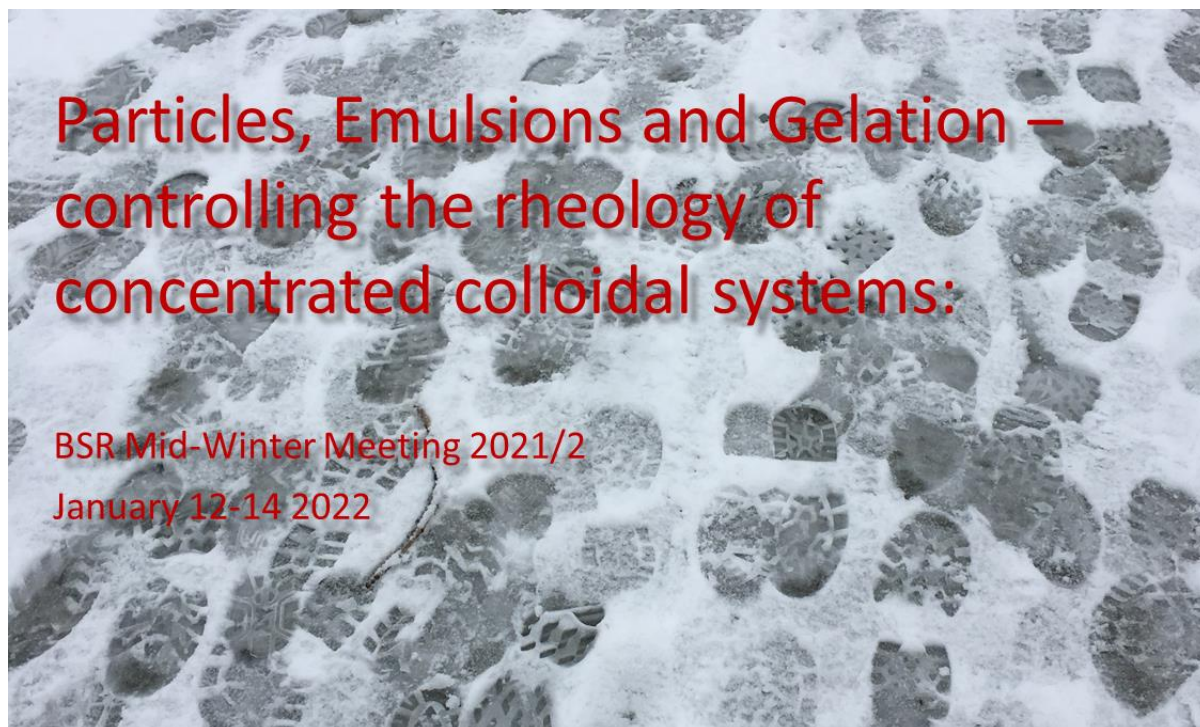




## Programme



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# The British Society of Rheology

Day 1 - Wed 12th				Day 2 - Thurs 13th				Day 3 - Fri 14th			
				Length	Start	end					
							Chair				
							Claire McIlroy				
				00:05	09:00	09:05	Welcome day 2				
				00:40	09:05	09:45	Helen Wilson				
				00:25	09:45	10:10	Carlos Torres-Ulloa				
				00:25	10:10	10:35	Romain Mari				
				00:25	10:35	11:00	Franco Tapia				
				00:20	11:00	11:20					
							Chair				
							Richard Watson				
				00:40	11:20	12:00	<b>Olav Romcke</b>				
				00:25	12:00	12:25	Thomas Larsen				
				00:25	12:25	12:50	Thanasis Athanasiou				
				00:00	12:50	12:50	---				
						12:50					
Length	Start	end		Length	Start	end		Length	Start	end	
			Chair				Chair				Chair
			Shona Marsh				Simon Cox				Richard Thompson
00:10	13:00	13:10	Welcome	00:05	14:00	14:05	BSR prizes intro	00:05	13:00	13:05	Welcome day 3
00:40	13:10	13:50	<b>Daniel Bonn</b>	00:40	14:05	14:45	<b>Dan Curtis</b>	00:40	13:05	13:45	<b>Sebastien Manneville</b>
00:25	13:50	14:15	James Richards	00:05	14:45	14:50	Award	00:25	13:45	14:10	Vincenzo Calibrese
00:25	14:15	14:40	Beibei Zhou	00:35	14:50	15:25	<b>Ana Mari Fuentes Capparos</b>	00:25	14:10	14:35	Henry Lockwood
00:25	14:40	15:05	Rut Besseling	00:05	15:25	15:30	Award	00:00	14:35	14:35	---
00:20	15:05	15:25	break	00:20	15:30	15:50	break	00:20	14:35	14:55	break
			Chair				Chair				Chair
			Phil Threfell-Holmes				Manlio Tassieri				Simon Cox
00:40	15:25	16:05	<b>Malcolm Faers</b>	00:40	15:50	16:30	<b>Emanuela Del Gado</b>	00:40	14:55	15:35	<b>John Royer</b>
00:25	16:05	16:30	Joerg Lauger	00:25	16:30	16:55	Reza Foudazi	00:25	15:35	16:00	Olivia Pabois
00:25	16:30	16:55	Andrew Clarke	00:25	16:55	17:20	A Darras	00:25	16:00	16:25	John Hone
00:25	16:55	17:20	Joseph Cousins	00:25	17:20	17:45	Abhishek Rajbanshi	00:05	16:25	16:30	Meeting conclude
	17:20				17:45				16:30		

All papers to be given via Zoom.

Speakers, please ensure your talk finishes within, at most, 20mins. Your timeslot allows for your starting up zoom sharing, your talk and questions. There will be a hard stop.

All registrants will be emailed connection details ahead of the meeting.



## 1 Day 1 Wed 12<sup>th</sup> pm

### 1.1 Repulsive colloidal emulsions, hard or soft particle dispersions

	<p><b>Towards a constitutive equation for yield stress fluids</b> <b>Daniel Bonn</b> <i>University of Amsterdam</i></p> <p>Yield stress materials such as emulsions are very frequently encountered in everyday life, but we do not really know how to predict their flow behavior. I will present a systematic study of the flow behavior of emulsions as a function of the volume fraction of the dispersed phase. A yield stress is observed above a critical volume fraction, the jamming transition. I will show that a simple rescaling of the flow curves with the distance to jamming yields a universal behavior. In addition, the stress scale is shown to be given by the Laplace pressure of the emulsion drops. This means that once the drop size, interfacial tension and volume fraction are known, the shear rheology can be predicted. I will also extend this to the normal stresses and elongational viscosity, allowing to formulate a constitutive equation for emulsion rheology that predicts the flow behavior for arbitrary flows.</p>
	<p><b>Characterising the yielding of soft solids on the microscopic level without particle tracking</b> <b>James A Richards, Vincent A Martinez and Jochen Arlt</b> <i>University of Edinburgh</i></p> <p>Microscopic dynamics reveal the origin of the bulk rheological response in complex fluids. In model systems particle motion can be tracked from microscopy, but for industrial samples this is often impossible. Here we complement rheological measurements of the yielding of a silicone oil emulsion with information on the microscopic dynamics from rheo-confocal imaging without particle resolution. By adapting differential dynamic microscopy to study flowing highly concentrated systems, we probe both the rate of shear-induced rearrangements and the local flow velocity in oscillatory and steady shear. Yielding is seen to happen in two steps: with droplet mobilisation marking the limit of linear visco-elasticity, followed by the development of shear localisation and macroscopic yielding. Using this suite of techniques, such insight could be developed for a wide variety of challenging complex fluids.</p>
	<p><b>Flow behaviour of oil/water high internal phase emulsions (HIPes) at high shear rate under confinement</b> <b>Beibei Zhou, Stephan Drusch and Sean A. Hogan</b> <i>Teagasc Food Research Centre and Technical University of Berlin</i></p> <p>High shear rheometry has been used to achieve very high shear rates (<math>&gt; 10^4 \text{ s}^{-1}</math>) at narrow gaps (of micrometre length scale). Following considerations of various sources of errors and data artefacts, the effects of protein concentration and pH of continuous phase on the flow behaviour of whey protein isolate (WPI) stabilised high internal phase emulsions (HIPes) have been studied using this method. Narrower gaps enhanced the solid-like behaviour for the emulsions. Higher protein concentrations resulted in smaller droplets with a tighter network structure, leading to higher viscosity and yield stress. The HIPes can be transformed from thixotropic to anti-thixotropic system by increasing the protein concentration. The magnitude of the latter was greater at acidic pH compared to neutral pH, which is likely due to more extensive, confinement-induced ageing. Emulsions exhibited greater stability against extreme</p>



	<p>shearing conditions and creaming at pH 3 than at pH 7. This can be attributed to more efficient adsorption of whey proteins and large deformability of the oil droplets under the former conditions.</p>
	<p><b>Spatially Resolved DLS for inline characterization of concentrated nano-emulsions during High Pressure Homogenization</b> <b>R. Besseling, R. van Tuijn, M Hermes, C. Schuurmans, A. Gerich</b> <i>InProcess-LSP</i></p> <p>Nano-emulsions are widespread as intermediate or end-products in food, cosmetics, pharmaceutical and chemical industries. A popular method for their manufacturing is High Pressure Homogenization (HPH) due to its ease of tuning droplet size and up-scaling. Nevertheless, there remain challenges, e.g. in developing and understanding HPH processes and formulations in an efficient manner, and in real-time process control for complex emulsions. Despite advances in HPH modelling [1], for specific cases direct inline monitoring ('Process Analytical Technology', PAT) of HPH process can be crucial to obtain nano-emulsions with controlled size characteristics and functionality.</p> <p>Detailed inline size characterization of nano-dispersions was previously hardly possible due to limitations in characterization methods. We have introduced an instrument based on Spatially Resolved DLS (SR-DLS), the NanoFlowSizer (NFS), which can measure the size of nanoparticles in real-time, under flow conditions, for concentrated emulsions up to very high turbidity. By implementing the NFS inline in HPH processes, the droplet size can be directly monitored during processing, the effect of changes in formulation and process parameters can be established efficiently and process parameters may be tuned to obtain the desired size characteristics.</p> <p>I will describe both this novel measurement method and PAT technology, as well as the application to monitor and characterize HPH of model oil-water emulsions, focussing on effects of droplet interactions on inline size characterization and on the effective mechanism of droplet size reduction.</p> <p>[1]Gupta, A., et al, 2016. Controlling and predicting droplet size of nanoemulsions: Scaling relations with experimental validation. <i>Soft Matter</i> 12, 1452–1458. [2]Besseling, R., et al, 2019. New unique PAT method and instrument for real-time inline size characterization of concentrated, flowing nanosuspensions. <i>Eur. J. Pharm. Sci.</i> 133, 205–2.</p>

## 1.2 Applications

	<p><b>Crop protection suspension formulation design – applying rheology and colloid science to understand the complex performance and stability challenges.</b> <b>Malcolm Faers,</b> <i>Bayer AG, Formulation Technology, Monheim, Germany.</i></p> <p>Designing crop protection formulations is a complex challenge, the final product must fulfil several different criteria such as performance, innovation, differentiation, safety, be registerable, cost, sustainability, stability and be robust for manufacture for example. These criteria often compete against each other during formulation design and finding effective solutions in the design space is complex. This raises the question of how can solutions be found efficiently? The number of recipe components, process variations and product criteria make it highly unlikely that solutions will be found that could be foreseen. Colloid science and rheology</p>
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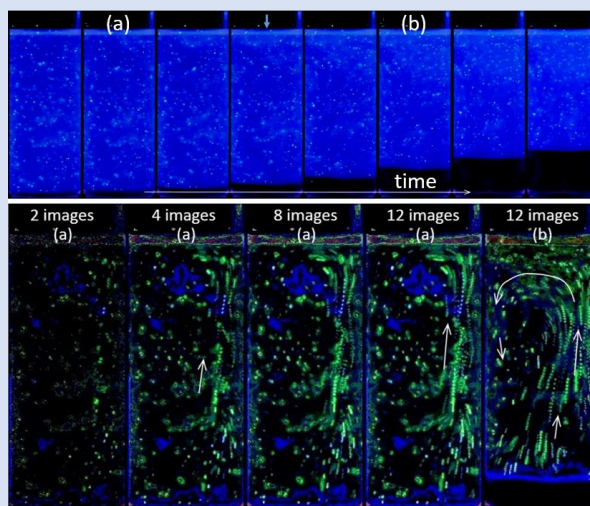
are valuable tools here in the formulation design process to better understand the large and complex design variable space.

Recently unmanned aerial systems (UAS) or drones have emerged (rapidly in APAC) as alternative and potentially disruptive methods to apply products more sustainably with the opportunity to reduce the CO<sub>2</sub> footprint of spray application but with the consequence of limited carrying capacity for the spray liquid (~10-30L), resulting in spray volumes down to ~8-30 L/ha (from ~100-1000 L/ha). At these low spray volumes, the low number of spray droplets (typically VMD 100 to 250 microns) impacts the deposition and coverage, which can result in reduced efficacy. This creates interesting opportunities for formulation design where the higher concentration of surfactants and other formulants in the spray droplets can be utilised to enhance wetting, spreading and biodelivery of active ingredients to the target.

Optimisation of such recipes with many formulation components is complex regarding both performance and stability during the product's lifetime, which is typically 2-4 years. These suspensions are weakly arrested gels that resist gravitational separation through the presence of particle networks (e.g., from depletion flocculation of the active ingredient particles and/or gelling clays). These particle networks show ageing of the network and can show delayed gravitational collapse.

Index matched PDMS emulsions with non-adsorbing polymers are convenient model arrested gel network systems to study that show collapse to be a random process demonstrating both height and density dependence, indicating it to be stress driven and that the mechanical properties ( $G'$ , static yield stress) are important elements for the stability of suspensions. In-situ low invasive vane rheology measurements curiously show that the gel network increases in strength prior to collapse, demonstrating that the collapse is not due to weakening of the network but an increase in the internal stress in the sample. The inclusion of tracer particles reveals remarkably that internal structural changes on the macroscopic scale (as well as microscopic) occur for significant periods of time prior to collapse and ultimately when collapse occurs that it is a highly chaotic process.

Low invasive vane rheology is a valuable predictive technique which can sample the evolving structure in suspensions during ageing, provide information on stability and accelerate the design of stable commercial suspensions.



Time-lapse image series showing changes in the interface height and internal movement both pre-collapse (a) and post-collapse (b). Sample: Depletion flocculated PDMS emulsion ( $\phi$  0.3) with HEC (1.4 g/L). Bottom: Composite images from regions (a) and (b) showing internal movement of tracer particles between successive images.

(PDMS = polydimethylsiloxane, HEC = hydroxyethyl cellulose)

## Advances in rheo-optical methods

**Joerg Lauger,**

*Anton Paar Germany*

Simultaneous use of rheological and optical techniques, i.e. of rheo-optical methods, is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. Different optical methods such as small angle light scattering, microscopy (polarized, fluorescence,



confocal), spectroscopy (NIR, IR, Raman), birefringence and dichroism, as well as pure visualization techniques have been employed.

In this paper, the use of rheo-optical techniques suited for a variety of materials is discussed. Microscopy and especially polarized microscopy and SALS at elevated temperatures provide structural information in the micro meter range on flow induced orientation or phase transition phenomena. A rheo polarized imaging techniques called SIPLI (shear induced polarization light imaging) combines a visualization technique with measurements of local stresses through the detection of the birefringence [1]. By employing parallel-plate geometries, different shear rates are present throughout the sample, from a maximum shear rate at edge of the sample to a zero-shear rate in the center of the plate. With SIPLI the whole plate is observed and the birefringence can be displayed over the full range of shear rates within one single experiment. Applications presented include simultaneous SIPLI and the rheology of the oriented lamellar phase of block copolymers, cellulose and block copolymer solutions as well as shear orientation effects in liquid crystals, nanocellulose and clay suspensions. In addition, flow-induced crystallization of semi-crystalline polymers was investigated with SIPLI.

During phase transitions the physical as well as the chemical properties of materials can change dramatically. While the viscoelastic properties can usually be characterized with a rheometer, no chemical information is obtained by the mechanical testing. The interpretation of rheometric results often relies on empirical models and a more phenomenological approach. For directly relating the changes in rheological behaviour to chemical changes, we employ Raman spectroscopy in situ with rheology [2]. The phase transition from the crystalline to liquid state for different polymers was monitored for a temperature range from 70 to 150 °C. This phase transition resulted in a higher viscosity, as well as an alteration of vibrational bands in the Raman spectrum, reflecting the conversion from a crystalline to an amorphous structure. Having both viscoelastic and spectroscopic information on a sample allows a detailed characterization, and interpretation of the sample behaviour on the molecular level. Special emphasis has been given to an accurate temperature control up to 400°C in order to take full advantage of the potential of the various rheo-optical techniques for polymeric applications.

#### References

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2. Fleissner, F.; Napp, K.E.; Wezislá, B.; Völker-Pop, L. *Spectroscopy* 2019, 34(9), 2-8.

#### **Gel breakdown in a formulated product via accumulated strain**

**Andrew Clarke**

*Schlumberger Cambridge Research*

We study the breakdown of a gelled formulated product, a drilling fluid, under the action of repeated deformation, i.e. weakly nonlinear oscillation. Our data may be rationalised by postulating that the fluid behaves as an arrested phase separating material whose natural slow structural evolution, aging and coarsening, is accelerated by the imposed sinusoidal strain consistent with previous work on well characterised systems. During the observed evolution the elastic modulus exhibits a maximum which appears correlated with a maximal connected heterogeneity of structure.



## **Weak-anchoring effects in a pinned ridge of nematic liquid crystal**

**Joseph R. L. Cousins**, Akhshay S. Bhadwal, Lindsey T. Corson, Brian R. Duffy, Ian C. Sage, Carl V. Brown, Nigel J. Mottram, Stephen K. Wilson

*University of Glasgow / University of Strathclyde*

Motivated by the need for further understanding of nematic liquid crystal (nematic) weak-anchoring effects in systems that involve interfaces between the nematic, a solid substrate, and an atmosphere of gas, a theoretical investigation of a thin pinned static ridge of nematic is undertaken and supported by new experiments.

Specifically, it is found that the value of the Jenkins--Barratt--Barbero Barberi critical thickness determines the energetically preferred solutions for the nematic director.

It is also found that, in general, anchoring breaking occurs in edge regions adjacent to the nematic--substrate--gas three-phase contact lines, and the director alignment in these regions is uniform and determined by the interface with the strongest anchoring.

The analysis is compared with physical experiments using a thin pinned static ridge of the nematic 4'-pentyl-4-biphenylcarbonitrile (5CB) and new insight into the weak anchoring of the air--5CB interface is obtained.



## 2 Day 2 Thurs 13<sup>th</sup> am

### 2.1 Non- colloidal non-granular athermal particles -constitutive modelling

	<p><b>Modelling the first effects of viscoelasticity on suspensions and emulsions</b> <b>Helen Wilson &amp; Liam Escott,</b> <i>UCL</i></p> <p>Most theoretical models of two-phase materials yield governing equations that are too complex for any but rheological researchers to easily use. Here we show how to approximate three different two-phase materials using the second-order fluid model. In each case, the continuous phase is a weakly viscoelastic fluid; the inclusions may be rigid or soft solid particles, or liquid droplets. We use a mean-field approximation to produce semi-empirical models which are expected to capture the broad trends of behaviour some way beyond the strictly-dilute limit.</p>
	<p><b>Viscous froth model applied to the motion and topological transformations of two-dimensional bubbles in a channel: The three-bubble case</b> <b>Carlos Torres-Ulloa &amp; Paul Grassia,</b> <i>University of Strathclyde</i></p> <p>The viscous froth model can be used to predict the rheological behaviour of a two-dimensional liquid-foam system comprised of three bubbles confined between two glass plates (Hele-Shaw cell). The model incorporates three physical phenomena, namely the viscous drag force, the pressure difference across foam films, and the surface tension acting with curvature along with them, converting any mismatch between the pressure and film curvature to film motion. In the so-called infinite staircase structure, the system does not undergo any topological bubble neighbour-exchange transformations, for any imposed driving back pressure. Bubbles then flow out of the channel of transport in the same order in which they entered it. In contrast, in a simple single bubble staircase or so-called lens system, for higher imposed back pressures, topological transformations do occur, helping to relax the system. The case studied here, i.e. the three-bubble case, aims to interpolate between the infinite staircase and simple staircase/lens. To determine at which driving pressures and at which velocities topological transformations might occur, and how the bubble areas influence their occurrence, steady state propagating three-bubble solutions are obtained for a range of bubble sizes and imposed back pressures. As an imposed back pressure increases quasistatically from equilibrium, complex evolution is exhibited as the systems undergo either topological transformations, reach saddle-node bifurcation points, or asymptote to a geometrically invariant structure which ceases to change as the back pressure is further increased.</p>
	<p><b>Dynamics of microstructure anisotropy and rheology of soft jammed suspensions</b> <b>Nicolas Cuny, Eric Bertin, Romain Mari</b> <i>Univ. Grenoble-Alpes / CNRS</i></p> <p>We develop a constitutive model for rheology of two-dimensional soft suspensions above jamming. Starting from a statistical description of the particle dynamics, we derive, using a set of approximations, a stress evolution for arbitrary flows, whose coefficients are expressed in terms of the packing fraction and of particle-level parameters. This constitutive model rooted in the microscopic dynamics qualitatively reproduces a number of salient features of the rheology of jammed soft suspensions, including the presence of yield stresses for the shear component of the stress and for the normal stress difference. Within our model the orientation of the anisotropy of the</p>





	<p>microstructure, governed by an interplay between advection and contact elasticity, plays a key role at yielding and in flow. It generates normal stress differences contributing significantly to the yield criterion and Trouton ratio. It gives rise to non-trivial transients such as stress overshoots in step increases of shear rate, residual stresses after flow cessation. Finally, it explains the collapse of storage modulus as measured in parallel superposition for a yielded suspension</p>
	<p><b>Rheology of non-colloidal dense suspensions: friction and shape matters</b> <b>Franco Tapia</b>, Mie Ichihara, Olivier Pouliquen, Elisabeth Guazzelli <i>University of Tokyo</i></p> <p>The fundamental understanding of dense granular flows of non-colloidal particles suspended in a fluid matrix still remains a challenge, even in the simplest case of spherical particles immersed in a Newtonian fluid. The collective character, spatial disorder and out-of-equilibrium state of these systems make difficult to establish a set of constitutive equations to describe them. However, important progress in experimental and numerical studies give us some interesting clues about how particle-particle (roughness and shape) and fluid-particles interactions (interstitial fluid viscosity) could affect the macro-rheology of granular suspensions, in particular how the relative viscosity evolve as a function of the solid volume fraction close to the jamming transition.</p> <p>The presence of solids particles in suspension increases the anisotropy of the system, leading to non-zero stress difference. Inspired from granular mechanics, a frictional description presents as an interesting tool to complement classical rheology. Thus, the rheology is described by two dimensionless quantities: the effective friction and the global packing fraction. Since a simple dimensional analysis, these parameters are mainly ruled by the viscous number <math>J</math> in over-damped flows and by the inertial number <math>I</math>, once particle inertia takes place (Bagnold regime).</p> <p>We present here a brief description of how the rheological properties of non-colloidal particles evolve as a function of its mechanical and geometrical features. Well-controlled experiments under pressure and volume imposed conditions are performed to describe how geometrical properties of solid particles modify the algebraical function in the neighbourhood of the jamming transition. Additionally, by varying systematically the interstitial fluid, we show that the viscous-inertial transition takes place at a specific Stokes number, which is independent of the packing fraction. The algebraic power law for the viscosity divergency is also shown to follow a frictional behaviour and be independent of the regime.</p>

## 2.2 Non- colloidal non-granular athermal particles -constitutive experiments

	<p><b>Strain and surface texture on a dense cornstarch suspension</b> <b>Olav Rømcke</b>, Ivo R. Peters (<i>University of Southampton</i>), R. Jason Hearst (<i>Norwegian University of Science and Technology</i>)</p> <p>Dynamic jamming by shear in dense suspensions is caused by the formation of a frictional contact network between grains as stress increases. Given a high enough stress and packing fraction, the suspension will appear solid-like. Previous studies have revealed how a jamming front propagates through the suspension, leaving a jammed state in its wake. Experimentally, this has been done with a single perturbing body and relatively simple geometries. What happens to the state of the suspension when two jamming fronts collide remains an open question.</p>
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# The British Society of Rheology

	<p>Here we present experimental results of colliding jamming fronts that are generated by two cylinders moving in parallel. Using Particle Image Velocimetry (PIV) and high-speed footage of the surface texture, we show that the region in between the cylinders, where the jamming fronts first collide, appears to relax back to its quiescent state, while the jammed region in the far-field keeps growing.</p> <p>We further quantify the surface texture by a Fourier transform of localized windows of the surface images, which reveals the local directionality of the surface features. These structures correlate well with the direction of the eigenvectors of the accumulated strain tensor.</p> <p>Using this knowledge we show that the shape of the unjammed pocket that develops after the fronts collide is outlined by the eigenvectors of the accumulated strain tensor.</p>
	<p><b>Rheology of materials for bipolar plates and electrocatalytic inks in high temperature polymer electrolyte membrane fuel cells</b> <b>Thomas Larsen</b>, Søren Juhl Andreasen, Tom Larsen and Jesper de Claville Christiansen <i>Aalborg University/Advent Technologies A/S</i></p> <p>Highly filled polymer composites are used as bipolar plates (BPPs) for fuel cell applications due to their high electrical and thermal conductivities provided by fillers such as graphite and carbon black. However, the commercial production of BPPs require large quantities of powdered fillers, and to keep costs down the fillers are often polydisperse and irregularly shaped. Research carried out at Advent Technologies A/S has thus investigated the rheological behaviour of model polydisperse flake-graphite-in-oil suspensions. A strong dependence of the flow history on the viscosity is found, leading e.g. to the failure of the Cox-Merz rule. Future research aims to explore the effect of various filler particle size distributions and compound preparation methods on filler dispersion, rheology, and electrical conductivity.</p> <p>Electrocatalytic inks consisting of platinum nano particles, carbon blacks and various additives and solvents, are coated onto carbon substrates in order to manufacture fuel cell electrodes. The coated layers have special requirements when it comes to final morphology, surface structure, balance between triple phase boundaries and hydrophobicity. These properties are highly dependent on the processing parameters of the inks both during mixing, but also during coating and solvent evaporation. Viscosity is highly affected by different treatment steps, and different techniques can be applied in the industrial processing of the inks, such as mechanical mixing, high shear mixing, ultrasonication and vacuum treatment. Structured analysis is examined in order to optimize ink treatment and coating quality in the effort of creating electrodes of a higher cost and a better performance.</p>
	<p><b>High frequency Optimally Windowed Chirp rheometry in fast evolving systems.</b> <b>Thanasis Athanasiou</b>, George Petekidis <i>FORTH/IESL</i></p> <p>Frequency-modulated excitation waveform, known as Chirp, has emerged recently as promising way to interrogate the linear viscoelastic properties of time-evolving materials. With this method the linear viscoelastic spectrum can be obtained very fast compared to classic frequency sweeps.</p> <p>However, the ability of the software-controlled motor of commercial rotations rheometers, to impose such a complex strain waveform has limitations. We utilize frequency- and amplitude-modulated strain waveform [1] in conjunction with a home-made sliding plate piezo-operated rheometer [2] to probe the linear viscoelasticity of time –evolving materials. The simplicity of the setup due to the absence of any kind of</p>



firmware and the microsecond actuator-sensor response prove this device an ideal case study of the advantages of this technique. The high frequency capability of this piezo-rheometer allows us to extend the accessible linear viscoelastic spectrum and most importantly, to shorten the length of the interrogating strain signal (Chirp) at a subsecond scale. Therefore the duration of the scan is short compared to the evolution of moduli (mutation time) keeping the mutation number ( $N_{mu}$ ) [3] sufficiently low, even in fast evolving systems.

To this end, we provide proof of concept, by capturing the solidification of fast evolving soft matter composites such as vinylester resin and vinylester resin-fumed silica nanocomposite during curing process. The LVE spectrum is accessed almost every second portraying the rapid evolution of moduli with adequate time resolution. Comparison of the Chirp utilization in commercial rotational and piezo based rheometer provides further information on the applicability of the technique.

Work in collaboration with Michela Geri and Gareth H McKinley (MIT)

#### References

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- [3] Mours, M., & Winter, H. H. (1994). Time-resolved rheometry. *Rheologica Acta*, 33(5), 385-397



## 3 Day 2 Thurs 13<sup>th</sup> pm

### 3.1 Awards

#### 3.1.1 Annual Award Prof. Dan Curtis

**On weird and wonderful relaxation spectra in superposition rheometry**

**Dan Curtis<sup>1</sup>, Russell Davies<sup>2</sup>, Alex Holder<sup>1</sup>, Rebecca Hudson<sup>1</sup>, Ade Ogunkeye<sup>1</sup>**

*(1) Complex Fluids Research Group, Department of Chemical Engineering, School of Engineering and Applied Sciences, Swansea University, SA1 8EN*

*(2) School of Mathematics, Cardiff University*

Superposition rheometry, in which small amplitude oscillatory perturbations around a non-equilibrium flow condition are used to probe flow induced microstructural changes, can be implemented in either orthogonal or parallel configurations. Orthogonal superposition data (in terms of the orthogonal 'storage' and 'loss' moduli), are often interpreted as per their linear viscoelastic counterparts. However, the complexity of the flow in parallel superposition experiments means that the parameters characterising the oscillatory response are more difficult to interpret. Consequently, the use of a comparison of the moduli measured in orthogonal directions is rarely seen in the literature as a measure of flow induced anisotropy. To facilitate such a comparison, the authors have recently published a series of papers which consider the problem of interconversion between orthogonal and parallel superposition data. If possible, such an interconversion facilitates a valid comparison of the parallel and orthogonal superposition moduli. In this presentation, we will consider how interconversion can be undertaken using some well known constitutive equations via discrete relaxation spectra with interesting, and unexpected, properties before applying the models to the study of worm like micelles.



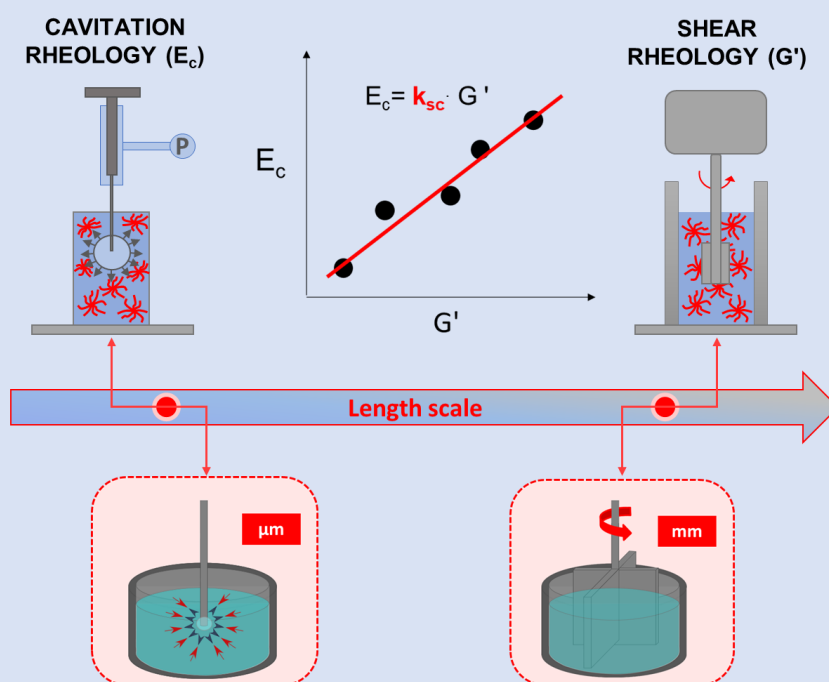
Vernon Harrison Award Ana M. Fuentes Caparrós

## Exploiting Rheology to Understand the Mechanical Properties of Multi-layered 3D Printed Hydrogel Systems

Ana M. Fuentes Caparrós

University of Strasbourg

Hydrogels are present in our everyday life: electronic devices, hygiene products, water purification systems, biomedical sciences, and so on. The characterisation of the mechanical properties of such class of soft material is key in determining whether these materials are potentially suitable for specific applications. Hydrogels used for tissue engineering, for example, are committed to 3D scaffolds that mimic the natural extracellular matrix, which supports cell adhesion, migration, differentiation and proliferation. As such, there is special interest in the study of the mechanical properties of hydrogels. Over the last few decades, 3D (bio)printing has emerged as a promising technology to construct biomaterials over layer-by-layer deposition with precise shape, structure and architecture of target tissues and organs.



**Figure 1.** Schematic representation of a cavitation rheometer (top left) and a shear oscillatory rheometer (top right). The relationship between both techniques is given by a proportionality constant,  $k_{sc}$ , determined by the ratio of the moduli obtained from the two techniques (top middle). Closer diagram showing how both techniques work at different length scales (bottom).

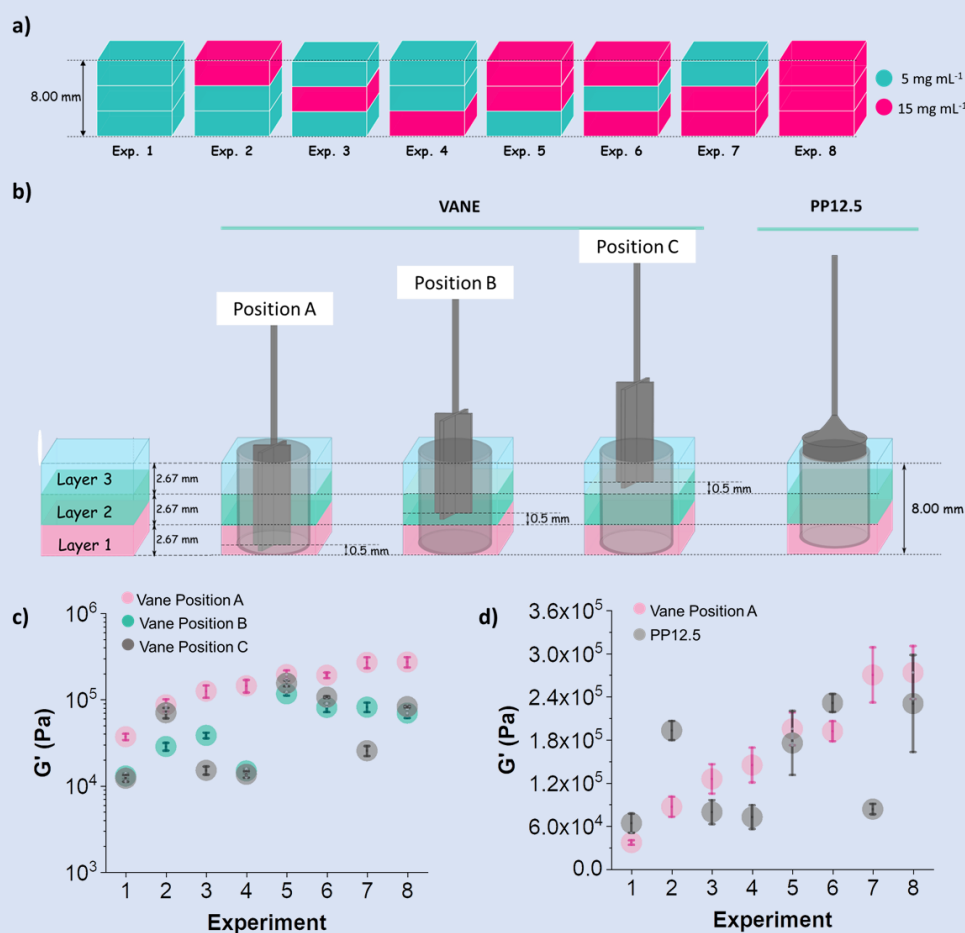
Thus, a wide range of hydrogels have been reported to be suitable for 3D printing. In most cases, the mechanical properties of such hydrogel's candidates are assessed before the 3D printing process, with little if any rheological characterisation of the gels after they have been printed. Thus, it is normally assumed that the resulting mechanical properties of the printed materials are not affected by the printing process. This lack of measuring post-printing is undoubtedly due to the difficulty in carrying out such measurements.





Furthermore, the mechanical properties of hydrogels are normally measured using traditional shear rheology, which needs millilitres of sample and assesses the bulk properties of the material. However, very often in biology, for example, the volume of gels samples for rheological characterisation is limited. As such, their characterisation using traditional shear rheology is restricted. Furthermore, it is important to not only measure the bulk mechanical properties, but also interpret the properties of hydrogels at a smaller length scale, especially if they want to be used in biomedical sciences.

In my thesis, I focused on developing rheological methods to characterise multi-layered hydrogels for 3D printing technology as well as finding a way to characterise the mechanical properties of hydrogels at multiple length scales. Specifically, we used traditional shear rheology and cavitation rheology to assess the mechanical properties of a series of hydrogels at the mm and  $\mu\text{m}$  scales respectively (Figure 1).



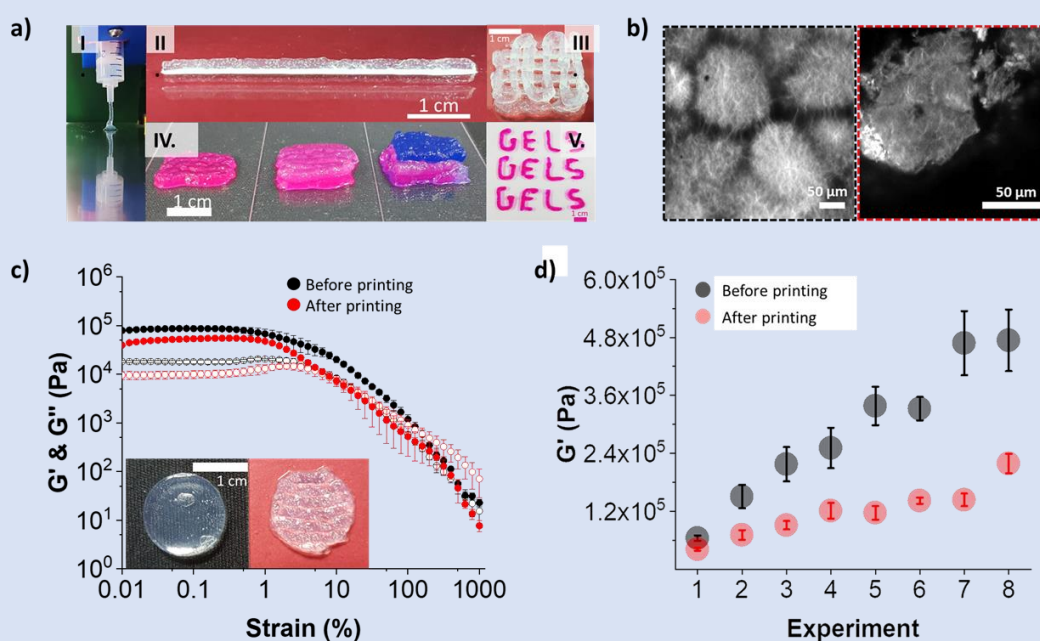
**Figure 2.** (a) Cartoons showing gel layers in experiments 1-8. Each gel stack is made up of 3 layers, where the cyan and deep pink layers represent 5 mg mL<sup>-1</sup> and 15 mg mL<sup>-1</sup> of the gelator respectively. The different concentrations result in different gel stiffnesses. (b) Schematic representing three different positions used for the vane measurements in an 8 mm three-layered gel; position A, B and C correspond to the vane located at 0.5 mm above the bottom surface of layers 1, 2 and 3 respectively. (c)  $G'$  values for experiments 1-8 in log scale using the vane in position A (pink circles), B (green circles) and C (grey circles). (d) Comparison of  $G'$  for experiments 1-8 using both the vane in position A (pink circles) and the PP12.5 (grey circles). The error bars represent the standard deviation of three different measurements.



We analysed the quantitative relationship,  $k_{sc}$ , to interconnect between both rheological techniques.  $k_{sc}$  was assessed for gels with different microstructures and we found that the resulting values were dependent on the type of microstructure present in our gel. The resulting measurements showed that cavitation rheology gives a greater insight into the networks that have been formed as compared to bulk rheology where the slight differences in absolute moduli are difficult to interpret.

Furthermore, we developed a rheological method to characterise the mechanical properties of multi-layered hydrogels with a high degree of control. We demonstrate that not only the mechanical properties of individual layers within a multi-layer gel system can be measured, but also the contribution of each layer to the combined gel can be assessed as well as the contribution of the neighbouring layers (Figure 2).

Lastly, we demonstrated the effect of 3D printing on the mechanical properties of the resulting multi-layered hydrogels (Figure 3).



**Figure 3.** (a) Photographs of 3D printed gels at a concentration of  $5 \text{ mg mL}^{-1}$ ; (a.I.) A 50 mm printed line. (a.II.) Deposition of a gel filament onto the printing bed; (a.III.) Scaffold of three printed layers; (a.IV.) (left to right) 1-layer, 2-layer and 3-layer systems using a serpentine pattern and dyed with Rose Bengal (layer 1), no dye (layer 2) and Nile Blue A (layer 3). (a.V.) Printed text. All scale bars represent 1 cm. (b) Confocal images for a gel at a concentration of  $5 \text{ mg mL}^{-1}$  (left) before and (right) after printing. The scale bars represent  $50 \mu\text{m}$ . (c) Strain sweep for a gel at a concentration of  $5 \text{ mg mL}^{-1}$  and 2 mm height before printing (black data) and 1 layer after printing (red data). The rheological measurements were carried out using the vane at a measuring position of 0.5 mm. The insets show photographs of a gel at concentration of  $5 \text{ mg mL}^{-1}$  (left) before and (right) after printing. (d) Evolution of  $G'$  for experiments 1-8 (black data) before and (red data) after printing. The error bars represent the standard deviation of three different measurements.



## 3.2 Attractive colloidal emulsions, hard or soft particle dispersions

	<p><b>Elasticity, rigidity and rheology of soft particulate gels</b> <b>Emanuela Del Gado</b> <i>Georgetown University</i></p> <p>Many materials we eat, spread, squeeze, or 3D print are gels, soft amorphous solids whose solid component is constituted by a network of self-assembled particles or agglomerated smaller units (proteins, polymers, or other particulates). The understanding of the emergence of rigidity and of the role of stress localization in the mechanics of this type of gels has just started, but it is clearly key to designing and expanding their performances and functions.</p> <p>I will discuss new insight into the fundamental physics that control rigidity, elasticity and rheology of soft particulate gels. Mechanical heterogeneities, often not recognizable from structures and morphologies, translate into stress and strain localization when the material is deformed or under load. The outstanding questions are whether there exist organizing principles in the gel microstructures that can encompass different compositions and gelation processes, and whether it is possible to identify common underlying mechanisms in the rheological response.</p>
	<p><b>Rheology of macro- and nano-emulsions in the presence of micellar depletion attraction</b> Neda Sanatkaran, Muchu Zhou, <b>Reza Foudazi</b> <i>University of Oklahoma</i></p> <p>In this work, we study the rheological behaviors of oil-in-water emulsions from micro- to nano-size droplets with different volume fractions above the CMC of the surfactant. We then discuss the rheological properties of these emulsions by considering the calculated interdroplet forces in terms of van der Waals, electrostatic, and depletion interdroplet interactions. Then, we present glass and gel states of studied emulsions in yield stress vs droplet size diagram. A model is proposed to describe the yield stress in attractive glass and gel regimes by considering contributions from Brownian motion and interaction between droplets.</p>
	<p><b>Erythrocytes sedimentation: collapse of a high-volume-fraction soft-particle gel</b> <b>A. Darras, T. John, L. Kaestner, C. Wagner</b> <i>Saarland University</i></p> <p>Erythrocytes sedimentation rate (ESR) is a physical parameter which is often checked in medical diagnosis. It is indeed well known that in case of inflammation, the increase in fibrinogen and other proteins induces a higher ESR.</p> <p>Until now, researchers thought that the increase of fibrinogen accelerates the ESR by creating larger aggregates of red blood cells (RBC). Fibrinogen is indeed an aggregation supporting agent of RBCs, and bigger aggregates tend to sediment faster in Stokes regime. However, modeling the ESR measurements with this hypothesis is challenging and often requires physical assumptions specific to this system.</p> <p>Besides, modern colloidal science has shown that attractive particles can form percolating aggregates, as wide as the container. The sedimentation of those colloids then follows a so-called "colloidal gel collapse" regime. Here, we show that RBCs actually follow the same behavior. We present detailed measurements of experimental ESR curves, and original microscopic pictures supporting this claim. We also demonstrate that such assumption naturally leads to efficient colloidal modeling for the sedimentation curve of RBC.</p>



## **Polymeric surfactants enabling thermoresponsive emulsions**

**Abhishek Rajbanshi<sup>1</sup>, Marcelo Alves da Silva<sup>1</sup>, Darragh Murnane<sup>1</sup>, Cecile A Dreiss<sup>2</sup>, Michael T. Cook<sup>1</sup>**

*1 School of Life and Medical Sciences, University of Hertfordshire, Hatfield, UK*

*2 Institute of Pharmaceutical Sciences, Kings College London, London, UK*

“Engineered emulsions” transition between liquid and gel states in response to a stimulus. Whilst there are several reports of pH-responsive engineered emulsions (Weaver, Rannard and Cooper, 2009), temperature-responsive materials of this type are uncommon and would have a tremendous potential in topical drug delivery system. These materials could transition from liquid to gel at body temperature, enabling in situ gelation and thus enhanced retention and therapeutic effect (Cook et al., 2021).

The main objective of the study is to investigate the use of polymeric surfactants to enable thermoresponsive emulsions. In this study, thermoresponsive branched copolymer surfactants (BCSs) were synthesised by free radical polymerisation aiming to generate thermoresponsive engineered emulsions. A “thermoresponsive” monomer exhibiting a lower critical solution temperature, di(ethylene glycol) methyl ether methacrylate (DEGMA), was combined with hydrophilic poly(ethylene glycol) methyl ether methacrylate (PEGMA), a cross-linker and different carbon length thiols acting as chain transfer agents. Thermoresponsive PDEGMA-co-PEGMA copolymers were synthesised with varying amount of crosslinker (ethylene glycol dimethacrylate, EGDMA) and the effect of polymer architecture on BCSs properties was explored. These thermoresponsive BCSs were characterised by NMR, GPC and SANS. GPC analyses revealed relatively systematic decrease in molecular weight and polydispersity with lowering the amount of crosslinker whilst keeping the stoichiometry of the monomer to chain transfer agent constant allowing for control over this parameter. This supports the generation of highly branched structures at high cross-linker concentrations.

Oil-in-water emulsions were then prepared by homogenising the aqueous solutions of thermoresponsive BCSs ranging in concentrations of 2.5-15 wt% with an equal volume of dodecane oil phase. However, at high polymeric concentrations of 15 wt% in aqueous phase, the emulsification was hindered. The dispersed-to-aggregated phase transition in surface-functional emulsions was tracked by monitoring the relative magnitude of the storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of temperature. This demonstrated that the BCSs could form thermoresponsive engineered emulsions. It was also found that crosslinker concentration, molecular weight, hydrophobic chain ends, and polymer concentration are able to tune the temperature at which the thermoresponsive emulsions transitions to a gel and the ultimate rheology of the gel phase. At around 49°C, the cross-over point when solid-like behaviour first appears occurs ( $G' > G''$ ), which most likely corresponds to the formation of an inter-droplet gel network indicating the aggregation of engineered emulsion gel due to intermolecular associations. Reversible thermoresponse was observed resulting in a dispersed conventional emulsion fluid upon cooling. The rheology of the engineered emulsion stabilised by the polymer synthesised with half the amount of crosslinker showed thermogelation at two events, 25°C and 50°C. However, during the first event, the thermogelation plateau was not stable with  $G'$  declining after 30°C indicating collapse of aggregated emulsion droplets. Polymer synthesised without crosslinker did not exhibit any thermoresponsive activity, indicating that this component is essential in



the design of these emulsions. It was also found that both molecular weight of the copolymer and length of hydrophobic tail groups enhanced the ability of the BCSs to form thermoresponsive engineered emulsions with a broad plateau in the gel phase. Furthermore, thermoresponsive activity was also enhanced with increase in polymer concentration. 10% polymer concentration was identified as the optimum concentration to show better thermoresponse and prolonged gel stability.

Overall, this study has demonstrated the ability of PDEGMA BCSs to generate thermoresponsive engineered emulsions and identified several design principles for these highly functional materials. These systems have the potential to be optimised further to gel at body temperature and generate thermoresponsive engineered emulsions for topical drug delivery.

#### References

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Weaver, J. V. M., Rannard, S. P. and Cooper, A. I. (2009) 'Polymer-mediated hierarchical and reversible emulsion droplet assembly', *Angewandte Chemie - International Edition*, 48(12), pp. 2131–2134. doi: 10.1002/anie.200805448.





## 4 Day 3 Fri 14<sup>th</sup> pm

### 4.1 Yielding of colloidal gels

	<p><b>Creep dynamics of colloidal gels : Reversible yielding versus irreversible rupture</b> Thomas Gibaud, Thibaut Divoux, and <b>Sébastien Manneville</b> <i>Physics Laboratory at Ecole Normale Supérieure</i></p> <p>Colloidal gels are formed through the aggregation of attractive particles, whose size ranges from 10 nm to a few micrometers, suspended in a liquid. Such gels are ubiquitous in everyday life applications, from food products to paints or construction materials, in particular thanks to their ability to easily “yield,” i.e., to turn from a solid to a liquid under the application of a weak external load. Understanding and controlling the mechanical response of colloidal gels is, therefore, of prime importance. Depending on the details of the system, however, the resulting gel networks present different microstructural organizations that may lead to widely different mechanical responses. This raises important challenges in fully characterizing yielding and in uncovering the mechanisms of nonlinear response in colloidal gels.</p> <p>In this talk, I will focus on the creep dynamics on colloidal gels, i.e., on their response to a constant shear stress. I shall distinguish between two classes of colloidal gels showing respectively reversible yielding, where the gel network reforms upon load release, and irreversible yielding, where the network is fully destroyed through fractures and phase separation. This broad, empirical distinction is achieved by coupling rheology and local measurements at a mesoscopic scale, intermediate between the network characteristic size and the sample size. I will describe the series of events that successively lead from the initial soft solid to a yielded, liquidlike suspension. Time permitting, I will further discuss “fatigue” experiments, where the shear stress is periodically modulated, and how the experimental observables, such as the yielding time, may be modeled to predict yielding. I will also highlight open questions and future research directions in the domain.</p>
	<p><b>Structure-property relationship of a soft colloidal glass in simple and mixed flows</b> <b>Vincenzo Calabrese</b>, Stylianos Varchanis, Simon J. Haward, John Tsamopoulos, Amy Q. Shen <i>Okinawa Institute of Science and Technology (OIST)</i></p> <p>Under specific conditions, rod-like cellulose nanocrystals (CNC) can assemble into structurally ordered soft glasses (SGs) with anisotropy that can be controlled by applying shear. However, to achieve full structural control of SGs in real industrial processes, their response to mixed shear and extensional kinematics needs to be determined. We hypothesise that by knowing the shear rheology of the CNC-based soft glass and adopting a suitable constitutive model, it is possible to predict the structure-property relationship of the SG under mixed flows.</p> <p>We use an aqueous suspension with 2 wt% CNC at 25 mM NaCl to form a structurally ordered SG composed of a CNC network containing nematic domains. We combine rheometry and microfluidic experiments with numerical simulations to study the flow properties of the SG in shear, extension, and mixed flow conditions. Extensional flow is investigated in the Optimised Shape Cross-slot Extensional Rheometer (OSCER), where the SG is exposed to shear-free planar elongation. Mixed flow kinematics are investigated in a benchmark microfluidic cylinder device (MCD) where the SG flows past a confined cylinder in a microchannel.</p>



	<p>The SG in the MCD displays a velocity overshoot (negative wake) and a pronounced CNC alignment downstream of the cylinder. Simulations using the thixotropic elasto-visco-plastic (TEVP) model yield near quantitative agreement of the velocity profiles in simple and mixed flows and capture the structural fingerprint of the material. Our results provide a comprehensive link between the structural behaviour of a CNC-based SG and its mechanistic properties, laying foundations for the development of functional, built-to-order soft materials.</p>
	<p><b>Long-term memory and delayed shear banding in soft glassy materials</b> <b>Henry Lockwood</b>, Matthew Carrington, Prof. Suzanne Fielding <i>Durham University</i></p> <p>We study theoretically the dynamics of soft glassy materials during the process of stress relaxation following the rapid imposition of a shear strain. By detailed numerical simulations of a mesoscopic soft glassy rheology model referenced against a simplified continuum fluidity model, we show that a dramatic shear localisation instability arises, in which the strain field suddenly becomes heterogeneous within the sample, accompanied by a precipitous drop in the stress. Remarkably, this instability can arise at extremely long delay times after the strain was applied, due to the long-term memory inherent to glassy systems. The finding that a catastrophic mechanical instability can arise long after any deformation could have far reaching consequences for material processing and performance, and potentially also for delayed geophysical phenomena.</p>

## 4.2 Mixtures of attractive and repulsive components

	<p><b>'Mechanorheological' memory suspensions from colloidal gels with granular inclusions</b> <b>John Royer</b> <i>University of Edinburgh</i></p> <p>We describe a new class of bistable 'mechanorheological' fluids that can be reversibly switched between rigid solid and flowing liquid states via mechanical shear. This smart material, analogous to field-tuneable electrorheological and magnetorheological fluids, is formed from a simple colloidal gel with embedded inclusions of non-Brownian 'granular' particles. While most complex fluids are mechanorheological in the sense that their rheology is rate dependant, our bistable mechanorheological suspensions remember their state after the removal of the external mechanical stimulus, so that shear acts as a switch between stable solid and liquid states.</p> <p>Direct imaging reveals this rheological change is driven by a clear transition in the suspension microstructure; the colloidal gel collapses into compact, disjoint blobs over a finite stress range to give the liquid state, and these blobs then redisperse at higher stress allowing the rigid gel to reform. We map out the state behaviour of these materials varying an array of suspension properties (sizes, concentrations, interactions) and demonstrate this phenomenon in two distinct model systems, suggesting generic phenomena with implications for an array of industrial products and processes.</p>
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	<p><b>Novel lubricating microgel-reinforced hydrogel as a saliva substitute</b> <b>Olivia Pabois, Jing Hu and Anwasha Sarkar</b> <i>University of Leeds</i></p> <p>Xerostomia, or dry mouth resulting from a reduction/absence of salivary flow/lubricity, affects at least 1 in 10 adults, with rates as high as 30% in elders and 80% in institutionalised elders. This condition, which can be a side effect of cancer-related radiations, has a detrimental impact on the ability to eat and speak, ultimately causing malnutrition and affecting the quality of life of elders.</p> <p>Inspired by the structure of human saliva [1], we have developed [2] and filed a patent application [3] for an innovative super-lubricious colloidal formulation, composed of a proteinaceous microgel-reinforced biopolymeric hydrogel.</p> <p>The capacity of this aqueous lubricant to provide both boundary and fluid film lubrication was assessed by tribology, using both smooth and 3D-textured elastomeric tribocontact surfaces, the latter being a biomimetic emulation of the real human tongue surface [4]. This surface replicates the size and spatial distribution of fungiform/filiform papillae, thus mimicking the human tongue roughness, stiffness and hydrophobicity. The viscoelastic and adsorption properties of the formulation were characterised using, respectively, rheology and quartz-crystal microbalance, and its mesoscopic structure was resolved using a combination of small-angle X-ray/neutron scattering and atomic force microscopy.</p> <p>Results show that our novel formulation reduces drastically the friction between two dry mouth-mimicking surfaces in contact, and performs strikingly better than the naturally lubricating human saliva, therefore demonstrating its high potential as an effective salivary substitute. Its remarkable lubrication performance was attributed to an optimal synergy between the two electrostatically binding components: the efficiently adsorbing microgel particle, promoting boundary lubrication, and the highly viscous hydrogel nanofibrils, generating hydrodynamic lubrication.</p> <p>References [1] Xu et al., <i>Adv. Mater. Interfaces</i>, 2020, 7, 1901549. [2] Hu et al., <i>ACS Macro Lett.</i>, 2020, 9, 1726. [3] Pabois et al., GB Priority Patent Application No. 2007546.1, 2020; International Patent Application No. PCT/GB2021/051212, 2021. [4] Andablo-Reyes et al., <i>ACS Appl. Mater. Interfaces</i>, 2020, 12, 49371.</p>
	<p><b>Structure and Settling in Agrochemical Suspensions</b> <b>John Hone</b> <i>Syngenta</i></p> <p>Serum and sediment formation are key failure mode in agrochemical products with suspended agrochemically active ingredient particles. Here we will look at how the anti-settling systems employed interact with the particle in suspension to alter the rheology and give robust formulations.</p>