British Society of Rheology Midwinter Meeting 2016: Polymer Dynamics & Rheology

and

Symposium on “The Science of Alexei Likhtman”

12th-14th December 2016, Palmer Building, 1.09 Lecture Theatre, Whiteknights Campus, University of Reading
Preface

The BSR Midwinter Meeting 2016 has a general theme of *Polymer Dynamics and Rheology*, and incorporates a minisymposium entitled "*The science of Alexei Likhtman*". This one-day symposium is inspired by Professor Alexei Likhtman, and incorporates contributions from many who have worked with him.

Organising Committee

Joseph L. Keddie (Surrey)
Tom McLeish (Durham)
Daniel Read (Leeds)
Zuowei Wang (Reading)
Helen Wilson (UCL)
PROGRAMME

Monday 12 December

[11.00-11.45] REGISTRATION and COFFEE

**Rheometry**

Chair: Helen Wilson

[11.45-12.10] *i*-Rheo GT: Transforming $G(t)$ obtained from molecular dynamics simulations into the materials' linear viscoelastic properties without artefacts.
Manlio Tassieri (University of Glasgow).

Oleksandr O. Mykhaylyk (University of Sheffield).

[12.35-13.00] Relative humidity as a new parameter in rheological testing.
Joerg Laeuger (Anton Paar Germany GmbH).

[13.00-14.00] LUNCH

**Polymer dynamics**

Chair: Daniel Reid

[14.00-14.25] Rheology and relaxation dynamics in a chain-length series of methacrylates ranging from oligomer to entangled polymer.
Matthew Reynolds (University of Leeds).

Vassilis Kontogiorgos (University of Huddersfield).

Alessio Zaccone (University of Cambridge).

Guanghui Cui (University of Leeds).

[15.40-16.10] TEA
**Chair: Zuowei Wang**

**[15.45-16.10] Anomalous self-diffusion in associating telechelic star polymers.**
Dr. Jorge Ramirez (Universidad Politécnica de Madrid).

**[16.10-16.35] From dilute to concentrated polyelectrolyte solutions: understanding sodium carboxymethyl cellulose chain dynamics in water with rheology and light scattering measurements.**
Juliette Behra (University of Leeds).

**[16.35-17.00] Elasticity dominated surface segregation in polymer gel mixtures.**
Dr. Buddhapriya Chakrabarti (Durham University).

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**Tuesday 13 December**

**The Science of Alexei Likhtman**

**Chair: Helen Wilson**

**[9.00-9.10] Opening remarks.**
Tom McLeish (Durham University).

**[9.10-9.35] Challenges in the dynamics of entangled polymers in strong flows and in confinement.**
Dimitris Vlassopoulos (University of Crete).

**[9.35-10.00] Coarse-graining in description of entanglement relaxation.**
Hiroshi Watanabe (Kyoto University).

**[10.00-10.25] Analysing time-dependent homogeneous ows of entangled linear polymers.**
Richard Graham (University of Nottingham).

**[10.25-10.50] Entanglements and dynamics of ring polymer melts.**
Scott Milner (Penn State University).

**[10.50-11.20] COFFEE**

**Chair: Joe Keddie**

Wim Briels (University of Twente).
A Molecular View on Supramolecular Chain and Association Dynamics. Dieter Richter (Forschungszentrum Jülich GmbH).

Light-induced self-assembly processes in solutions of triarylamines. Alexander N. Semenov (Institut Charles Sadron, CNRS, University of Strasbourg).

Linear Viscoelasticity of Associating Ionomers. Ralph Colby (Penn State University).


[12.35-13.00] Linear Viscoelasticity of Associating Ionomers. Ralph Colby (Penn State University).

[13.00-14.00] LUNCH

Chair:


[15.15-16.15] TEA and POSTERS

Chair: Daniel Read


[16.40-17.05] The Effects of Molecular Structure and Rheology on Film Blowing Characteristics of Bimodal HDPEs. Choon Chai (INEOS).

[17.05-17.25] Closing Remarks. Zuowei Wang (University of Reading).

[19.00 for 19.30] CONFERENCE DINNER
**Wednesday 14 December**

**Non-Newtonian fluid mechanics**

Chair: Tom McLeish

[09.00-09.25] *Edge fracture instabilities in polymeric fluids.*
Ewan Hemingway (Durham University).

Claire McIlroy (Georgetown University).

[09.50-10.15] *Rivulet flow of generalised Newtonian fluids.*
Stephen Wilson (University of Strathclyde).

[10.15-10.40] *Shear banding in large amplitude oscillatory shear of soft glassy materials.*
Suzanne Fielding (Durham University).

[10.40-11.10] COFFEE

**Volcanology / Awards**

Chair: Helen Wilson


[11.15-13.00] Joint Lecture of BSR Annual Award and Vernon Harrison Award

*Multiphase magma rheology: theory, experiments, and implications for volcanic processes.*
Ed Llewellin and Jen Truby (University of Durham).

[13.00] CLOSE
Abstracts for Contributed Talks

Monday

[11.45-21.10] i-Rheo GT: Transforming $G(t)$ obtained from molecular dynamics simulations into the materials’ linear viscoelastic properties without artefacts.

Manlio Tassieri (a), Jorge Ramírez (b), Yuichi Masubuchi (c) and Sathish K. Sukumaran (d)

[a] Division of Biomedical Engineering, School of Engineering, University of Glasgow, Glasgow G12 8LT, UK; [b] Departamento de Ingeniería Química, ETSI Industriales, Technical University of Madrid, José Gutiérrez Abascal 2, 28006 Madrid, Spain; [c] National Composite Center, Nagoya University, Nagoya 4648603, Japan; [d] Graduate School of Organic Materials Science, Yamagata University, Yonezawa, 992-8510, Japan.

E-mail: Manlio.Tassieri@glasgow.ac.uk

We present a simple new analytical tool for educing the materials' linear viscoelastic (LVE) properties from (atomistic and quasi-atomistic) molecular dynamics simulations (MDS) describing the temporal behaviour of the materials' shear relaxation modulus $G(t)$. The new tool allows the evaluation of the materials' complex shear modulus $G^*(\omega)$ over the widest range of experimentally accessible frequencies, without the need of 'preconceived' models, such as a generalised Maxwell model. This is achieved by means of the analytical method introduced by Tassieri et al. [1,2] to evaluate the Fourier transform (FT [...] ) of raw data, via:

\[
G^*(\omega) = \mathcal{F}\left[\frac{dG(t)}{dt}\right] = io\hat{G}(\omega),
\]

where $\hat{G}(\omega)$ is the Fourier transform of $G(t)$ and $\omega$ is the angular frequency. The analytical method has been implemented into a new open access executable named ‘i-Rheo GT’ (Figure 1), enabling its use to a broad scientific community. The effectiveness of the new rheological tool has been corroborated both by analysing the dynamic response of a model system (i.e., a single Maxwell mode) and by direct comparison with bulk-rheology experimental data. i-Rheo GT offers the opportunity to gain new insights into the materials’ LVE properties, especially at high-frequencies (i.e., in the glassy region and beyond); where (i) conventional tools (e.g., Reptate or Iris) struggle to ‘interpret’ the data and (ii) MDS actually provide the most accurate predictions of $G(t)$. Interestingly, these frequency regions are commonly ‘unexplored’ by the rheology community. Nevertheless, having access to atomistic and quasi-atomistic MDS represents both a challenge and a springboard for theoreticians to develop comprehensive models able to predict the materials’ LVE properties over the widest range of experimentally accessible frequencies; hence, the importance of the new rheological tool.
Figure 1. Front panel of the LABVIEW (National Instruments) executable i-Rheo GT.

References:

Keywords: Stress relaxation, molecular dynamics, linear rheology, complex fluids

[12.10-12.35] Shear-induced polarized light imaging (SIPLI) - a technique for mechano-optical rheology of polymeric materials.

Oleksandr O. Mykhaylyk

Soft Matter Analytical Laboratory (SMALL), Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

Since polymeric liquids subjected to an external field (flow) often respond with a related anisotropy of their refractive index and stress, flow birefringence is commonly used for structural characterization of these materials. In this respect, rotational geometries are well suited for visual observations of the flow and, consequently, mechano-optical rheology of polymeric liquids. The potential of these geometries, commonly used in rheology, has not yet been entirely explored for these applications. A new rheo-optical method based on a combination of rotational rheology and a recently developed optical technique – shear-induced polarized light imaging (SIPLI) is presented. Simultaneous rheo-optical studies using mechanical rheology coupled with SIPLI visualization and/or quantitative birefringence measurements will be demonstrated for various materials including semicrystalline polymers, self-assembled copolymers and liquid crystals. The results are compared with small-angle x-ray scattering (SAXS) measurements. In addition, the SIPLI techniques provides a unique opportunity to control sample loading and monitor sample state during rheological measurements in plate-plate and cone-and-plate geometry.
Relative humidity as a new parameter in rheological testing

Joerg Laeuger, Gunther Arnold

Anton Paar Germany

In addition to temperature and pressure the water content of a sample as well as the relative humidity of the ambient air are important parameters influencing the rheological behavior of many complex fluids such as, for example, gels, biomaterials, polymeric systems, food products, and adhesives.

A combination of a modified convection oven and an external humidity generator enables to work under defined relative humidity (RH) and temperature (T) in the ranges of RH = 5 to 95% and T = 5 to 120°C. Traditional convection ovens are mainly equipped with electrical heaters. For lower temperatures a cold gas (e.g. LN2) is brought into the chamber and the oven heats against the cold gas. In the new humidity system the convection oven is based on Peltier elements allowing to set temperatures below ambient without the need of a cold gas as input to the oven chamber. In order to control the relative humidity a humidity sensor is located in the oven and the external humidity generator provides the needed moisture of the gas flowing into the chamber. The humidity sensor and the humidity generator are fully integrated into the operating software for the rheometer, allowing the programming of combinations of T and RH including ramps in RH at constant T or ramps in T at constant RH, respectively. Various standard geometries like parallel-plate, cone-and-plate, solid bar for torsional DMTA, extensional tools for DMTA and steady extensional rheological testing, a ball on three plate geometry for tribological investigations, as well as a newly designed modified ring geometry. The later consists of two broken rings in which the sample is placed on some small portions of the ring and has the advantage of a large surface to volume ratio, enabling a fast penetration of moisture into the sample. Applications examples in the different geometries show the importance of the relative humidity on the rheological behavior of many complex fluids.
Rheology and relaxation dynamics in a chain-length series of methacrylates ranging from oligomer to entangled polymer

Matthew Reynolds, Daniel Baker, Chinmay Das, Johan Mattsson

Dept. of Physics and Astronomy, University of Leeds.

Glassy polymers are commonly used in a wide variety of industrial applications. Both their macroscopic and microscopic behaviours are often strongly affected by processing history, and the link between rheology and relaxation behaviour is important and often complex. This presentation will outline recent work to determine the variation of the rheological response and relaxation dynamics of a molecular weight series of oligo and poly(methyl methacrylates). Rheology data covering a wide temperature range will be presented alongside results from broadband dielectric relaxation spectroscopy and modulated and standard differential scanning calorimetry. The results will be presented in the context of recent models and behaviour previously reported for other polymer systems in the literature.

Relaxation dynamics in hydrated gluten networks

Vassilis Kontogiorgos

Department of Biological Sciences, University of Huddersfield, Queensgate, HD1 3DH, UK

Thermomechanical and microstructural properties of hydrated gluten networks were studied by rheometry (stress relaxation), differential scanning calorimetry (DSC, MDSC), imaging (cryo-SEM, TEM, CLSM, μ-CT) and theoretical modeling. This work was undertaken to investigate the thermal and mechanical relaxations observed in hydrated gluten and relate them to its microstructure. The Defay–Prigogine theory for the depression of melting point of fluids confined to capillaries was used to explain the calorimetric results and provide in-depth understanding of gluten microstructure. Results of the present investigation showed that is impossible to assign a specific glass transition value for hydrated gluten because of the wide temperature range over which the gluten matrix vitrifies. Stress relaxation was followed over a wide temperature range (0 - 70 °C) and modulation of intermolecular bonds was achieved with urea, DTT or ascorbic acid in an effort to elucidate the presiding intermolecular interactions over gluten network relaxation. Temperature played a significant role in relaxation, allowing the construction of mastercurves and calculation of shift factors. Numerical calculation of stress relaxation spectra using Tikhonov regularization and the L-curve criterion identified three relaxation regimes. Relaxation commences with a well-defined short-time regime where Rouse-like modes dominate, followed by a power law region displaying continuous relaxation concluding in a terminal zone. In the latter zone, poroelastic relaxation due to water migration in the nanoporous structure of the network also contributes to the stress relief in the material. Stress relaxation is independent of compositional differences, however, hydrogen bonding between adjacent protein chains was identified as the determinant force that influences the relaxation of the networks. Utilization of theoretical frameworks from macromolecular dynamics coupled by calorimetric and imaging techniques allowed in-depth understanding of the rheological properties of gluten with the aim to improve its industrial performance.
Nonlinear nonaffine theory of stress overshoots in the start-up shear of semiflexible filament networks

A. Zaccone and E.M. Terentjev

Department of Chemical Engineering and Biotechnology, and Cavendish Laboratory, University of Cambridge, Cambridge U.K.

One of the most important contributions of Alexei Likhtman to polymer physics has been the implementation of complex multi-chain dynamic effects (including non-trivial non-bonded excluded volume effects) into single-chain models and convective strain-release models to predict stress-strain constitutive relations and complex stress relaxation in polymer melts [1]. The ubiquitous stress-strain overshoot observed in the start-up shear of most polymer materials is interpreted microscopically as a consequence of the shear-induced breakup of entanglements. Here we propose a different theoretical framework that arrives at a microscopic description of the same phenomena for polymer networks. The starting point is a microscopic elasticity theory for disordered systems where nonaffine motions of network nodes are important as microscopic mechanisms of localized stress release [2]. The origin of nonaffine motions lies in the local absence of inversion-symmetry in amorphous lattices, which makes the sum of forces transmitted by chains to a node not equal zero, as it would be, instead, in a centrosymmetric lattice [3]. We choose a 3-chain constitutive model of semi-flexible polymer networks which also accounts for filament pre-tension [4], and we implement it within the nonaffine deformation formalism extended here to finite deformations using a neo-Hookean model. Assuming a shear-induced mechanism to break up non-bonded interactions governed by convective Smoluchowski dynamics [5], the theory is able to explain the stress overshoot as due to the competition between affine (positive) and nonaffine (negative) contributions to the free energy of deformation, whereas the final Newtonian-like plateau sets in due to the build-up of dissipative contributions to the stress within a simple Maxwell mode. The theoretical predictions are in excellent agreement with experimental data of different cross-linked polymers.

Comb-like statistic copolymers based on 2-ethylhexyl acrylate (EHA) and ureidopyrimidinone (UPy) units are synthesized via RAFT polymerization. While the former gives to the chain the comb structure leading to its moderate extension, the latter generates supramolecular interactions (H-bonds) leading to the formation of strong UPy dimers providing the materials enhanced mechanical properties. In this work, we investigate the multi-scale dynamics (over about ten decades in time) of five of such supramolecular co-polymers containing 0, 2, 6, 9 and 14% molar in UPy units by means of broadband dielectric spectroscopy (BDS), (modulated) differential scanning calorimetry ((M)DSC), rheology and stochastic simulations. From X-rays scattering, nuclear magnetic resonance and chromatography experiments, we further provide structural evidences (such as the UPy dimer size or their number density) allowing then to discuss unambiguously the structure-properties relationship. As expected, increasing the density of the physical cross-links dramatically affects the rheological behavior of the polymer. It notably delays its terminal relaxation time by more than four decades when the UPy content is set to 14% molar, a feature well captured by our sticky-Rouse model. In addition, it qualitatively changes the macroscale dynamics from following a WLF behavior to an Arrhenius one \((E_a \approx 192 \text{ kJ/mol})\) that we rationalize in terms of H-bonds density. More surprisingly, the supramolecular interactions are found to play an important role at the segmental level (1-5 nm). Both BDS and DSC clearly reveals that increasing their density results in a strong broadening of the glass-to-melt transition jointly with a jump of the corresponding temperature \(T_g\) by more than 10 °C and a higher fragility. In contrast, at a more local scale (0.5 nm), the UPy units seem to enhance the side groups dynamics leading to an unusual decoupling of the \(\alpha\) and \(\beta\) relaxation processes.
Supramolecular polymer networks differ from their chemically crosslinked counterparts by the fact that the intermolecular bonds between associating groups can be created and destroyed reversibly, and this has a very strong effect on the dynamical properties and relaxation response of these materials. A detailed understanding of the effect that the association and dissociation kinetics of the reversible junctions have on the self-diffusion of associating networks is still missing, and it is important in order to predict and understand the mechanical properties, stability and self-healing capabilities of these type of soft materials. In a recent series of publications [1-2], the diffusion of linear and star polymers with associating groups was studied by means of forced Rayleigh scattering, showing an unexpected superdiffusive behaviour over a wide range of time and length scales. In this talk, we explain the origin of the observed superdiffusive behaviour, by means of scaling arguments, analytical theory and simulations.

REFERENCES:

Sodium carboxymethyl cellulose (Na CMC) is widely used in industry for its thickening and swelling properties. Applications are very broad and include pharmaceutical, food, home and personal care products as well as the paper industry, water treatment and mineral processing. Na CMC is a linear negatively charged water-soluble polymer derived from cellulose. Its behaviour in water is known to be very complex and a function of several parameters including the characteristics of the polymer itself such as molecular weight and degree of substitution as well as the solution concentration and dissolution conditions (e.g. addition order of the system components). While Dynamic Light Scattering (DLS) has been widely used to study the behaviour of polyelectrolytes, relatively few DLS studies have been conducted on Na CMC and, to our knowledge, none in pure water. Moreover, for relatively concentrated solutions, no oscillatory data has been collected over a wide enough range of frequencies to reveal the terminal zone (i.e. low-frequency region). The aim of the present study was to investigate the behaviour of Na CMC chains (Mw = 700,000 g/mol; DS = 0.9) in pure water using both DLS and rheology measurements. Viscosity measurements were run to identify the different concentration regimes (see Figure 1), facilitating comparisons to the behaviour typically found for
polyelectrolytes. DLS and oscillatory measurements were then performed to cover the four concentration regimes. Preliminary results have shown interesting correlations between both rheology and light scattering measurements.

![Figure 1](image)

Figure 1 – Specific viscosity ($\eta_{sp}$) as a function of Na CMC concentration $\eta_0$: zero-shear viscosity (obtained from the Carreau model); $\eta_s$: solvent viscosity (experimental value); the values below the names of the different concentration regimes are the expected exponents of the power laws of the specific viscosity as a function of the polyelectrolyte concentration; the values above the curve are the best fit slopes. Though the experimental exponents are slightly higher than the theoretical ones, they are in agreement with the literature about Na CMC [1, 2].


**[16.35-17.00] Elasticity dominated surface segregation in polymer gel mixtures**

J. Krawczyk, S. Croce, T. C. B. McLeish, B. Chakrabarti

Dept. of Mathematical sciences, Durham University, Durham DH1 3LE, UK

We study the phenomenon of migration of the small molecular weight component of a binary polymer mixture (of which one component is a reticulated network) to the free surface using mean field and self-consistent field theories. By proposing a free energy functional that incorporates matrix elasticity explicitly, we compute the migrant volume fraction and show that it decreases significantly as the sample rigidity is increased. Estimated values of the bulk modulus suggest that the effect should be observable experimentally for rubber-like materials. This provides a simple way of controlling surface migration in polymer mixtures and can play an important role in industrial formulations, where surface migration often leads to decreased product functionality.
Wednesday

[09.00-09.25] Edge fracture instabilities in polymeric fluids

Ewan Hemingway, Halim Kusumaatmaja and Suzanne Fielding

Soft Matter and Biological Physics Group, CMP, Department of Physics, Durham University, DH1 3LE, UK

There exists an ongoing controversy regarding whether monodisperse linear entangled polymers exhibit shear banding, or whether apparent instabilities can be attributed instead to edge fracture. Experiments by Li et al. [J. Rheol. 57, 1411 (2013)] suggest that edge fracture instabilities can cause velocity profiles that appear shearbanded close to the interface but which return to homogenous shear flow as measurements are taken further into the sample bulk. In wormlike micellar surfactants, which unambiguously do shear band, flow curve measurements are typically interrupted above a critical strain rate, often with the sample being physically ejected from the rheometer. While both sets of experiments show that edge fracture and shear-banding phenomena are intimately linked, the details of the relationship and the nature of causality remain unclear. We first analyse the linear stability properties of a free surface between a bulk polymeric fluid under shear and the air. This allows us to explore the mechanisms that drive the edge fracture instability, and to characterise the critical shear rate at which it first appears. Our analytics provide insight into how edge fracture might be avoided experimentally.

These predictions are complemented by full 2D hydrodynamical simulations in the flowgradient/vorticity plane, using a diffuse interface approach to correctly capture the dynamics of the contact line where the air/fluid interface meets the solid wall of the flow cell. By tuning the properties of our coarse-grained polymeric model, we can control whether the fluid exhibits bulk shear-banding or not. Even when bulk shear-banding is not present, we observe non-linear velocity profiles sufficiently close to the free surface. In bulk shear-banding fluids, our results show that secondary flows in the region where the shear-banded interface meets the air play a crucial role in determining edge fracture.

Snapshots from our nonlinear simulations showing dynamics of the edge fracture instability.
[09.25-09.50] An Application of the Rolie-Poly Model: Polymer Behaviour during 3D Printing

Claire McIlroy and Peter Olmsted

Department of Physics, Georgetown University

3D printing has the potential to transform manufacturing processes, yet improving the strength of printed parts, to equal that of traditionally-manufactured parts, remains an underlying issue. The most common method, fused deposition modelling, involves melting a thermoplastic, followed by layer-by-layer extrusion of the molten viscoelastic material to fabricate a three-dimensional object.

The key to the ensuring strength at the weld between these layers is successful inter-diffusion. However, as the printed layer cools towards the glass transition temperature, the time available for diffusion is limited. In addition, the extrusion process significantly deforms the polymer microstructure prior to welding and consequently affects how the polymers “re-entangle” across the weld.

We have developed a simple model of the non-isothermal printing process to explore the effects that typical printing conditions and amorphous polymer rheology have on the ultimate weld structure. In particular, we incorporate both the stretch and orientation of the polymer using the Rolie-Poly constitutive equation to examine how the melt flows through the nozzle and is deposited onto the build plate. We then address how this deformation relaxes and contributes to the thickness and structure of the weld.

[09.50-10.15] Rivulet flow of generalised Newtonian fluids


Department of Mathematics and Statistics, University of Strathclyde, Livingstone Tower, 26 Richmond Street, Glasgow G1 1XH, UK

The previous work by Al Mukahal et al. [1, 2] concerning rivulet flow of a power-law fluid provided a rare analytical benchmark for the study of rivulet flow of non-Newtonian fluids; however, it is of limited applicability to the flow of realistic non-Newtonian fluids. Thus, in the present work we analyse rivulet flow of generalised Newtonian fluids. Gravity-driven flow of a thin uniform rivulet of a generalised Newtonian fluid down a vertical planar substrate is considered. We derive the parametric solution for any generalized Newtonian fluid whose viscosity is specified as a function of the shear rate (including, in particular, the solution for a Carreau fluid), and the explicit solution for any generalised Newtonian fluid whose viscosity is specified as a function of the shear stress (including, in particular, the solution for an Ellis fluid). We use these solutions to describe rivulet flow of a Carreau fluid and of an Ellis fluid, highlighting the similarities and differences between the behaviour of these two fluids. In particular, the surprisingly complicated behaviour of strongly shear-thinning Carreau and Ellis fluids is described. We also demonstrate that the non-monotonic variation of the viscosity of an Ellis fluid with the parameter that measures the degree of shear thinning leads to a more complicated dependence of the behaviour of the rivulet on this parameter than on the other parameters in the Carreau and Ellis models.
References


[10.15-10.40] Shear banding in large amplitude oscillatory shear of soft glassy materials

Suzanne Fielding and Rangarajan Radhakrishnan

Department of Physics, Durham University

We study shear banding in soft glassy materials subject to a large amplitude oscillatory shear flow (LAOS). By simulations of the soft glassy rheology model, supplemented by more general physical arguments, we demonstrate strong banding over an extensive range of amplitudes and frequencies of the imposed shear rate, even in materials that do not permit banding as their steady state response to a steady imposed shear flow. Counter intuitively, banding persists in LAOS even in the limit of zero frequency, where one might a priori have expected a homogeneous flow response (consistent with the requirement of homogeneous flow for a strictly zero frequency steady imposed shear flow). We explain this in terms of an alternating competition within each cycle between glassy aging and flow rejuvenation. Our predictions have far reaching implications for the flow behavior of aging yield stress fluids, suggesting a generic expectation of shear banding in flows of even arbitrarily slow time-variation.
Abstracts for Posters

[P1] Dynamics of Packed Soft Colloids

Tom Ridley

University of Leeds, UK

We aim to computationally probe coordinated movement in highly packed soft colloid systems and investigate how considering deformable particles alters packed behaviour, building on previous experimental work on polymer microgels. We model the colloids as deformable viscoelastic solids subject to thermal fluctuations, suspended in a viscous medium. The method is based on the “Fluctuating Finite Element Analysis” technique developed by Oliver et al. (2013, Journal of Computational Physics, 239, 147-165). This method was originally developed for simulating globular biomolecules, but here we apply it to microgels by treating each colloidal particle as a viscoelastic sphere constructed from tetrahedral finite elements. Short-range forces between particles are comprised of volumetric steric forces that discourage overlap between particles and Lennard–Jones forces, with periodic boundary conditions applied at the boundaries of the computational domain. In this poster we give an outline of the method and present preliminary results.

[P2] Rheology of viscoelastic magnetic fluids

A. E. A. S. Evangelopoulos1, P. Ilg1,*

1Department of Mathematics and Statistics, University of Reading, Reading RG6 6AX, UK. *p.ilg@reading.ac.uk

The magnetic-field-- and shear-dependent rheology of fluids containing ferromagnetic nanoparticles suspended in a Newtonian solvent, known as ferrofluids, has opened possibilities in a range of industrial and medical applications, such as magnetic dampers and magnetic drug delivery [1]. Building upon the fundamental model [2] of a ferrofluid in the presence of an external magnetic field and aspiring towards a new class of materials of higher complexity and technological potential, we employ a generalized Langevin equation [3] to incorporate viscoelastic effects of a surrounding Maxwell medium. This introduces the complexity of magneto-mechanical coupling between the magnetic particles and their viscoelastic environment [4]. Details of this coupling are largely unknown to date and this project aims to contribute towards a better fundamental understanding and, ultimately, discover ways of optimizing field-induced rheological changes in industrial applications. We perform numerical simulations to study the magneto-mechanical coupling as a result of both rotational effects of individual, non-interacting, particles, as well as due to chain or cluster formation of interacting particles. We compare findings to experiments where magnetic nanoparticles have been used as probes to measure local rheological properties [5].

We have studied the control and manipulation of tuneable sub-micron scale equilibrium structures in urethane/urea elastomer films [1], spheres [2,3] and fibres [4,5]. These are obtained by UV-irradiation of the elastomers followed by mechanical deformation or swelling in a solvent. The chemistry is standard and no complex deposition techniques are required. The resulting textures have been investigated using atomic force microscopy, scanning electron microscopy, small-angle light scattering and polarised optical microscopy. They can be interpreted by assuming that each film or sphere consists of a thin, stiff surface layer (“skin”) lying atop a thicker, softer substrate (“bulk”). The skin’s higher stiffness is hypothesized to result from the more extensive cross-linking of the polymer chains located near the surface by the UV radiation. Textures then arise from competition between the effects of bending the skin and compressing the bulk, as the applied stress is removed or the solvent evaporates. In the case of spheres [2], this provides a very convenient route for the fabrication of Janus particles with hierarchical wrinkling [3], which we describe in some detail. In the case of fibres, the wrinkling only starts after the fibre has curled into a well-defined helical shape. A simple analytical model is proposed to find the curling curvature and wrinkle wavelength, as well as the transition between the “curling” and “wrinkling” regimes [4]. This new instability resembles that found in the tendrils of climbing plants as they dry and lignify. Finally, we establish under what conditions the wrinkles will be across or along the fibre axis [5].

References
Sodium carboxymethyl cellulose (Na CMC) is the most widely used cellulose derivative. It is used in pharmaceutical, food, home and personal care products, as well as in the paper industry, water treatment and mineral processing. Na CMC is a linear negatively charged water-soluble polymer. Its behaviour in water is known to be very complex and a function of several parameters including the characteristics of the polymer itself such as molecular weight and degree of substitution, as well as solution concentration and dissolution conditions (e.g. addition order of the system components).

Physical ageing of Na CMC solutions has been reported in a few previous research studies, although a thorough understanding of time-dependent solution changes is still lacking. Typically, a more or less significant decrease with time in the low-shear viscosity is usually observed even though increases in the viscosity over time have also been reported for some systems. To more completely understand these phenomena, we have investigated the rheological behaviour of a 0.2% and a 1.5% Na CMC solutions (Mw = 700,000 g/mol; DS = 0.9) over long time periods. The least concentrated solution shows a decrease in the viscosity over time, which is consistent with reports in the literature. However, the most concentrated solution shows a significant increase in the viscosity as well as a change in the shape of the viscosity curve (i.e. viscosity versus shear rate or shear stress). Additional measurements involving solution stirring the day before the rheology measurements have been conducted to obtain a greater insight into these interesting results.

We study the conformational properties of single diblock polyampholytes (PAs) that are overall neutral by satisfying $N_+ f_+ = N_- f_-$, where $N_+$ is the number of monomers on the respective positive or negative block and $f_+/-$ is the fraction of charged monomers on the blocks. We fix $N_+ f_+$ but vary $N_-$ and $f_-$ thus increasing the block asymmetry to investigate how these architectures affect the overall and individual block conformations. Replica Exchange Molecular Dynamics (REMD) simulations with configuration swaps in the electrostatic interaction strength (Bjerrum length) space were performed. We find that the conformations of the diblock PA chains transfer from being globular in the symmetric case to a densely charged polyelectrolyte chain surrounded by a cloud of oppositely charged but connected counterions in the highly asymmetric case.

We investigate the conformation and rheology of ubiquitous sodium carboxymethyl cellulose (NaCMC) aqueous solutions. NaCMC is the most abundant cellulose polyelectrolyte derivative, with a wide range of applications in the oil, paper and food industries[1,2]. Small angle neutron scattering (SANS) and rheology are employed to study NaCMC of three degrees of substitution (D.S.) as a function of polymer mass (Mw)and polymer and salt concentration [3]. Scaling laws for the overlap and entanglement concentrations are established. NaCl is found to screen electrostatic interactions but not hydrophobic ones, while NaOH screens both. In salt free and NaCl solution, a NaCMC sample with D.S. = 1.2 displays typical polyelectrolyte and neutral polymer in good solvent behaviour respectively. The viscosity in NaOH solutions is to that in NaCl. Two samples with D.S. = 0.8 display hydrophobic behaviour above the entanglement concentration in salt free and NaCl solution, becoming thixotropic gels at high concentrations. However, the viscosities in NaOH are identical to those of the more substituted sample due to solubilisation of unsubstituted cellulose patches. SANS data indicate that the polymer conformation is not significantly affected by the increased hydrophobic interactions. By varying the ionic strength and pH of aqueous solutions, it is possible to tune the polymer-solvent interactions for NaCMC samples. This allows us to separate the effects of entanglements, electrostatic repulsion and hydrophobic interactions on the solution rheology of NaCMC.


Jian Zhu, Alexei E. Likhtman and Zuowei Wang*

School of Mathematical, Physical and Computational Sciences, University of Reading, Reading RG6 6AX, UK

The study of dynamics and rheology of well-entangled branched polymers remains a challenge for computer simulations due to the exponentially growing terminal relaxation times of these polymers with increasing molecular weights. We present an efficient simulation algorithm for studying the arm retraction dynamics of entangled star polymers by combining the coarse-grained slip-spring (SS) model with the forward-flux sampling (FFS) method. This method is first applied to simulate symmetric star polymers in the absence of constraint release (CR). The reaction coordinate for the FFS is determined by comparing the simulation results on the terminal relaxation times of mildly entangled stars with those obtained from direct SS model simulations and finding less than 5% relative difference between them. The FFS simulations are then carried out for strongly entangled stars with arm lengths up to 16 entanglements which are far beyond the accessibility of direct simulations in the no-CR condition. Apart from the terminal relaxation times, the same method can be applied repeatedly to generate the relaxation spectra of all entanglements along the arms which are desired for the development of quantitative theories of entangled branched polymers. Furthermore, we propose a numerical route to construct the experimentally measurable relaxation correlation functions by effectively linking the data stored at each interface during the FFS runs. The obtained star arm end-to-end vector relaxation functions \( \Phi(t) \) are found to be in good agreement with direct simulation results, while the stress relaxation data \( G(t) \) show a systematic error, which could be attributed to the conformational bias on the interfaces. Finally we demonstrate that this simulation method can be conveniently extended to study arm-retraction problem in the presence of CR by modifying the definition of reaction coordinate.

[P8] Extrudate Swell of Monodisperse Polystyrenes

Ben Robertson [a], Richard Thompson [a], Tom McLeish [b]

[a] Department of Chemistry, Durham University
[b] Department of Physics, Durham University

E-mail: benjamin.robertson@durham.ac.uk

This work aims to achieve a molecular understanding of extrudate swell (also called ‘die swell’). We present predictions of extrudate swell using the tube-model-based Rolie-Poly constitutive equation combined with the Lagrangian finite element solver flowSolve. We find a molecular weight independence of the swelling when the flow speed is scaled by the Rouse Weissenberg number. The roles that both chain orientation and stretch play in determining extrudate swell are clearly identifiable from plots of swelling ratio against Weissenberg number. We also present complementary experimental results performed isothermally inside a Multi-Pass Rheometer. The predictions for swelling ratios of monodisperse polystyrene closely match those from experiments up to Rouse Weissenberg numbers of \( \sim 7 \) above which swelling is over predicted by flowSolve. Simulations of a bidisperse melt are also presented where an increased chain stretch time for the longer component results in a better fit to experimental data than an uncorrected simulation.
[P9] Analysing molecular Dynamics trajectories with Markov Chain Monte Carlo method

Changqiong Wang, Richard Everitt, Zuowei Wang, Patrick Ilg, Alexei Likhtman

School of Mathematical, Physical and Computational Sciences, University of Reading, UK

Polymer melts generally demonstrate complicated dynamic and stress relaxation behaviours, which are usually difficult to be described by theoretical models and typically involve many parameters. We propose to apply the Markov Chain Monte Carlo (MCMC) method to facilitate the selection of the most appropriate models from potential models. We apply this algorithm to analyse the trajectory of the center of mass of polymer chains obtained from molecular dynamic simulation of linear polymer melts. This allows us to achieve the posterior distribution of a series of Generalized Langevin Equation models and corresponding parameter estimations together with uncertainty assessment, which can be applied to develop coarse-grained simulation models of various polymer melts.

[P10] The flow-induced phase change during the natural spinning of silk fibres

Peter Laity and Chris Holland

Department of Materials Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin St, Sheffield.

It is widely accepted that, irrespective of the species involved and the application desired by the animal, the natural spinning of silk fibres under ambient conditions is achieved through a flow-induced phase change. Yet the details remain elusive. Rheology provides a powerful tool for characterising the native silk feedstock and observing its conversion to a solid under various conditions and has generated an extensive body of literature. Nevertheless, progress towards a full understanding has been slow. Part of this may be ascribed to the difficulties in handling the native silk feedstock and apparent inconsistencies in its flow behaviour. Moreover, explanations offered hitherto have not taken full account of the wealth of information on this material emerging from the many diverse experimental methods used.

Our recent work has concentrated on rheological characterisation of native silk feedstock from the domesticated silkworm (Bombyx mori). Although considerable systematic variation has been observed, apparently linked to the onset of cocoon construction, it was found that oscillatory data measured between different feedstock specimens could be removed by normalisation against the cross-over point, while measurements at different temperatures (between 2 and 55°C) could be condensed onto a master-curve through time-temperature superposition (TTS). Rather than the complex behaviour frequently claimed for silk feedstocks, our work has indicated rheological simplicity, consistent with a well-dissolved polymer.

In combination with data from other techniques, this has led us to propose a new explanation for the silk phase change process.
[P11] Near-wall Velocimetry on a Rheometer by Evanescent Wave Dynamic Light Scattering

Antonio Giuliani, Ruel McEnzie, and Benoit Loppinet

IESL, FORTH, HERAKLION, Crete 71110, Greece

Assessing the near wall velocity profile can be important in a number of situations, in particular in the context of the possible occurrence of slip of complex fluids at the wall. We present the implementation and use of evanescent wave dynamic light scattering for near-wall velocimetry on a rotational rheometer. With this technique, we gain access to both a near-wall velocity as well as to the near-wall shear rate (in a range of 100 nm from surface). The technique takes advantage of the penetration depth (order of 500nm) of light at total internal reflection to resolve the velocity gradient of colloidal tracers (220nm) in the penetration depth as well as the velocity of the slowest tracers nearest to the glass bottom plate of the rheometer. The tool can be relatively easily implemented on commercial rheometers. We describe the principles of the technique [1] and demonstrate its use on various fluids, including simple Newtonian fluids, colloidal suspensions and polymer solutions. Linear no slip flows are observed for Newtonian fluids. Visco-elastic fluids were found to present near wall shear rate different from the macroscopic shear rate, and non-zero slip velocities and lengths. The presence and onset of slip is shown in the case of Laponite dispersion.


[P12] Origin of dynamic contact angle at the nanoscale

A.V. Lukyanov, A.E. Likhtman

School of Mathematical and Physical Sciences, University of Reading, Reading RG6 6AX, UK

Generation of a dynamic contact angle in the course of wetting is a fundamental phenomenon of nature. Dynamic wetting processes have a direct impact on flows at the nanoscale, and therefore, understanding them is exceptionally important to emerging technologies. Here, we reveal the microscopic mechanism of dynamic contact angle generation, which is demonstrated using large-scale molecular dynamics simulations of bead–spring model fluids. It has been shown that the main cause of local contact angle variations is the distribution of microscopic force acting at the contact line region. We were able to retrieve this elusive force with high accuracy to understand its nature and its characteristic physical parameters. It has been directly established that the force distribution can be solely predicted on the basis of a general friction law for liquid flow at solid surfaces first formulated by Thompson and Troian on the basis of molecular dynamics simulations of Lennard-Jones liquids. The relationship with the friction law provides both an explanation of the phenomenon of dynamic contact angle and a methodology for future predictions. The mechanism is intrinsically microscopic with characteristic length scale of the friction force distribution of about 3 nm, universal, and irreducible and is applicable to a wide range of problems associated with wetting phenomena.
[P13] Chain dynamics in polymer melts at flat surfaces

Jack Kirk and Patrick Ilg

Department of Mathematics and Statistics, University of Reading, RG6 6AX, UK

We investigate a single-chain theoretical model for describing the influence of steric hindrance on the dynamic properties of non-entangled chains in polymer melt near a flat surface. The Rouse model is extended by an additional potential that results from the assumption that chain conformations coincide with reflected random-walk statistics, as first advocated by Silberberg\(^1\).

The results for end-to-end vector and Rouse mode correlation functions compare well with those obtained from molecular dynamics simulations of multi-chain systems using the Kremer-Grest bead-spring model\(^2\). Even though the additional potential is parameter-free, we show that the accuracy of the model for surface chains is comparable to that of the Rouse model for bulk chains. An analytic dumbbell model accurately describes the longest Rouse mode correlation function of surface-tethered "mushroom" chains immersed in a polymer melt at low grafting density.


[P14] Unsteady Flow of Thixotropic Fluid in a Slowly Varying Pipe

Andrew I. Croudace, David Pritchard, Stephen K. Wilson

Department of Mathematics and Statistics, 26 Richmond Street, University of Strathclyde, Glasgow, G1 1XH, Scotland, United Kingdom

e-mail: andrew.croudace@strath.ac.uk

We use lubrication theory to develop the governing equations for unsteady axisymmetric flow of thixotropic fluid along a circular pipe of slowly varying radius. The strength of thixotropy is described by advective and temporal Deborah numbers, which are the ratios of the structure response timescale to, respectively, the timescales of advection and of an unsteady applied pressure gradient. In the regimes of ‘weak thixotropy’, in which the Deborah numbers are comparable to the small aspect ratio of the pipe, we follow the expansion method proposed by Pritchard et al. [1] to obtain the effects of thixotropy and antithixotropy as perturbations to a generalised Newtonian flow. We present illustrative results for the Moore–Mewis–Wagner rheology [2, 3]. Pritchard et al. [1] showed that in a widening channel (or, by analogy, a decelerating flow), thixotropy increases the fluid velocity near the centre of the pipe and decreases it near the wall, while antithixotropy has the opposite effect. These results are generic for steady pipe flow (see Figures 1(a) and (b) for thixotropic and antithixotropic fluids, respectively). However, unsteady pipe flow of an antithixotropic fluid is more complicated and the velocity profile depends on some subtle dynamical balances. We show that for some rheological models the velocity perturbation for a strongly antithixotropic fluid mimics that for a thixotropic fluid (see Figures 1(c) and (d) for thixotropic and strongly antithixotropic fluids, respectively). This casts doubt on the extent to which generic statements can be made about the effects of antithixotropy on lubrication flow.
Figure 1: Profiles of the streamwise velocity perturbation $w_1$ for the steady flow of a thixotropic fluid (a) and an antithixotropic fluid (b), and the unsteady flow of a thixotropic fluid (c) and a strongly antithixotropic fluid (d).

References


Keywords: Thixotropy, antithixotropy, slowly varying flow, Moore–Mewis–Wagner model.

[P15] Flow phenomena in the XY model

R M L Evans(a), C A Hall(a), R A Simha(b), T S Welsh(a), J Hulks(a)

[a] University of Leeds, United Kingdom; [b] IIT Madras, Chennai, India

e-mail: r.m.l.evans@leeds.ac.uk

It was shown in [PRL 114, 138301 (2015)] that one of the standard models of statistical mechanics, the classical one-dimensional XY model, exhibits many of the flow regimes typical of non-Newtonian fluids. So this simplest of models may reveal universal physics relevant to all complex fluids. Here we present further results and investigate the order parameters that control flow-induced phase transitions.

The XY model has transitions between four steady-state behaviours: uniform flow, shear-banding, solid-fluid coexistence, and slip-planes/fractures. These archetypal non-Newtonian flow regimes can be seen in many real complex fluids (foams, dense colloids, surfactant solutions, polymer melts), that have very little in common, in terms of the specific details of their constituent particles and their interactions.

The defining features common to all complex fluids are: (i) that their constituents are large enough to behave classically, governed by Newtonian dynamics (ii) that their constituents are small enough to be Brownian, governed by statistical mechanics, (iii) that their interaction energies are comparable to the thermal energy scale, so that their phenomenology is governed by both energetic and entropic effects. The 1D XY model with conserved angular momentum is the simplest classical, Brownian system with a bounded, non-zero interaction potential, and therefore qualifies as a complex fluid.