological behavior, are of great interest in the field of dermatological products. Recent studies have shown the influence of the rheological features of a vehicle on the release of drugs and active compounds from the formulation. In this context, the aim of this study was to evaluate the influence of the rheological features of two different emulsion formulations on the release of alpha-lipoic acid. Alpha-lipoic acid (ALA) was chosen for this study because of its potent antioxidant characteristics, which could be useful for the prevention of skin diseases and aging. The rheological behavior and the in vitro release profile were assayed. The rheological analyses were performed in a Haake RS-1 rheometer, using the cone-plate sensor (C35/2ºTi). The in vitro release of ALA from the formulations was determined using Franz modified cells. The results showed that there is a strongly correlation between the rheological features, such as viscosity, thixotropy and compliance, and the release of ALA from the emulsions. Also, was verified that the presence of a hydrophilic polymer in one of the emulsions was an important factor affecting the rheology and, therefore, the release of ALA. Thus, the choice of a suitable system in which to incorporate a drug or active substance is of fundamental importance for the stability and availability of the drug at the application site and, therefore, for its effectiveness.

Wednesday 5:30 Salons Fontaine C-H PO90

The sequencing of dynamic rheological measurements

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Dynamic oscillatory rheological tests have become a staple tool used to investigate responses of soft materials and complex systems. The prevalence of linear oscillatory tests in materials science research can be attributed to the ease with which the tests can be performed and the firm theoretical foundations upon which their results rest. However, many real-world uses of complex soft systems apply conditions ill-suited for this analysis. There has consequently been a burgeoning interest in systematic studies of the nonlinear oscillatory behavior of soft complex materials. A number of recent publications have suggested that a better understanding of soft materials can be obtained by viewing responses to nonlinear tests as being the results of sequences of physical processes. Such ideas are in contrast with the most widely-used Fourier-based analysis concepts, which view nonlinear responses as linear superpositions of potentially infinitely-many material states. This poster introduces a quantitative analysis scheme for all oscillatory rheological data that takes its cue from the phenomenological studies. The new scheme defines three, not two, time-dependent viscoelastic material parameters to account for all of the information encoded in a response. Two of the terms are 'regular' viscoelastic material parameters; moduli, viscosities, compliances, or fluidities. The third, an entirely new concept for viscoelastic analysis, accounts for yield strains and stresses, and the shifting of the equilibrium point from which meaningful strain is acquired. The quantitative analysis allows for comprehensive physical interpretations of all responses to oscillatory deformations including those of steady alternance to any applied amplitude, thixotropic and anti-thixotropic materials, and time-dependent oscillatory shear startup responses.

Wednesday 5:30 Salons Fontaine C-H PO91

Rheological behavior of hydrate forming THF-water solutions

Michela Geri and Gareth H. McKinley
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Clathrate hydrates represent a major issue in natural gas/oil transport. They are inclusion compounds with a water-based crystalline structure stabilized by guest molecules of certain gases or volatile liquids. Their formation is promoted by low temperatures (273 K) and high pressures (1-10MPa), conditions which are commonly established in the operation of subsea pipelines. The study of clathrate hydrates is a real challenge due to the extreme conditions required for their formation. This issue can be partially overcome when using particular hydrate-forming molecules, i.e., tetrahydrofuran (THF) or cyclopentane (CP), which can form hydrates at atmospheric pressure. While CP is soluble in organic solvents, THF is miscible with water and it therefore gives the unique opportunity to study an extremely simple system: a binary mixture of THF and water. This particular solution has been investigated in the past, especially to understand the process of hydrate formation, but the mechanical behavior of THF-water hydrate slurries has never been clearly defined. Although the nature of water in crude oil emulsions is fairly different from that of a binary solution, the behavior of these hydrate forming systems is impressively similar in terms of viscosity evolution. Such observation has motivated the present study which is intended to provide a thorough experimental investigation of THF-water solutions during hydrate formation. The rheological fingerprint of these systems is determined by probing them under different conditions, e.g., steady state flow and oscillatory shear, with the aim of elucidating the main characteristics of their behavior. These results will help to understand what features can other hydrate-forming systems develop, as well as to establish a reliable protocol than can be used in future experiments.

Wednesday 5:30 Salons Fontaine C-H PO92

Soap film hydrodynamics: In color & in black & white

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

Iridescent colors of soap bubbles or films arise due to interference between light reflected from two surfactant-laden surfaces that are 100 nm - 10 micron apart. Sandwiched between these interfacial layers is a fluid that drains primarily under the influence of gravitational and capillary or interfacial forces, including disjoining pressure. Below 50 nm the thin films appear as black. We experimentally follow the drainage kinetics of soap films using imaging & color science and UV-Visible spectroscopy. We find fascinating examples of two-dimensional hydrodynamics and unexplained, if not unprecedented, drainage kinetics.

Wednesday 5:30 Salons Fontaine C-H PO93

The rheological properties of the oil in diesel engines

Israel Ibarra Solis[1], Ma. del Carmen Salazar Hernandez[2], and Juan C. Rodriguez Sierra[3]
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In the present work, we investigated the rheological properties of oils used in transit buses in the city of Silao Gto. Mexico, the aim of this research was to relate changes in the effective viscosity of the oil (fluid) in engine wear on buses. Maximum particle concentration of Fe and Cu from the frictional wear of the engines as it was determined by atomic absorption spectroscopy. The rheological properties of the oils are determined by varying the concentrations of particles determined by zero to maximum in oils, for these studies we used a Modular Compact Rheometer Physica MCR-300 Viscotherm VT2 with temperature control using a double gap geometry DG / 26. It is expected to obtain results indicating a dependency of the effective viscosity in oils with increasing Fe and Cu particles in oils as well as a direct connection between engine wear and the value of effective viscosity.

Wednesday 5:30 Salons Fontaine C-H PO94

Impact of temperature and thermal history on rheological properties of municipal digested sludge

Ehsan Farno[1], Rajarathinam Parthasarathy[1], Jean Christophe Baudez[2], and Nicky Eshtiaghi[1]
[1]Civil, Environmental and Chemical Eng., RMIT, Melbourne, VIC 3000, Australia; [2]Irstea, Montoldre, France

Municipal digested sludge is a non-Newtonian fluid which its rheological characteristics are highly thermal dependant. The rheological characteristic of digested sludge can irreversibly change by increasing temperature. This study investigated the irreversible effect of changing temperature on rheology of digested sludge in terms of thermal history effect. The sludge collected from Mount Martha sewage treatment plant and subjected to change of temperature from 20-80°C and then cooled down to 20°C. The rheological measurement was performed using stress controlled rheometer which is connected to water bath. Sludge composition also studied using chemical oxygen demand (COD) tests on sludge liquor obtained in different temperature. The yield stress and the apparent viscosity has been measured and compared for sludge with different thermal history. The result showed that the yield stress decreased by increasing the temperature, however, the yield stress did not recovered to original value by cooling the heated sludge. In addition, the sludge liquor COD increased by increasing the temperature, similarly, the solubilised COD did not come back to its original value. The Herschel-Bulkley model of non-Newtonian liquid has been successfully used to model data.

Wednesday 5:30 Salons Fontaine C-H PO95

Impact of increasing secondary sludge content on the rheological behaviour of blends of primary and secondary sludge

Nicky Eshtiaghi[1], Flora Markis[2], Kevin Hii[2], Jean Christophe Baudez[3], and Paul Slatter[2]
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Engineering rheological property of sludge inside anaerobic digesters for wastewater treatment for good mixing and biogas production is a challenging task and less understood. An understanding of sludge rheology during anaerobic digestion can greatly improve digester performance. However, the "black box" nature of digesters limits the knowledge sludge flow behaviour, once it enters the digester. A study on the flow properties (i.e. apparent viscosity and yield stress) as well as the yielding and restructuring behaviour of primary, secondary and blends of primary and secondary sludge was carried out. The primary and secondary sludge samples were collected from one of Melbourne wastewater treatment plant (Australia). Flow curve, creep tests (below and above yield stress) and shear stress sweep tests (at various times of rest from 60 to 3600s) were conducted to study the yielding and restructuring behaviour of the individual sludge types at 5% total solids concentration using a stress controlled rheometer. Primary sludge (5% TS) was then mixed with secondary sludge (5% TS) at different ratios (0 - 80%) and their flow properties analysed at 20 °C. The Herschel-bulkley model was used to model their flow properties. It was shown that primary sludge acted as a jammed material whose rheological parameters (apparent viscosity, yield stress and shear thinning properties) were lower than secondary sludge at approximately the same total solids concentration. The viscosity, yield stress and shear thinning behaviour of blends of primary and secondary sludge increased with increasing ratio of secondary sludge to primary sludge.

Wednesday 5:30 Salons Fontaine C-H PO96

Effect of curing pathways on rheological and mechanical properties of dual curable clearcoats for automotive applications

Samuel Park[1], Ji Won Hwang[1], Kyung Nam Kim[2], Seung Man Noh[2], and Hyun Wook Jung[1]
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In this study, rheological and mechanical characteristics of dual curable clearcoats, as curable oligomeric systems in automotive application, with several crosslinkers were compared through several curing pathways: UV mono-curing, thermal mono-curing, UV-thermal dual curing, and thermal-UV dual curing. SMBI (silane-modified blocked polyisocyanate), blocked HDI-based polyisocyanate, and blocked IPDI-based polyisocyanate were involved as crosslinkers. It was possible to find the optimal curing pathway for enhancing clearcoat properties from the transient patterns of rheological modulus data for different clearcoats, focusing on the role of crosslinkers on the formation of crossliked polymeric networks inside clearcoats. Mechanical properties of cleracoats with different crosslinkers were successfully elucidated from the nano-scratch test (NST) and three-dimensional scratches captured by AFM.

Wednesday 5:30 Salons Fontaine C-H PO97

Coating flow dynamics of shear thinning liquids in stripe slot coating process

Won-Gi Ahn[1], Lee Si Hyung[1], Ji Ho Suk[1], Nam Jaewook[2], and Jung Hyun Wook[1]
[1]Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea; [2]School of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

Coating process has been regarded as one of the core processing technologies in manufacturing flat panel displays, Li-ion secondary batteries, and fuel/solar cells. Among the coating processes, the slot coating with high precision and fast processing time has been importantly applied. This process also can manufacture the multi-lane coated products by implementing the stripe shim inside the slot die. The most significant task in this process is to uniformly coat various liquids onto the web or substrate without any defects by controlling rheological aspects of liquids and die internal/external designs. It is the goal of this study to theoretically and experimentally investigate flow dynamics of non-Newtonian shear thinning liquids in stripe slot coating, especially focusing the effect of rheological property and shim configuration. Especially, three-dimensional calculations of both inside die and coating bead flow regions have been conducted to scrutinize flow characteristics and multi-lane coated patterns of Newtonian (a mixture of glycerin and water) and non-Newtonian liquids (a mixture glycerin and water with xanthan), using Fluent CFD solver. Also, operability coating windows, demarcating leaking and bead breakup defects from the uniform state, have been established.

Wednesday 5:30 Salons Fontaine C-H PO98

Rheology and stability of waterborne nanoparticle dispersions for paper coating

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The processing of coating formulations onto the papermachine are characterized by the occurrence of high shear rates ranging from 10,000 s^{-1} (size press coater) over 100,000 s^{-1} (rod coater) to over 500,000 s^{-1} (blade coater). We have previously illustrated that organic nanoparticles in aqueous dispersion can be favourably used for the functionalization of paper surfaces with a nanostructured coating. The synthesis conditions for the nanoparticle dispersions were optimized to provide aqueous dispersions with solid content of 35 to 65 wt.-% and appropriate viscosity. Although the nanoparticles provide hydrophobic properties, they are fully stabilized in an aqueous environment without using supplementary surfactants, due to close control of the synthesis conditions. However, problems in stability of the nanoparticle dispersion can be expected under extremely high coating speed conditions, leading to eventual splitting of a continuous coating film due to shear thinning. In order to provide application procedures for the nanoparticle dispersion that are compatible with the paper coating process and the nanoparticle dispersion, this study focusses the determination of an optimum processing window by further rheological characterization of nanoparticle dispersions. Therefore, different coating compositions were evaluated and under various conditions of shear rates, using different types of rheometers. Under different testing conditions, the range of linear response was first determined. The special case of rheograms for colloids with high solid contents provide different characteristic behaviours as a function of shear rate, including shear thinning, a Newtonian plateau, dilatancy or shear thickening and finally second shear thinning effects at extremely high shear rates.

Wednesday 5:30 Salons Fontaine C-H PO99

Extrusion of plastic scintillators with high fluorescent dopant loading

Pascale Meysing[1], John R. Dorgan[1], Adam Mahl[2], and Uwe Greife[2]
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Plastic scintillators used to detect nuclear radiation can be produced by adding large concentrations of the fluorescent compound 2,5-diphenyloxazole (PPO) in common plastics. The impact on rheological properties of the incorporation of PPO in concentrations up to 20 wt.% in polystyrene and polycarbonate was investigated. The glass transition temperature of the blends is reduced by up to 30°C by PPO incorporation. Master curves of the rheological properties were created using the principle of time-temperature superposition over a wide range of shear rates and the viscosity function was fitted to the Carreau Yasuda model. Determination of the rheological properties serves as a basis for developing extrusion processes needed to produce low-cost, high volume detectors for homeland security applications.

Wednesday 5:30 Salons Fontaine C-H PO100

Capillary imbibition of a yield stress fluid

Catherine Barentin and Baudouin Géraud
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We study the capillary imbibition of a complex fluid which is here a simple yield stress fluid. Using a relevant set up, we show that the knowledge of the final imbibition height allows measuring both the values of the surface tension and the yield stress. These measurements can also give information about the flow boundary conditions. The imbibition height of complex fluid is indeed strongly affected by the existence or not of slippage, which is directly linked to the roughness of the capillary walls. More other, we show that the imbibition's dynamic allows giving relevant rheological information, in particular in the limit of low shear rates. To summarize, the important results of our study is that, contrary to simple fluids, the final imbibition height of yield stress fluids corresponds to a dynamical arrest, depends strongly on the wall roughness and does not depend on the capillary gap in the limit of high yield stresses.

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Plenary Lectures and Award Presentation

Monday, October 14 *8:30 AM, Westmount*	**Rheology of cellulose hydrogels** Theo van de Ven[1], Leila Jowkarderis[2], and Reghan Hill[2] *[1]Chemistry and [2]Chemical Engineering, McGill University*
Tuesday, October 15 *Bingham Lecture* *8:30 AM, Westmount*	**Power-law gels, Scott-Blair and the fractional calculus of soft networks** Gareth H. McKinley *Hatsopoulos Microfluids Laboratory, MIT*
Wednesday, October 16 *8:30 AM, Westmount*	**Rheological characterization of polymer nanocomposites** Pierre Carreau *Chemical Engineering, École Polytechnique de Montréal*
Thursday, October 17 *Metzner Award Presentation* *8:00 AM, Westmount*	**Active matter: Suspensions of self-propelled particles** Patrick T. Underhill *Chemical and Biological Engineering, Rensselaer Polytechnic Institute*

Social Program

Sunday, October 13	**Welcoming Reception** 6:30 PM – 8:30 PM *Hosted by TA Instruments*	Salon Bonaventure (lobby level)
Monday, October 14	**Industry/Faculty/Student Forum and Mixer** ***Rheology in the Real World*** 6:00 PM – 7:30 PM	Salon Lachine
Tuesday, October 15	**Society Business Meeting** 12:05 PM	Salon Westmount
	Awards Reception 7:00 PM – 8:00 PM *Sponsored by a generous contribution from Xpansion Instruments*	Salon Bonaventure (lobby level)
	Awards Banquet 8:00 PM	Outremont Ballroom (lower level)
Wednesday, October 16	**Poster Session Reception** 5:30 PM – 7:30 PM *Sponsored by a generous contribution from Anton-Paar USA* *Poster competition prizes are sponsored by the Canadian Society of Rheology.*	Salons Fontaine C-H (lower level)

The Society gratefully acknowledges the generous support of
Anton-Paar USA, TA Instruments, Xpansion Instruments
and the Canadian Society of Rheology.