

Day 1: OIST (Day) and Seaside House (Evening)

INTERFACE AND INSTABILITIES

Two-dimensional foam under shear: bubble migration, size segregation and evolving rheology

James J. Feng

Department of Chemical and Biological Engineering and Department of Mathematics, University of British Columbia, Canada

In this talk I will describe experiments on two-dimensional bidisperse and polydisperse foams sheared in a Couette device. The bubbles tend to segregate according to their size, with larger ones in the middle of the gap and smaller ones closer to the walls. To explain this behavior, we first study the migration of a single large bubble in a sea of small monodisperse bubbles. Treating the small bubbles as an effective continuum, we find that the Chan-Leal theory for lateral migration of drops can be adapted to predict the bubble migration in our sheared foam. Furthermore, the theory can be applied to bidisperse foams, where the larger bubbles also interact among themselves. Modeling this interaction as an effective diffusion, we are able to predict the observed bubble distributions accurately. We also observed, somewhat to our surprise, that the size-based segregation always results in a decrease in the apparent shear viscosity for the foam, regardless of the initial morphology. Finally, we probe the effects of the foam rheology in a wide-gap Couette device. Generally, shear-thinning pushes a large bubble inward, whereas the first normal stress difference does the opposite. The bubble migration is governed by this competition.

Asphaltenes at oil-water interfaces and their role in coalescence

Maria Merola¹, Simone Bochner², Gerald Fuller², Dimitris Vlassopoulos¹

¹ *FORTH and University of Crete, Institute of Electronic Structure & Laser, Heraklion, Crete, Greece*

² *Stanford University, Department of Chemical Engineering, Stanford, CA, USA*

Using a combination of interfacial tensiometry, interfacial rheology, scattering characterization and microscopy-based droplet coalescence and film drainage measurements, we explore systematically the role of asphaltenes at the oil/water interface. We find that, with increasing concentration of deposited material, asphaltenes aggregate and form stiff layers that hinder coalescence of water drops. However, at high concentrations coalescence is promoted at long aging times, hence allowing to tune this process. We believe that the formation of microemulsion droplets (apparently due to spontaneous curvature) and reorganization of asphaltenes in the bulk and at the interface are at the origin of this unexpected phenomenon.

Properties of self-propelled droplets in a Leidenfrost state on liquid substrates

S. D. Janssens,^{1, 2, a} S. Koizumi,^{1, 3} and Eliot Fried²

1)National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

2)Okinawa Institute of Science and Technology Graduate University (OIST), Tancha, Onnason, Okinawa 904-0495, Japan

3)Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), c/o AIST, Tsukuba, Ibaraki 305-8568, Japan

It is demonstrated that non-coalescent droplets of acetone, methanol, and ethanol can be formed on liquid substrates. The fluid flows around and in an acetone droplet hovering on water are recorded to shed light on the mechanisms which might lead to non-coalescence. For sufficiently low impact velocities, droplets undergo a damped oscillation on the surface of the liquid substrate but at higher velocities clean bounce-off occurs. Comparisons of experimentally observed static configurations of floating droplets to predictions from a theoretical model for a small non-wetting rigid sphere resting on a liquid substrate are made and a tentative strategy for determining the thickness of the vapor layer under a small droplet on a liquid is proposed. This strategy is based on the notion of effective surface tension. The droplets show self-propulsion in straight line trajectories in a manner which can be ascribed to a Marangoni effect. Surprisingly, self-propelled droplets can become immersed beneath the undisturbed water surface. This phenomenon is reasoned to be drag-inducing and might provide a basis for refining observations in previous work.

The stabilizing effect of shear thinning on the onset of purely elastic instabilities in serpentine microflows

Laura Casanellas, Manuel A. Alves, Robert J. Poole,^d Sandra Lerouge and Anke Lindner

We determine both experimentally and numerically the onset of elastic flow instabilities in viscoelastic polymer solutions with different levels of shear thinning. Previous experiments realized in microfluidic serpentine channels using dilute polymeric solutions showed that the onset of elastic instabilities strongly depends on the channel curvature. The scaling dependence is well captured by the general instability scaling criterion proposed by Pakdel and McKinley [Phys. Rev. Lett., 1996, 76, 2459:1–4]. We determine here the influence of fluid shear thinning on the onset of such purely-elastic flow instabilities. By testing a set of polyethylene oxide solutions of high molecular weight at different polymer concentrations in microfluidic serpentine channels we observe that shear thinning has a stabilizing effect on the microfluidic flow. Three-dimensional numerical simulations performed using the White–Metzner model predict similar trends, which are not captured by a simple scaling analysis using the Pakdel–McKinley criterion.

Flow of wormlike micellar solutions around confined microfluidic cylinders

Ya Zhao,¹ Simon J. Haward,² & Amy Q. Shen²

Department of Mechanical Engineering, University of Washington, WA 98195, USA

Wormlike micellar (WLM) solutions are frequently used as fracture and proppant-carrying fluids in enhanced oil and gas recovery applications in porous rock beds where complex microscopic geometries result in mixed flow kinematics with strong shear and extensional components. Experiments with WLM solutions through model microfluidic porous media have revealed a variety of complex flow phenomena that can occur under such conditions, including the formation of stable gel-like structures known as a Flow-Induced Structured Phase (FISP). Such microstructural transitions undoubtedly play an important role in applications of WLM fluids, but are still poorly understood. An important first step in understanding flows of WLM fluids through porous media can be made by examining the flow around a single micro-scale cylinder aligned on the flow axis. Here we study flow behavior of an aqueous WLM solution consisting of cationic surfactant cetyltrimethylammonium bromide (CTAB) and a stable hydrotrope 3-hydroxy naphthalene-2-carboxylate (SHNC) in microfluidic devices with three different cylinder blockage ratios, β . Flow of WLM solutions around confined cylinders results in the onset of a sequence of low Re flow instabilities, which depend on both Wi and β . Instabilities upstream of the cylinder are associated with high stresses in fluid that accelerates into the narrow gap between the cylinder and the channel wall, while upstream vortex growth is reminiscent of that seen in microfluidic contraction geometries. Instabilities downstream of the cylinder are associated with stresses generated at the trailing stagnation point and the resulting flow modification in the wake, coupled with the onset of time-dependent flow upstream and the asymmetric division of flow around the cylinder.

Heat Transfer Recovery on a Surfactant Drag-Reducing Flow

^{1*}Hiroshi Suzuki, ²Ruri Hidema and ¹Yoshiyuki Komoda

¹*Complex Fluid and Thermal Engineering Research Center (COFTEC), Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan*

²*Complex Fluid and Thermal Engineering Research Center (COFTEC) Organization of Advanced and Integrated Reseach, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan*

Drag reduction technologies with surfactants in water have been utilized in district heating/cooling systems, building air-conditioning systems and so on, because some kinds of surfactants can reduce at maximum 80 % drag in a pipe flow. However, the heat transfer in a heat exchanger is also reduced. This problem severely affects the design of the heating/cooling applications. Surfactant drag reduction is caused by the formation of rod-like micelles and of the higher-order structures of them and the heat transfer recovery is caused by the same reason. One of ideas is that the heat transfer recovery can be obtained when the rod-like micelles are broken at the inlet of the heat exchangers. When the re-formation time of the rod-like micelles is enough long, the heat transfer can be recovered in the heat exchanger and the drag reduction occurs in a pipe for transporting the heat media. In order to find the surfactants, which have long formation time after broken-up, the effects of hydrophilic head of surfactant molecules on the formation time of rod-like micelles have been investigated. The rod-like micellar structures were also researched by use of a fluorescence probe method. From the results, a large hydrophilic surfactant is found to be easily broken and to have a long formation time of rod-like micelles. It was also found from the fluorescence probe method that the number of counter-ion composing rod-like micellar structure is small in the case of large hydrophilic head, due to the structural disturbance. The

other idea for the heat transfer recovery is the method using the viscoelasticity of the surfactant drag-reducing fluid. Generally, heat transfer promoters like ribs are mounted on the heat transfer walls in order to expand the heat transfer surfaces. In such a complex flow path, there exist cavities where the heat transfer coefficient is low in cases when Newtonian fluid is used. On the other hand, the viscoelastic fluid shows the Barus effect at a sudden expanded flow path like cavities. Thus, the flow deeply penetrates into the cavity and the effective heat transfer surface can be expanded. In order to investigate the present heat recovery method by using Barus effect of surfactant drag-reducing fluid, which has strong viscoelasticity, heat transfer and flow visualization experiments and numerical computations have been performed. It was found from the results that the heat transfer coefficients in cavities when the viscoelastic fluid is used shows larger values than those in the case of water in a range of low Reynolds number. However, the pressure loss was found to show the much higher values compared with those in cases of water. On the other hand, a certain unique flow in the mid-range of Reynolds number, called bulge structure in ICR, was found in the cavity. In this stage, it has not yet unknown that the structure is effective for heat transfer recovery of the drag-reducing flow, but will be reported here.

Day 1: OIST and Seaside House

COLLOIDAL SYSTEMS AND MICROSTRUCTURE FORMATION

(Hydro)Dynamics of camphor boats at air-water interfaces.

M. Bandi

Okinawa Institute of Science and Technology Graduate University, Japan

Camphor is a waxy hydrocarbon that forms a loose van der Waals solid and undergoes sublimation at room temperature. When a camphor tablet is introduced at the air-water interface, camphor spreads radially outwards on the surface and locally reduces surface tension. When the axisymmetric spreading of camphor is distorted by ambient fluctuations, the surface tension gradients sharpen and impart a force to the camphor particle which propels itself like a boat over the air-water interface. Since its first recorded observations in 1686, this curious phenomenon has attracted the attention of many scientists including Volta, Franklin, Venturi, Biot and Lord Rayleigh. Despite this rich history, camphor boats still afford many puzzles relevant in the modern context of Hydrodynamics (viscous marangoni propulsion), Statistical Mechanics (Active Matter), and Biology (Chemomechanical transduction in biological and molecular motors).

In this talk, I will explain two experiments we performed to understand the self-propulsive mechanics of camphor boats. The first experiment was performed on a stationary camphor boat held rigid to study the initial (transient) and later (steady-state) interfacial camphor spreading dynamics. Despite not being a surfactant, the radial front $R(t)$ of camphor initially spreads with time as $R(t) \sim t^{0.5}$, just like volatile surfactants. The camphor spreading eventually approaches a steady-state condition where the camphor influx from the tablet onto

the surface is balanced by its outflux via bulk dissolution. Liquids spreading at air-water interface where bulk diffusion is as dominant as surface spreading predict a steady state radial velocity profile $u(r) \sim r^{2/3}$. In contrast, we experimentally observe $u(r) \sim r^{3/5}$ profile for the steady-state radial velocity, which can only be explained if surface spreading dominates over bulk dissolution. Our theoretical, numerical and experimental results strongly indicate there may be substances like camphor, which albeit not being surfactants, do possess a strong affinity for interfaces which renders them surface active in a non-traditional sense.

In the second experiment, we studied the self-motion of a free camphor particle. We observe three distinct modes of motion: a harmonic mode where the boat velocity varies sinusoidally, a continuous mode where boat velocity is constant, and a relaxation oscillation mode where the camphor boat remains static for a while before suddenly jumping to a new position. Whereas several studies have reported each of these modes separately, we experimentally show all three modes are part of a common description. The modes arise from a mismatch between the marangoni force that drives the camphor boat and the viscous drag force which inhibits the motion.

Hydrodynamics of copepod locomotion, feeding, and sensing

Daisuke Takagi, University of Hawaii

Marine animals generate diverse and intriguing flows which are sources of inspiration for soft matter research. Copepods, arguably the most numerous animal group on the planet, have developed remarkable adaptations in form and behavior that are needed to survive in challenging marine habitats. In this talk I present how these tiny organisms can effectively swim, feed, and sense through microscale flows. Theoretical and experimental studies reveal that copepods are well-adapted to rapidly escape from predators and capture food particles in dilute suspensions. The design principles in nature could be applied to novel sensors and actuators in technological applications.

Steady and transient rheology of Graphene Oxide solutions

F. Del Giudice¹, B. Cunning^{2,3}, Rodney S. Ruoff^{2,3,4}, A.Q. Shen¹

¹*Okinawa Institute of Science and Technology Graduate University, Japan*

²Center for Multidimensional Carbon Materials, Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea

³Department of Chemistry and School of Materials Science and Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

Graphene Oxide (G-O) dispersions in water are aqueous suspensions containing chemically modified graphene sheets. G-O sheets or aqueous G-O dispersions have been used for studies of hydrogen storage, sensing, and biomedical applications, among many others. Understanding the rheological behavior of aqueous (and other) G-O dispersions is fundamentally interesting and also important for certain applications. However, conflicting

reports of rheological behavior of G-O dispersions have recently appeared in the literature. We present preliminary results from shear and transient rheology of aqueous G-O dispersions at several mass concentrations. Bulk rheology measurements were conducted with both glass parallel plates and Couette geometries. Steady shear rheology suggests the presence of a yield stress at G-O concentration $c > 0.04\%$ w/w. By using the Couette geometry, a flow-induced instability is observed at various shear rates, the nature of which is not clear yet. Transient rheology of G-O dispersions, at low imposed shear rate and in parallel plates, shows that the shear viscosity does not reach a steady-state value in two to ten hours. These time scales are much longer than those usually considered for steady-state measurements of shear. Furthermore, steady shear measures cannot be considered as a trustworthy index for the material characterization, particularly at low shear rate. Transient measurements in the Couette configuration show that flow-induced instabilities disappear over time.

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Patterning surfaces with colloid-bottlebrush polymer suspensions

Michel Cloitre¹, Charlotte Pellet¹, Jean-Marc Suau²

¹ Soft Matter and Chemistry, CNRS, ESPCI Paris, PSL Research University, 10 rue Vauquelin, 75005 Paris, France

² Coatex SAS, 35 Rue Ampère, 69727 GENAY, France

The deposition of colloidal particles from liquid droplets on solid substrates is a widespread surface technology for fabricating biological, electronic or optical devices. One current limitation is the difficulty to achieve uniform patterns during solvent evaporation because the particles tend to accumulate at the droplet periphery resulting in a ring-like morphology, known as the coffee-ring effect [1]. Recently the origin and modeling of the coffee ring effect have stimulated a lot of research [2] but its suppression remains an important challenge for applications.

We describe a new method for inhibiting coffee ring defects in colloidal suspensions using bottlebrush polymers as additives. The bottlebrush polymers we use consist of a highly charged polyelectrolyte backbone and hydrophilic pendant chains densely tethered to it. This specific architecture confers remarkable rheological properties to bottlebrush solutions: low viscosity up to high concentrations, insensitivity to pH and ionic strength variations. When added at extremely low concentrations to colloidal calcium carbonate suspensions, bottlebrush polymers totally suppress the coffee ring effect and produce very uniform defect-free patterns [3]. We will present the new mechanism which is at the origin of coffee ring inhibition by bottle brush polymers and discuss the applicability of the method to other colloidal suspensions.

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[3] C. Pellet, “Nouvelles fonctionnalités de copolymères en brosse dans les suspensions minérales concentrées”, PhD Thesis, Université Pierre et Marie Curie, 2015.

RHEOLOGY AND DYNAMICS OF COMPLEX FLUIDS

“3D printing with polymers”

Peter Olmsted

Georgetown University

3D printing, also known as Additive Manufacturing, is rapidly growing in multiple areas of manufacturing. Despite intense activity using entangled polymers, there has been very little scientific study of the process, and in many cases the produced parts have poor mechanical properties. I will present a study using the Rolie-Poly model of the extrusion and cooling process that underlies “fused filament fabrication”, also known as “fused deposition modeling”, which will eventually help understand the welding of filaments and eventually lead to improved materials” .

Dynamics of semidilute polymer solutions

J. Ravi Prakash

Monash University, Melbourne, Australia

Many important phenomena in both industrial and biological contexts involve semidilute polymer solutions. However, the behaviour of polymer solutions is presently well understood only in the dilute and concentrated solution limits. I review the investigations of the dynamics of semidilute solutions of DNA in our group, through experiments and computer simulations, over the past few years. The experiments probe the linear and non-linear viscoelastic behaviour in a wide range of molecular weights (25-289 kilobasepairs), temperatures and concentrations. The dependence of the zero shear rate viscosity on concentration is observed to display universal behaviour that can be understood within the framework of the blob theory for semidilute polymer solutions. Further, the shear rate dependence of viscosity at various temperatures and concentrations can be collapsed onto master curves when understood in terms of a relaxation time that depends on concentration. Computational prediction of the static and dynamic properties of semidilute polymer solutions requires the simulation of a large system of polymer chains interacting with each other through excluded volume and hydrodynamic interactions. We describe the development of a Brownian dynamics simulation algorithm that uses a fast implementation of the Ewald summation method to predict the behaviour of flowing polymer solutions at finite concentrations. In particular, we use the algorithm to study the existence of non-monotonic coil-stretch hysteresis with varying concentration, and to examine the response of single chains in a semidilute solution when subjected to a step-strain deformation followed by cessation of flow. A systematic comparison of simulation predictions is carried out with the experimental observations of Sridhar’s group on semidilute polystyrene solutions undergoing uniaxial

extensional flow in a filament stretching rheometer, and with the observations of Schroeder's group, who have recently used single molecule techniques, in the context of semidilute solutions flowing in a cross-slot cell, to investigate the stretch-relaxation of individual λ -phage DNA chains.

Viscoelastic properties of supramolecular polymer melts end-functionalized with coordinative interactions

F. Zhuge, J-F Gohy, E. van Ruymbeke

*Institute of Condensed Matter and Nanosciences (IMCN), Bio and Soft Matter Division (BSMA),
Université catholique de Louvain, Belgium.*

We study the linear viscoelastic properties of a series of low dispersity index poly (*n*-butyl acrylate) chains end-functionalized with 2,2',6',2"-terpyridine, able to self-associate by metal-ligand coordination. Depending on the architecture and topology of the chains, the polymers with low dispersity index ($\mathcal{D} < 1.3$) can self-assemble and form metallo-supramolecular structures in the melt state once metal ions are added. For linear chains (mono-functional or bi-functional), the polymers form longer chains. For four-arm star chains, the polymers form a network. The properties of obtained materials can be tuned depending on the length of the polymer chains and the type of metal. In this respect, a good control is gained over the dynamics of this class of metallo-supramolecular terpyridine functionalized networks. We then develop a tube-based model in order to describe their viscoelastic behavior and to further understand how association dynamics and disentanglement dynamics interact in the relaxation of these supramolecular networks.

EVENING SESSION

Evolution of miscible liquid sessile and pendant drops

Daniel J. Walls, Simon J. Haward, Amy Q. Shen, and Gerald G. Fuller

Miscible liquids commonly contact one another in natural and technological situations in the form of sessile and pendant drops. In the sessile case, where a drop of one liquid finds itself on a solid surface and immersed within a second, miscible liquid, it will spread spontaneously across the surface. We show experimental findings of the spreading of sessile drops in miscible environments that have distinctly different shape evolution and power-law dynamics from sessile drops that spread in immiscible environments, which have been reported previously. We develop a characteristic time to scale radial data of the spreading sessile drops based on a drainage flow due to gravity. This time scale is effective for a homologous subset of the liquids studied. However, it has limitations when applied to significantly chemically different, yet miscible, liquid pairings; we postulate that the surface energies between each liquid and the solid surface becomes important for this other subset of the liquids studied. Experiments performed with pendant drops in miscible environments

support the drainage flow observed in the sessile drop systems. The result is a remarkable “jetting” phenomena where the droplet volumes diminish exponentially in time.

Quantitative MODELING of The Extensional Rheology of saliva using a sticky Finitely extensible network (SFEN) model

Caroline E. Wagner, Gareth H. McKinley, Hatsopoulos Microfluids Laboratory, Dept. Mechanical Engineering, Massachusetts Institute of Technology

There is increasing interest in using rheological measurements of saliva and other bodily secretions such as cervical and respiratory mucus as non-invasive diagnostics for pathology and disease. However, there is only limited literature available on the shear and extensional rheology of saliva, and nearly no consideration of its temporal stability in the face of enzymatic degradation. Indeed, capillary breakup extensional rheometry (CaBER) data of saliva samples at various ages shows that both the time to breakup and relaxation time of these highly elastic but low viscosity aqueous solutions decrease as a function of age. The viscoelastic properties of saliva can primarily be attributed to the presence of large glycoproteins (MUC5B mucins) in solution. It is well known that these ‘MUCmers’ physically associate and interact with each other and their surroundings via disulphide linkages, ion-mediated crosslinking and hydrogen bonding interactions to form a very weak hydrogel or ‘pre-gel’. This motivates the development of a Sticky and Finitely Extensible Network (SFEN) model for mucin-containing solutions. Building on earlier work of Tripathi et al [1] for synthetic HEUR associative polymer systems, the mucin macromolecules are modeled as a semi-dilute and semi-flexible network of physically-associated finitely extensible elastic segments. The resulting SFEN model features a new stretch-dependent ‘stickiness’ energy parameter that must be overcome in order for the chains to be able to reversibly dissociate from the rest of the network under imposed deformations. The model predicts an initial strain-hardening response in the transient extensional rheology followed by a sudden extensional-thinning and filament rupture as the chains approach their maximum extensibility and the tensile force between the junction points increases rapidly. We show that this model is able to accurately capture the capillary thinning and breakup behaviour of saliva using parameters that respect the known dimensions and properties of the mucin network, and can systematically account for temporal changes in the rheology through a progressive decrease in the molecular weight of the MUC5B chains.

[1] Tripathi, A., Tam, K.C. and McKinley, G.H., Rheology and Dynamics of Associate Polymer Solutions in Shear and Extension: Theory and Experiments, *Macromol.*, (2006), 39(5), 1981-1999.

Day 2: Seaside House

INTERFACE AND INSTABILITIES

Fracture in Polymeric Liquids

Ole Hassager

Understanding the mechanism of fracture is essential for material and process design. While the initiation of fracture in brittle solids is generally associated with the preexistence of material imperfections, the mechanism for initiation of fracture in viscoelastic fluids, e.g., polymer melts and solutions, remains an open question. We use high speed imaging to visualize crack propagation in entangled polymer liquid filaments under tension. The images reveal the simultaneous propagation of multiple cracks. The critical stress and strain for the onset of crack propagation are found to be highly reproducible functions of the stretch rate, while the position of initiation is completely random. The reproducibility of conditions for fracture points to a mechanism for crack initiation that depends on the dynamic state of the material alone, while the crack profiles reveal the mechanism of energy dissipation during crack propagation.

Elastically driven, intermittent microscopic dynamics in soft solids

Emanuela Del Gado

Soft amorphous solids such as particle gels tend to undergo a progressive aging over time, due to microscopic ruptures and rearrangements of their structure, with dramatic impact on the material properties. Contrasting behaviors have been observed in experiments, which detect in similar materials a slow, continuous evolution or instead sudden, fast rearrangements. Our computational study unravels that the fast, sudden rearrangements are the signature of large enthalpic stresses frozen-in, during solidification, in the microscopic structure of the material. In these conditions, exceedingly long time is required to relax stresses through thermal fluctuations and the microscopic ruptures and rearrangements underlying the aging are dominated by the elasticity stored in the material structure, which produces intermittent and strongly correlated dynamics.

Grain boundary kinetics during crystallization in magnetic colloidal monolayers

Ryohei Seto, An T. Pham, Benjamin B. Yellen, Eliot Fried
(OIST and Duke University)

A binary mixture of magnetic and nonmagnetic colloids in ferrofluid is rapidly cooled to a certain effective temperature by controlling an applied uniform magnetic field. Although the system favors a checker board lattice configuration below a certain critical temperature, nonmonotonic growth processes are observed due to grain boundary formation. Brownian simulations including magnetic dipole-dipole interactions can capture this crystallization process well. We study particle-scale processes associated with the formation and evolution of grain boundaries in an effort to understand such nonmonotonic crystallization.

Numerical portrayal of elastic flow instability, its possible remedy and a route to chaos with emphasis on melt fracture

Youngdon Kwon

*School of Chemical Engineering, Sungkyunkwan University
300 Cheoncheon-dong, Jangan-gu
Suwon, Gyeonggi-do 440-746, Korea*

Employing a finite element numerical scheme implemented onto the Leonov model for viscoelastic liquid, we describe various 2D elastic flow instabilities with particular emphasis on melt fracture for the extrudate exiting from the Poiseuille flow. This numerical approximation is shown to be possible, when a mathematically appropriate (evolutionary) constitutive equation is incorporated into the straightforward computation scheme (with no upwinding) with the tensor-logarithmic formulation. For robust computational modeling of various unstable flows such as vortex oscillation in contraction channel and unstable flow over a circular cylinder, the mathematical well-posedness (dissipative as well as Hadamard stability) of equations is proven crucial. According to this, the numerical scheme has to be consistently chosen (the direct mixed formulation without any algorithm of numerical diffusion may only be relevant at present). In examining planar extrudate flow from the contraction channel, four types of instability such as sharkskin, gross melt fracture, slow surface undulation and ripples are found, where each type of extrudate distortion is verified to result from the different cause, and thus geometric singularities and streamline vortices at die exit as well as contraction corner determine its specific type. In order to simplify the origin of melt fracture, we have considered the flow from the straight channel as well, in which the finite curvature of streamlines at the die lip solely incurs the extrudate instability. In this case, the melt fracture exemplifying typical sharkskin becomes exhibited as a Hopf bifurcation from steady symmetric into periodic symmetry-breaking flow dynamics at the critical Deborah number. As the Deborah number further increases, the flow dynamics attains a quasi-periodic or chaotic state. A possible remedy for the sharkskin is also suggested and demonstrated with numerical simulation.

RHEOLOGY AND DYNAMICS OF COMPLEX FLUIDS

Non-linear stress relaxation behavior of long chain polymer network and orientability of UHMWPE gels

Siu Yeung CHEUNG^a, Runlai Li^a, Weijia WEN^b and Ping GAO^a

^a *Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

^b *Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

The objective of this paper is to investigate the effect of microstructure on the ultimate molecular orientability of UHMWPE/petrolatum gel-precursors. Gel-fibers with and without extended fiber crystals prior to semi-solid state drawing were prepared by a model setup analogous to the gel-spinning die draw process. It was observed that the tensile strengths of the gel-fibers prepared from isotropic gel fiber precursors are 400% higher than those prepared from precursor fibers containing fiber crystals prior to gel crystallization. For example, we successfully prepared 10% UHMWPE/petrolatum gel fibers with tensile strength and young's modulus in excess of 600 MPa and 30 GPa, respectively from the initially isotropic gel fiber precursors. Full orientability recovery was observed upon melt annealing at temperatures higher than the fiber crystal melt transition temperature.

In order to elucidate the mechanisms of the observed orientability differences, we have carried out non-linear viscoelastic characterizations on the UHMWPE/petrolatum gels. It was observed that these gels exhibit an unusual stress relaxation behavior. A transient, but absolute plateau region after the imposition of a non-linear step strain was observed, and the magnitude of the plateau modulus is independent of temperature but decreases exponentially with increasing strain amplitude. In the meantime, the longevity of the plateau region increases with decreasing temperature. By invoking the cohesive entanglement concept originally proposed by Qian *et al.*,¹ we are able to model the newly observed stress relaxation behavior successfully. The pseudo-liquid crystalline interactions/or cohesive entanglement structures are locked into the fiber crystals upon melt drawing and lead to reduced drawability in the semi-solid state which is analogous to that of the main chain thermotropic liquid crystalline polymers.

References:

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Orientalional cross correlation in entangled polymers

Yuichi Masubuchi,

Nagoya Univ., Japan

Although it has not been frequently discussed, contribution of orientational cross correlation between chains (OCC) is significant in relaxation modulus of entangled polymers. Following the earlier study for the bead-spring simulation [1], we have investigated the OCC contribution in relaxation modulus using multi-chain slip-link simulations. It has been found that i) the amount of OCC contribution is almost independent of the molecular weight [2] and the long-chain branching of polymers [3], that ii) the OCC is affected by the density fluctuation of entanglement segment [4] and that iii) the time development of OCC may be varied by the molecular weight distribution [5].

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EVENING SESSION

Shear thickening in colloidal dispersions: colloidal hydrodynamics, dilatancy and/or friction

Norman J. Wagner,

University of Delaware

Reversible shear thickening is ubiquitous in stable colloidal suspensions and is marked by an increase in viscosity with shear rate at relatively high shear rates. Shear thickening colloidal suspensions have found application in a broad range of personal protective materials, such as: ballistic and multi-threat armor, impact protective materials, puncture resistant gloves, protection from micrometeoroids and orbital debris in space applications, and dynamic ligaments for biomedical devices. This wealth of applications necessitates formulating shear thickening fluids to meet specific performance requirements, which requires a quantitative understanding of the relationships between the rheological properties and the physiochemical properties of the particles and suspending fluid. These properties include: particle size, shape and polydispersity, nanoscale surface properties, interparticle interactions, and suspending media viscosity, as well as the presence of any additives such as surfactants or polymers, which may adsorb onto the particles. However, the development of quantitative, predictive relationships first requires understanding the physical mechanism responsible for the shear thickening viscosity. This presentation provides a summary of how measurements of suspension rheology can be used to distinguish between various mechanisms proposed for shear thickening in colloidal dispersions. Importantly, qualitative differences in the sign of the material functions corresponding to the first and second normal stress differences are shown to be sufficient to distinguish among various, dominant mechanisms. Direct measurements of the microstructure in the shear thickened state validate simulations and theory developed to explain these differences.

The Many Faces of Long End-Associative Polymers

Julie Kornfield, Caltech

We have been surprised in the course of our work on the rheology of long flexible chains with “sticky” ends (capable of hydrogen bonding). With backbones having at least 2000 backbone atoms (>260 Kuhn steps), the polymers we study are much longer than previously examined end-associative polymers (less than 400 backbone atoms (< 20 Kuhn steps)). Furthermore, we employ a highly flexible backbone, so that the individual chains contain many Kuhn steps (>260 , in contrast to prior literature <20) and many multiples of the melt entanglement molecular weight (≥ 14 , in contrast to prior literature ≤ 2). Simply using carboxylic acid groups and tertiary amine groups, we discovered a rich variety of behaviors in the melt and in solution. I’ll show melts with “truncated star-like” relaxation (with data from Akira Takagi of Taogosei and insights from Hiroshi Watanabe of Kyoto U.), solutions that behave like flow-like micelle networks and others that behave like entangled solutions. I look forward to discussing the physics and potential applications of these molecules with friends in the relaxing atmosphere of the Okinawa conference.

Day 3: Seaside House

MEASUREMENT AND MODELING TECHNIQUES

Moving from Time to Frequency domain without artefacts

Manlio Tassieri

Since the field of rheology was established, the frequency-dependent linear viscoelastic (LVE) properties of materials have been successfully correlated, both theoretically and experimentally, to their topological structure; from a macroscopic length scale (of the whole sample) at relatively low frequencies, down to an atomic length scale for frequencies of the order of THz. Hence, the importance of their knowledge over the widest possible range of frequencies to gain a full picture of the materials' structure.

Unfortunately, broadband rheology is still a challenge for conventional oscillatory measurements; limiting the number of explored frequencies to a few points per decade, often ranging from 0.1 to 100 Hz.

Nevertheless, wideband linear rheology is in principle still achievable if time-dependent rheological functions (e.g., the material's shear creep compliance or the mean-square-displacement of a suspended microsphere) are '*properly*' analyzed (i.e., Fourier transformed). Indeed, it has been shown that the passage from the time-domain to the frequency-domain via the Fourier transform of a finite set of data points, over a finite time domain, is nontrivial since interpolation and extrapolation from those data can yield artefacts that lie within the bandwidth of interest.

The solution to the above issue has been presented by Tassieri *et al.* [New Journal of Physics **14**, 115032 (2012)], while performing microrheology with optical tweezers of complex fluids. Moreover, the general validity of the proposed method has been corroborated recently by Tassieri *et al.* [J. Rheol. **60**, 649-660 (2016)], while analyzing conventional bulk rheology step-strain measurements performed on a series of complex materials having significantly different viscoelastic nature.

Onsager principle - A useful principle in soft matter dynamics -

Masao Doi

*Center of Soft Matter Physics and its Applications,
Internationa Research Center, Beihang University, Beijing, China*

In the celebrated paper on the reciprocal relation for the kinetic coefficients in irreversible processes, Onsager proposed a variational principle which holds for general irreversible processes[1]. It has been shown that many basic equations used in soft matter physics, Stokes equation for Newtonian fluid, Smoluchowskii equation for Brownian particles, hydrodynamic equation for phase separation dynamics(model H), elasto-diffusion equation for gels, Leslie-Ericksen equation for liquid crystals, are derived from this principle[2, 3]. It

has also been shown that the principle is useful in solving practical problem [4-7]. Here I will discuss the principle in connection with our ongoing problems.

Here I discuss how to use this principle in solving practical problems.

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Advances in Large-Amplitude Oscillatory Shear Flow of Polymeric Liquids

A. Jeffrey Giacomin

*Professor of Chemical Engineering
Professor of Mechanical and Materials Engineering
Polymers Research Group
Queen's University, Kingston, CANADA K7M 4M2*

Queen's University In 1935, Andrew Gemant conceived of the complex viscosity, a rheological material function measured by "jiggling" an elastic liquid in oscillatory shear [*Rheol. Acta*, **51**, 481 (2012)]. This test reveals information about both the viscous and elastic properties of the liquid, and about how these properties depend on frequency. The test gained popularity with chemists when John Ferry perfected instruments for measuring both the real and imaginary parts of the complex viscosity ["Ferry 1912-2002 ...," *Mem. Trib., NAE*, **17**, 96 (2013)]. In 1958, Cox and Merz discovered that the steady shear viscosity curve was easily deduced from the magnitude of the complex viscosity, and today oscillatory shear is the single most popular rheological property measurement. With oscillatory shear, we can control two things: the frequency (Deborah number) and the shear rate amplitude (Weissenberg number). When the Weissenberg number is large, the elastic liquids respond with a shear stress over a series of odd-multiples of the test frequency. In this lecture we will explore recent attempts to deepen our understand of the physics of these higher harmonics.

Coarse-graining in polymer rheology

Hiroshi Watanabe

ICR Kyoto Univ.

Coarse-graining is essential in simple description of rheological properties of entangled polymers. Comparison of viscoelastic and dielectric data of polyisoprene (PI) having type-A dipoles has established the importance of consistent coarse-graining of the length and time scales in successful description of those properties. Furthermore, recent experiments suggested that entangled polymer chains have two coarse-graining length scales, one defined along the polymer chain backbone to describe the stress level, and the other, along the chain backbone to determine the relaxation time.

Macro- and microscopic observation of dissolution process of cellulose into a few different ionic liquids.

Yoshiaki Takahashi and Xu Zhe

IMCE and IGSES, Kyushu University

Dissolution process of four representative cellulose, avicel, cosmetic cotton, nadelholz sulfur pulp and linter pulp into 1-butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium acetate are compared by macroscopic and microscopic observations to seek adequate condition to obtain uniform solution without severe damage for cellulose molecules. By macroscopic observation, minimum change in color of solution denoting oxidation and/or thermal degradation and uniform appearance are examined. Microscopic observation was used to see the difference in the early stage dissolution process of different cellulose samples and to check uniformity at the local level. It seems that cotton in 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride dissolves more mildly compared to other combinations. Observation of unique swelling pattern of cotton in these ionic liquids is still under the progress.

New Numerical Algorithms for the Identification of Linear Viscoelasticity of Polymers

Kwang Soo Cho

*Department of Polymer Science and Engineering,
Kyungpook National University,
Daegu, Korea*

All experimental methods for linear viscoelasticity have their own merits and demerits in accuracy, reproducibility and window of observation. Hence, data from various kinds of measurement are mutually complemented. Although linear viscoelastic theory provides exact relations, direct application of these equations does not guarantee the conversion from the data of a viscoelastic function to others because of the finite range of observation.

This talk introduces new numerical algorithms of data conversion and model identification which have been developed by our group. The talk consists of the followings:

- (1) Why is creep test better than other tests?

- (2) How to remove the inertia effect from creep data?
- (3) Importance of Laplace transform in data conversion
- (4) Identification of recovery compliance with a single creep test
- (5) Algorithms for conversion from static to dynamic data
- (6) Algorithms for conversion from dynamic to static data
- (7) Comparison with spectrum methods

POLYMERS AND TURBULENCE

Energy cascade in Reynolds' flashes

Pinaki Chakraborty

In 1883 Osborne Reynolds discovered a peculiar state for flow of water in a pipe. This state corresponds to the transition from the quiescent, laminar state at low Re (Reynolds number, a dimensionless measure of the flow velocity) to the roiling, turbulent state at high Re. The laminar state is devoid of fluctuations; the turbulent state is inundated by a broad range of fluctuations. The transition state is distinct from the laminar and turbulent states, and consists of localized patches---"flashes"---of fluctuations. Later work unveiled many features of these flashes: they can proliferate or fade away, maintain their shape or continually expand. The nature of the fluctuations in the flashes, however, remained unknown. We conduct experiments of flow of water in a pipe and focus on the fluctuations in the flashes. Our results suggest a startling conclusion: the fluctuations in the flashes partake in the well-known Richardson-Kolmogorov energy cascade, the signature of high Re turbulent state. To wit, transition is not a distinct state: flashes are turbulent.

This research is collaborative work with Rory Cerbus, Chien-chia Liu, and Gustavo Gioia.

Vortex Deformation on Two-dimensional Turbulence Affected by Polymers

Ruri Hidema¹, Hiroshi Suzuki²

¹*Organization for Advanced and Integrated Research, Kobe University*

²*Department of Chemical Science and Engineering, Kobe University*

A drag reduction effect has been a long-standing issue. In order to consider the background mechanism of the drag reduction effect, we focus on vortex deformation in turbulence and extensional rheological properties of the fluids in this study. A flowing soap film as a two-dimensional flow was adopted to avoid shear stress effects. Vortex generation in a 2D flow was visualized and how the vortices deformed by polymer additives were analyzed. Power spectra of the visualized 2D turbulence through interference patterns and velocity fluctuation obtained by a PIV analysis revealed the variation of energy transfer in 2D flow. A wavelet analysis was used to detect the variation of vortices in time. We considered how these variations were affected by a relaxation time of sample solution, and by several extensional rates added on the flow.

FLOW-INDUCED FRICTION REDUCTION AND TUMBLING EFFECTS IN ENTANGLED POLYMERS

Giovanni Ianniruberto^a, Qian Huang^b, Salvatore Costanzo^c, Giuseppe Marrucci^a, Ole Hassager^b, Dimitris Vlassopoulos^c

^aUniversity of Naples Federico II, Dept. Chemical, Materials and Production Engineering, Italy

^bTechnical University of Denmark, Dept. Chemical and Biochemical Engineering, Denmark

^cUniversity of Crete, Dept. Materials Science and Technology, Greece

The rheology of high-molar-mass polymers in the melt state or in concentrated solutions is controlled by topological interactions among neighboring chains called entanglements. This is confirmed by the fact that monodisperse linear polymers having the same number Z of entanglements per chain exhibit the same linear viscoelastic behavior. In the nonlinear range, however, the same Z value does not guarantee the same behavior, as indeed shown by recent uniaxial extensional data on polystyrene (PS) melts and solutions [1]. One possible source for this difference is related to differences in the entanglement molar mass M_e between melts and solutions, M_e ruling the finite extensibility of subchains between consecutive entanglements [1]. Recently, however, it was argued that the different behavior between PS melts and solutions with the same Z is mostly due to flow-induced friction reduction effects, that are expected to play a more important role in melts than in solutions, since solvent molecules do not in fact feel the orienting action of the flow [2].

We here report our recent work aiming at investigating if systems with the same Z behave differently also in fast shear flows [3]. Shear flows are indeed expected to be less effective in aligning polymer molecules, and hence less prone to induce friction reduction effects. However, the rotational nature of shear flows complicates the dynamics of polymer molecules, since it induces tumbling phenomena, as revealed by recent molecular dynamics simulations [4]. We here account for tumbling effects by modifying a tube-based constitutive equation in a simple, phenomenological way.

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Effect of rain-induced turbulent dissipation on hurricane intensity

Tapan Sabuwala

Hurricanes (better known as typhoons in Japan) are one of the most potent incarnations of atmospheric convection which conjure images of gusting winds and torrential rains. Japan, located in the northwest Pacific basin which hosts some of the most intense hurricanes, often bears the brunt of these powerful storm systems. In order to reduce the devastation caused by these powerful storms, we need to better predict both the path and intensity of a hurricane. However, attempts at modelling hurricane intensity using numerical models have failed to show a sustained and significant improvement, alluding perhaps that some key processes that influence hurricane intensity remain uncharted. In this talk, I will explore the effect of one such process – the role of turbulent energy dissipation due to rain, on the intensity of a hurricane. Each falling raindrop encounters resistance from the surrounding air, which leads to turbulent eddies that are generated in the wake of a drop. These eddies lead to energy dissipation. For an average hurricane, the rate of this energy dissipation, which I call rainpower, is of the same order of magnitude as the energy consumption rate of the entire Japanese economy. I investigate the role of this rainpower on hurricane intensity using a simple heat-engine model that predicts the maximum steady-state intensity of a hurricane. I will show that inclusion of rainpower leads to a significant change in the predicted intensity which nudges the predictions closer to observed data. Based on these results, I propose that rainpower plays a significant role in the energetics of hurricanes and needs to be included in current numerical models that aim to predict hurricane intensity.

This is collaborative work with Prof. Pinaki Chakraborty and Prof. Gustavo Gioia

Exact coherent structures in purely elastic turbulence

Alexander Morozov,

University of Edinburgh, UK

Newtonian fluids are known to exhibit hydrodynamic instabilities and/or transition to turbulence at large enough Reynolds numbers. Recently it has been discovered that in simple shear flows (like pressure-driven flows in a pipe or between two plates) there exist the so-called coherent structures which organize the turbulent dynamics close to the laminar-turbulent transition. In that region, their dynamics are low-dimensional and can be described by a few (order ten) well-chosen degrees of freedom.

On the other hand, complex fluids, in general, and polymer solutions, in particular, do not flow like Newtonian fluids. Their flows exhibit instabilities at very low Reynolds numbers which are driven not by inertia, but rather by anisotropic elastic stresses. Further increase of the flow rate results in a truly chaotic flow -- the so-called purely elastic turbulence. The mechanism of this new type of chaotic motion is poorly understood.

In this talk I will discuss our recent attempts to generalise the Newtonian theory of the transition to turbulence to the purely elastic case. We identify the relevant coherent structures and construct a viscoelastic self-sustaining process that can organise flow dynamics close to the transition.

Activation Energy of Associative Polymers

Zhijie Zhang, Chang Liu, Quan Chen*

*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied
Chemistry, Chinese Academy of Sciences, Changchun 130022, China
qchen@ciac.ac.cn*

Associative polymers contain stickers that can associate with each other. The lifetime of stickers within the association can be written as $\tau_s = \tau_0 \exp(E_a/kT)$, where τ_0 is characteristic time of a Kuhn segment and E_a is the activation energy for dissociation. In literature, there are usually two types of approaches to determine E_a : The first approach is based on a delay of terminal relaxation time of the physical gel formed from the association with respect to τ_0 ; The second approach is based on the temperature dependences of terminal relaxation time, viscosity, or linear viscoelastic shift factor. Nevertheless, inconsistency is frequently seen for E_a determined from these two types of approaches. In this study, we will explain sources of the inconsistency and provide an experimental solution.