Okinawa Institute of Science and Technology Graduate University

Flow & instability of self-assembled systems

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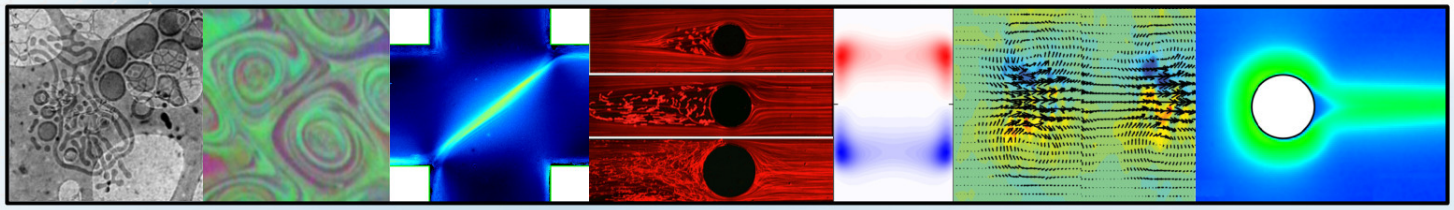
Organizers:
Amy Shen & Simon Haward



Mini-symposium

BOOK OF ABSTRACTS

Flow-induced demixing instabilities of viscoelastic multicomponent fluids

Tom C. B. McLeish

Department of Physics, University of York, Heslington, York, YO10 5DD, UK

The effect of viscoelasticity on the phase separation of binary fluids is still an unresolved challenge. Yet it is important for formulation, processing, and biophysics. The long timescales intrinsic to the fluids (high Deborah numbers of the flow) take some structural variables of the system potentially a long way from equilibrium. A two-fluid model approach within a Cahn-Hilliard framework shows that timescale mixing may occur. Model experimental results indicate that more is happening, but are challenging due to the highly anisotropic phase separated structures produced.

Flow-induced self-assembly of natural silk

Charley Schaefer

Department of Physics, University of York, Heslington, York, YO10 5DD, UK

Natural silk is a biological fibre with excellent mechanical properties that is produced from an aqueous solution of an intrinsically disordered silk protein. The transition from a viscous liquid to a high-performance solid fibre takes place while it is spewed from the gland of the animal through its spinnerette. While this is superficially a similar process as the industrial spinning of synthetic polymer fibres using elongational flow, the Bombyx Mori is remarkably more efficient in terms of both energetic costs and recycling of solvent. We investigate the underlying mechanism in a combined experimental and theoretical approach, where we view the silk protein as a sticky entangled polymer. Our findings suggest that the alignment of the intrinsically disordered protein in modest flow may be stabilised owing to the self-assembly of ionic bridges.

Flow instability of wormlike micelles as rheology modifiers

Yujun Feng

Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

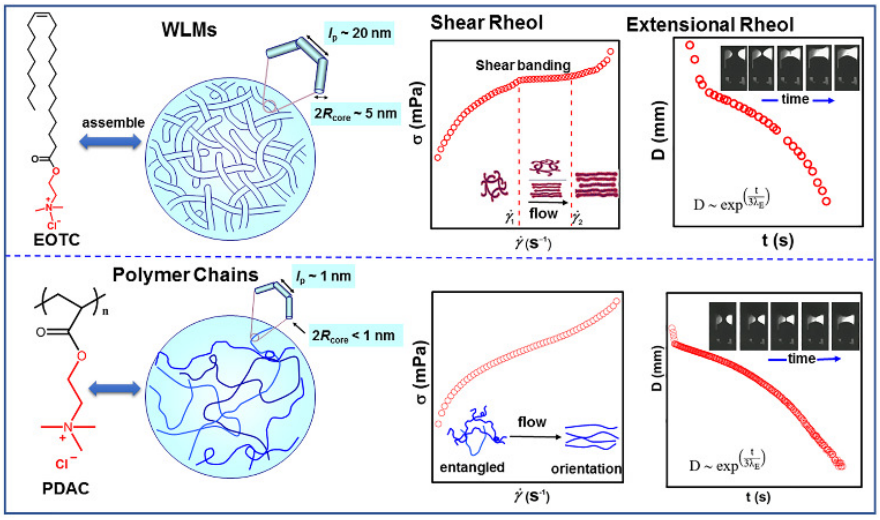
Wormlike micelles (WLMs) are typical soft materials self-assembled from surfactants in solution. Because of their peculiar viscoelastic behaviors and strong thickening capacity reminiscent of polymer solutions, WLMs have been widely used as rheology modifiers and are generally called "living polymers". However, no direct comparison between polymer solution and WLMs has been reported yet to date.

Herein, we systematically compared WLMs formed from various type of surfactants to polymers with different architectures, for example, polystyrene,[1] polyacrylamide,[2] from molecular level to macroscopic rheological response. To minimize the influence of molecular structure, more recently, we synthesized a C_{22}-tailed cationic surfactant, erucyl oxyethyl trimethylethanaminium chloride (EOTC) and a cationic polymer, poly(acryloyloxyethyl trimethyl ammonium chloride) (PDAC), both of which possess very similar molecular structure (Scheme 1). Then, the WLMs formed from EOTC without any hydrotropes and PDAC solutions were compared in terms of shear rheological behaviors, elongation properties and microstructures verified by small-angle neutron scattering (SANS).[3]

The shear rheological results demonstrated that both WLMs and PDAC showed strong thickening capacity and viscoelastic response in aqueous solution. In transient extensional experiments, filament made by WLMs or PDAC decayed exponentially with time, and showed strain-hardening behavior. These results confirmed that there are some similarities between WLMs and polymer solution, owing to the presence of three-dimensional network in both systems. However, significant differences were also evidenced from the two systems: WLMs solution showed typical characteristic of shear banding behavior, *i.e.,* the flow curve is composed of two branches corresponding to high and low viscosities separated by a stress plateau between two critical shear rates, whereas polymers did not. Moreover, extensional relaxation time (λ_E) and transient extensional viscosity (η_E) for the WLMs was significantly lower than those of PDAC. These differences were resulted from a distinct microstructural difference between flexible polymer and stiff WLMs, viz, relatively larger cross section core radius and longer persistence length in WLMs compared with PDAC. The present work can provide a guide for practical applications of WLMs and polymer. For example, compared to the stiff WLMs, the flexible polymer as rheology modifiers is especially advantageous for applications where a high elongational viscosity is required, such as ink-jet printing, fiber spinning or spray and atomization processes.

The rheological difference between WLMs and polymers is resulted from their microstructures in solution: the former is self-organized from low-molecular-weight surfactant monomers by hydrophobic interaction, which is a typical weak supramolecular force; while the latter act rheology modifiers by the coil-stretch conformation of single polymer chains which are connected covalently with numerous segments.

The non-covalent linkage of micelles inside WLMs impart them reversible formation and rupture. Such unique unstable rheological behavior of WLMs will be illustrated for their applications in oil production and anti-icing for aircrafts.



Scheme 1. Comparison of EOTC-based WLMs and PDAC polymer chains. The physical parameters underlying each type of structure are shown in the schematics. The WLMs are thicker than the polymer chains, i.e., their core radii R_{core} are much larger since they are formed by EOTC molecules in a cylindrical arrangement. In turn, the WLM filaments are much stiffer than the polymer chains, i.e., their persistence length l_p is also much larger. Both the WLMs and the PAM chains form transient networks at 25 °C. The shear and extensional rheology of these networks is compared in the plots.

[1] Raghavan, S. R.; Feng, Y. Wormlike micelles: solutions, gels, or both? In: Wormlike Micelles: Advances in Systems, Characterization and Applications, Soft Matter Series 6, edited by C. A. Dreiss and Yujun Feng. The Royal Society of Chemistry, London, 2017.

[2] Wang, J.; Feng, Y.; Agrawald, N. R.; Raghavan, S. R. Wormlike micelles versus water-soluble polymers as rheology-modifiers: similarities and differences. *Phys. Chem. Chem. Phys.* **2017,** *19,* 24458.

[3] Unpublished results.

A rheo-optical study on flow induced structure of wormlike micellar solutions

Tadashi Inoue

Department of Macromolecular Science, Osaka University, Osaka, Japan

Flow induced structure of entangled wormlike micellar solutions of CTAB/NaSal under a cone-plate fixture was investigated with the polarization imaging technique. At high shear rates, fluctuating cocylindrical vorticity bands were observed. Time dependence of 2D distribution of birefringence and extinction angle in the bands was determined with the polarization imaging camera. The stress-optical rule held well between the special average of the birefringence and the stress if the finite extensibility of wormlike micelles were considered, indicating that the segment of wormlike micelles is unvaried with formation of flow induced structure. The local stress distribution and its time evolution were calculated from the birefringence and they could be related with distribution of internal strain accompanied with distribution of entanglement density.

Microfluidics and wormlike micelles: Predicting elastic instabilities and secondary flows

Michael Cromer

School of Mathematical Sciences, Rochester Institute of Technology, Rochester, NY 14623, USA

In recent years, microfluidics has emerged as a versatile method of handling fluids at small length-scales. It not only provides a robust and efficient platform for rapid prototyping and cheap device fabrication, it is also straightforward to integrate different flow interrogation techniques with lab-on-a-chip. Microfluidic devices are typically composed of a series of planar channels involving either sudden changes in direction or variations of the flow area. The flows in these configurations are characterized by high deformation rates and small Reynolds numbers. In recent years, there has been intense investigations into the development of elastic instabilities and secondary flows in the flow of complex fluids in microfluidic devices. Investigations of instabilities and secondary flows in the vicinity of microbifurcations are particularly important in applications involving non-Newtonian fluids, ranging from polymer processing to diffusion/mixing processes in complex flows, or bio-engineering studies of corporal flows.

One class of fluids that has received a great deal of attention are wormlike micellar solutions. Wormlike micelles, like polymer chains, stretch and orient under flow; they have the additional ability to break and reform. In this work, we seek to understand how the breakage and reforming of micelles alters flow conditions with respect to that of polymer solutions. In particular, we focus our attention on simulations of the VCM constitutive model (Vasquez, McKinley and Cook (2007)), a two species, microstructural network model, which incorporates the breakage and reforming of two micellar chains. We consider two geometries: cross-slot and 90-degree bend. In cross-slot flow, it is well-known that an elastic asymmetric instability develops due to the stretching of polymeric chains. Using the VCM model, we show that the instability may be completely suppressed via chain scission. In addition, as observed in experiment, the VCM model predicts the formation of recirculation zones just upstream of where the inlet and outlet channels meet. One major question is how the vortices and instability interact. To move towards an answer to this question and to gain a better understanding of the vortices themselves, we also look at the development of the secondary flow in the 90-degree bend geometry. We consider the roles played by shear thinning, elasticity vs. inertia, and chain scission. The ultimate goal of this work is to determine the ability to design a material with physical properties specifically tailored to perform effectively and efficiently on a particular application.

Flow and instability of wormlike micellar solutions around microfluidic cylinders

Simon J. Haward

Okinawa Institute of Science and Technology Graduate University, Onna-son, Okinawa 904-0495, Japan

We present experiments on the flow of wormlike micellar solutions around novel microfluidic cylinder devices with low blockage ratios. Low Reynolds number flows are examined over a wide range of Weissenberg number (Wi) using quantitative time-resolved velocimetry and birefringence imaging. For cylinders pinned at both ends, flow remains steady and symmetric at low Wi but develops a steady asymmetry as Wi increases, with fluid choosing a preferential path around the cylinder. The asymmetry is characterized as a supercritical pitchfork bifurcation. As Wi increases, a Hopf bifurcation with period close to the fluid relaxation time precedes a sequence of period-doubling bifurcations. Eventually, a single characteristic frequency again emerges, but at a much higher frequency, possibly related to the relaxation of fragmented micelles. Finally, in analogy with vibrations due to vortex shedding around cylinders in Newtonian flows, we present preliminary results examining how these time-dependent elastic instabilities feed back on and affect the motion of a flexible micro-post pinned at only one end.

Vortex deformation in two-dimensional turbulent flows of drag reducing polymer solutions

Ruri Hidema

Fluid and Particle Engineering Laboratory, Organization of Advanced Science and Technology, Kobe University, Kobe, Japan

Addition of little amounts of polymer to water drastically reduces frictional drag in a pipe flow. It is well known as drag reduction phenomena. The most important feature of drag reduction is that the polymer additives do not simply suppress the turbulent motion: The turbulent fluctuation in the streamwise direction is increased, while the normal turbulent intensity is decreased. The anisotropic effect is due to deformation of vortices in the turbulent flow.

We have performed an experimental study to investigate the relationship between the extensional rheological properties of polymer solutions and the vortex shedding and the deformation in turbulent flow. In order to focus on the effects of the extensional properties, two-dimensional (2D) turbulent flow made of a self-standing flowing soap film was used. Vortex shedding and deformation in 2D turbulent flows were affected by polymer additives. We have found that the vortex deformation was categorized in three types, which was explained by extensional relaxation time of polymer solution. We discuss the relationship between such vortex deformation and drag reduction effects, and also energy transfer in 2D flows.

Microscopic investigation of vortex breakdown in a dividing T-junction flow

San To Chan

Okinawa Institute of Science and Technology Graduate University, Onna-son, Okinawa 904-0495, Japan

Axisymmetric vortex breakdown, the development of bubble-like regions inside which the flow recirculates, is possible when flow deceleration and vorticity decay are present in a swirling flow. Recently, it has been discovered that vortex breakdown also occurs in a dividing T-junction flow configuration, when the inlet Reynolds number Re exceeds the critical threshold Re_c [1,2]. Here, we microscopically investigate this phenomenon using a novel glass microfluidic T-junction device. First, by micro-Particle Image Velocimetry (μPIV), we visualize at the channel cross-section the formation of a pair of counter-rotating vortices, and explain it through the Dean instability. Second, by a method that enables high-contrast imaging of recirculating streamlines, we show that outflow imbalances of even just a few percent can significantly alter both the Re_c and structures of the vortex breakdown. Complementary numerical simulation reveals that these effects are due to variations in the net pressure difference across the two outlets. Our study highlights the risk of microfluidic design failure due to vortex breakdown, and implies that one can engineer the position and dynamics of recirculation within a dividing T-junction simply by varying the imbalance between the two outflows. Finally, we outline very recent preliminary work involving balanced outflows, but higher Re, demonstrating the onset of symmetry breaking between the vortex breakdown bubbles within the two outlet channels.

[1] Vigolo D, et al. (2014) Proc Natl Acad Sci 111: 4770

[2] Ault J T, et al. (2016) Phys Rev Lett 117: 084501

Inertioelastic flow instability at a stagnation point

Noa Burshtein

Okinawa Institute of Science and Technology Graduate University, Onna-son, Okinawa 904-0495, Japan

Recently it has been shown that flow of Newtonian fluids in cross-slot channels results in a steady spiral vortex instability as the Reynolds number, Re, is increased above a modest critical value Re_c (SJ Haward et al, Phys Rev E **93**: 031101, 2016). In this work we study how the onset and development of the spiral vortex is influenced when fluid elasticity is increased by the addition of high molecular weight poly(ethyleneoxide) (PEO) over a wide range of concentrations $0.0001 < c < 0.1$ wt%. The effects of fluid relaxation time λ; and viscosity ratio β; are decoupled by using solvents of various viscosity. Flow visualization is performed using quantitative micro-particle image velocimetry, from which vorticity fields in the cross-section of the spiral vortex are computed. The vorticity in the center of the spiral serves as a suitable bifurcation parameter to characterize the intensification of the instability with increasing Re. Our sensitive experimental set-up allows us to observe a significant change in Re_c at polymer concentrations as low as 0.0001 wt%, i.e. the concentration regime associated with polymer drag reduction (PS Virk & H Baher, Chem Eng Sci **25**: 1183, 1970). Our results show that as the polymer concentration is increased, Re_c and the intensity of the vortex are reduced. At sufficiently high polymer concentrations $c > 0.1$ wt%, we observe no vortex formation, but we encounter flow asymmetries due to the dominance of elastic effects at high Weissenberg numbers (Wi). Our data can be collapsed to describe a stability boundary in dimensionless Wi-Re-β; parameter space. Our results are supported by numerical simulations and constitute new data on stability of low to moderate elasticity fluids in elongational flow fields. Our experimental configuration allows direct and prolonged examination of a single steady vortex, providing new insight into the effects of drag-reducing concentrations of polymer on vortex formation and dynamics.

Instability of oscillatory pipe flow of wormlike micellar solutions

Jordi Ortín

Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Spain

Beyond a critical driving amplitude, the oscillatory pipe flow of wormlike micellar solutions is unstable against the formation of axisymmetric vortex rings. This instability is not driven by inertia, since the high viscosity of the solution ensures that the Reynolds number remains small. The basic parallel-shear flow, however, is markedly different from its Newtonian counterpart. Indeed, when the wavelength of the shear waves launched by the periodic driving is comparable to the radius of the pipe the flow is highly reversing. We show that this feature combines with the viscoelastic nature of the solution to render this flow unstable.

It is known that wormlike micellar solutions are shear-thinning at large strain rates. This property must be taken into account if a quantitative comparison to experiments is aimed. To this purpose we use a single-mode Giesekus equation. A simple analysis of the governing equations and numerical simulations of the base flow show that radial normal stresses diverge in this case. Using this divergence as a signature of the instability, we are able to reproduce quantitatively the instability threshold in the frequency-amplitude (or De-Wi) parameter space, and the amplitude dependence of the incubation periods required for vortex ring formation measured experimentally.

Flow instabilities of wormlike micelle solutions in microfluidics

Paul Salipante

National Institute of Standards and Technology, Polymers and Complex Fluids Group, Gaithersburg, Maryland 20899, USA

The pressure driven flow of non-Newtonian fluids through pipes is common in industrial processing and high shear rate rheological measurements. Wormlike micelle solutions are particularly susceptible to viscoelastic instabilities that can complicate measurements at high shear rate. In this talk, I will focus on measurements of flow instabilities of wormlike micelle solutions in microfluidic geometries where high shear rates can be achieved at low Reynolds number. In addition to 2-D fluorescent particle image velocimetry, I will introduce advancements in using digital holographic particle tracking velocimetry to measure 3-D flow fields with high temporal resolution. I will show results of volumetric flow rate measurements made using this technique, including a jetting instability of wormlike micelle solutions in rectangular microfluidic channels. I will also show results of flow behavior of wormlike micelle solutions in an axisymmetric capillary constriction, which produces a spatio-temporal instability affecting the flow throughout the fluid system. Velocimetry measurements in the entrance region show a transition to unstable flow above a critical flow rate, where large flow circulations are observed in the tapered geometry. This is further investigated using polarized light microscopy, which shows a rapid breakdown in micelle alignment at the onset of a flow spurt, indicating the importance of rapid micelle structural changes on the fluctuations. Finally, I will show ongoing work on two projects using 3D particle tracking: the characterization of polymer solutions around a micropost and measurement of wormlike micelle solution flow influenced by nonlocal stress at high shear rates.

Numerical simulation of flow and instabilities of complex fluids at microscale

Manuel A. Alves

Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr Roberto Frias s/n, 4200-465 Porto, Portugal

We present a numerical methodology based on the finite-volume method, using the open source OpenFOAM® toolbox, to simulate the microscale flow of complex fluids at low Reynolds numbers. The governing equations and the numerical discretization techniques are briefly presented, and illustrative results and current challenges are discussed, with emphasis on the use of the rheoTool library (https://github.com/fppimenta/rheoTool).

On the locomotion of planktonic microorganisms in a microfluidic environment

Chen-Li Sun

Department of Mechanical Engineering, National Taiwan University, Taipei 106, Taiwan

Planktonic micro-organisms play an important role in marine ecology, fishery, and the ocean carbon cycle. As the foundation of the oceanic food chain, phytoplankton and zooplankton form a complex food web, and their trophic interaction is vital to the prosperity of other marine life. In this talk, I will demonstrate how microfluidic devices can be employed to gain a better understanding of marine ecosystem in a single-cell level.

Focusing on studying the locomotion of plankton K. veneficum (CCMP426), we design different microlfuidic device to investigate the microhydrodynamic effects: stationary f/2-Si medium, steady flow, small and large temporal fluctuation of flow. After measuring the local flow field, we are able to determine the absolute and relative velocities of individual plankton cells, from which their rheotaxis can be derived. The probability density function is then calculated to statistically reveal the response of planktonic cells to various conditions of flow and shear rate. The experimental results show that K. veneficum is capable of maneuvering in a flow speed up to twice their swimming velocity and a preference of positive rheotaxis is found in weak flow. In the intermediate flow region, they tend to cut through the streamlines with small angle in order to escape. Once the current is too strong, their locomotion is dominated by the flow. Increasing the frequency of the flow fluctuation is also found to decrease the mobility of planktonic cells. The outcome of this study helps us to clarify how plankton cells respond to the very changeable flow condition in the ocean.

Solution rheology of polymerized ionic liquids in an ionic liquid solution

Atsushi Matsumoto

Okinawa Institute of Science and Technology Graduate University, Onna-son, Okinawa 904-0495, Japan

Polymerized ionic liquids (PILs) are a special type of polyelectrolytes and they are chemically described as polymers having constitutions of ionic liquids covalently attached to polymer backbones. The effect of electrostatic interaction on the rheological properties of ordinary polyelectrolytes in semidilute regimes has been well established with the scaling theory for electrically neutral polymers, assuming that the ion-ion interaction is negligible. However, the conformation and rheology of PILs in solutions are not well understood. In this study, we use a model system consisting of a polymerized ionic liquid (PC_4–TFSI: the poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide)) dissolved in a mixture of an ionic liquid (BmimTFSI) and a non-ionic (DMF) solvent. The ionic liquid BmimTFSI acts as both a solvent and a source of salt ions to regulate the charge screening, with the highest salt concentration c_{BmimTFSI} = 3.42 M when pure BmimTFSI is used as the solvent. The specific viscosity (η_{sp}) and relaxation time (λ) of PC_4–TFSI solutions in the semidilute unentangled regime are measured by using a combination of conventional and microfluidic rheometry. At low salt concentrations (c_{BmimTFSI} < 0.1 M), both η_{sp} and λ are initially constants but decrease with increasing c_{BmimTFSI}, consistent with the scaling prediction. However, at 0.1 M < c_{BmimTFSI} < 1 M, both η_{sp} and λ decrease with increasing c_{BmimTFSI} at slower rate compared to the scaling prediction. At c_{BmimTFSI} > 1 M, the values of η_{sp} and λ increase with c_{BmimTFSI} regardless of the polymer concentration. We propose that the electroviscous effect potentially influences the rheological behavior of PIL solutions at c_{BmimTFSI} > 1 M.

Microscopic origin of the elastic instabilities during flow of polymer solutions

Pouyan Boukany

Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands

Polymeric fluids exhibit a number of intriguing flow phenomena such as vortex formation, die swelling, stress overshoot, and drag reduction when the flow rate exceeds a certain critical value of flow rate (Typically when flow rate is larger than reciprocal of relaxation time of polymeric fluid or Wi > 1.0). The exact molecular picture behind many of these complex flow responses is not known yet and it is still under debate. This limits the design, control and optimization of the technological process related to polymer products. To overcome these technological limitations, it is required to develop novel methods that can relate the microscopic flow with the molecular conformation. Recently, the direct visualization of stained DNA inside microfluidics provides a unique opportunity for us to a conceptual framework for nonlinear polymer rheology in the fest flow rate regime (Wi > 1.0). For instance, we recently employed single molecule experiments to study the necking and pinch-off dynamics of polymeric droplets by combining microfluidics and ingle DNA observation. We demonstrated that the individual polymer molecules suddenly stretch from their coiled conformation at the onset of necking. The extensional flow inside the neck is strong enough to stretch polymer chains. Furthermore, we have unraveled the molecular process leading to dead-zone formation during flow of shear thinning polymer solutions through by similar approach. We believe that these single molecule experiments allow us to develop a realistic theoretical picture of polymer solutions during flow in porous media.