General Session 1

Monday 31 May 11:30 – 12:30

Semiflexible polymers under oscillatory shear flow

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The non-equilibrium structural and dynamical properties of semiflexible polymers confined to two dimensions under oscillatory shear flow are investigated by Brownian multi-particle collision dynamics. Two different scenarios will be considered: Filaments with both fixed ends [1] and wall-anchored chains [2]. The results of the numerical studies will be presented and discussed.

References

[1] A. Lamura, R. G. Winkler *Polymers* **2019**, *11*, 737. DOI:10.3390/polym11040737

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Rheological behavior of highly loaded suspensions for dense ceramics stereolithography application

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Ceramics stereolithography (SLA) consists of overlapping photopolymerized thin layers of a colloidal paste containing around 45vol.% of ceramic particles. This manufacturing method provides a high spatial resolution (ca. 10 µm), required for the design of complex and dense ceramic pieces notably useful in biomedical-engineering. The pastes are made of ceramic particles, multifunctional monomers, photo-initiators, dispersants, plasticizers, ... These numerous components, together with the very high solid content, make the mechanical response of the pastes quite difficult to rationalize without a fine structural analysis, particularly while flowing. [1]

During the process, the paste is dropped onto the support prior to be spread out and subsequently polymerized with a laser – the two latter steps being repeated for each material's layer. In this work, we focus on the spreading step, in which the paste is submitted to high shear rates, typically around 10-100 s-1, mainly because of the reduced thickness of the layers. Importantly, the paste viscosity should be high enough at rest to permit self-supporting of a layer while it must drop significantly during spreading to ensure the recoating at high shear rate (Figure 1b – the maximal shear rate is calculated through $\dot{\gamma}_{max} = \omega\gamma$). Interestingly, beyond the usual shear-thinning regime, a clear shear-thickening is observable in our SLA paste around $\gamma = 0.1$ ($\dot{\gamma}_{max}$=1 s-1). Although this phenomenon is mostly assigned to the reaggregation of particles upon shearing, it is far from being fully understood, while relevant for the SLA processing in terms of shear rate.

We will first define the notion of printability to emphasize the scientific and technological challenges behind this emerging technique. We will notably show the peculiar rheological behavior of our paste in response to various steady and oscillatory non-linear solicitations. A special attention will be paid to the handling of the ceramic paste enabling to obtain reproducible results. Beyond rheology, we will present some preliminary results regarding the quality of the pieces printed with SLA and their structural characterization through SEM. Also, we will emphasize the importance of the powder composition on the photo-polymerization. In fact, while Ce doped zirconia appears of great interest in biomedical applications for its remarkably high toughness, Ce absorbance is high at the pertinent wavelength, raising new challenges in this multidisciplinary field.

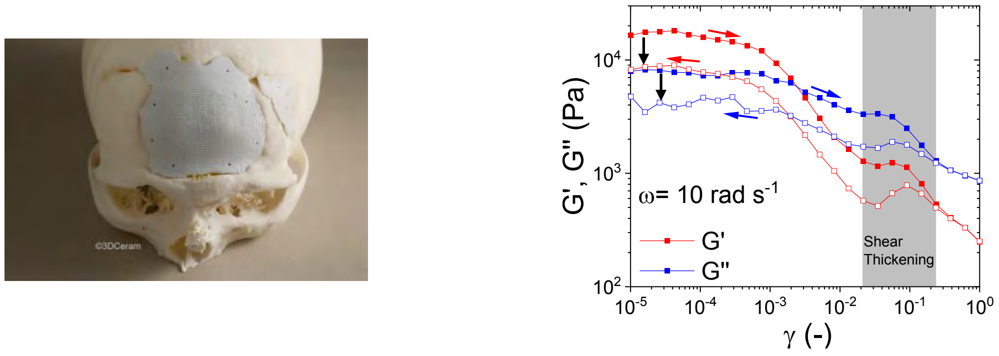

Figure 1: *a) A 3D-printed ceramic cranial implant made by SLA.* b) *Dynamic strain amplitude sweep of a commercial 3Y-TZP SLA paste.*

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Molecular mobility in skin and its relation to the presence of polar compounds

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The stratum corneum (SC) is the outer layer of the skin and protects the human body against both desiccation and penetration of harmful substances. To maintain the barrier properties of SC the biomembrane needs to be soft and pliable meanwhile tolerate deformation from physical strain and stress. In SC, these properties have shown correlation to both water content and presences of osmolytes, the latter commonly known as the natural moisturizing factor (NMF) [1]. Upon removal of NMF, i.e. through soaking of SC in water, the skin becomes stiff and brittle, which possibly is a result of reduced molecular mobility of its different components (keratin and lipids). In this study, we investigate how the molecular mobility in SC is affected by the removal of NMF and whether the induced changes can be reversed by a reintroduction of a simple polar molecule such as urea, pyrrolidone carboxylic acid or potassium lactate, which are compounds naturally present in NMF. NMR spectroscopy revealed that the mobility in the keratin filaments and a large fraction of the lipids in SC gradually vanished upon removal of NMF in comparison to untreated SC. Sorption measurements further showed a decrease in water uptake in SC when NMF was removed. Interestingly, when a polar compound was reintroduced to SC, for which NMF had been removed, mobility in both the keratin filaments and lipids was regained and the water uptake increased again. Taken together, the present study describes a general relation between the molecular mobility in SC and the amount of polar compounds present which is not necessarily dependant on the chemical origin of the NMF compounds. This finding contributes to the understanding of the biophysical properties of SC and are of value in the development of effective topical treatments.

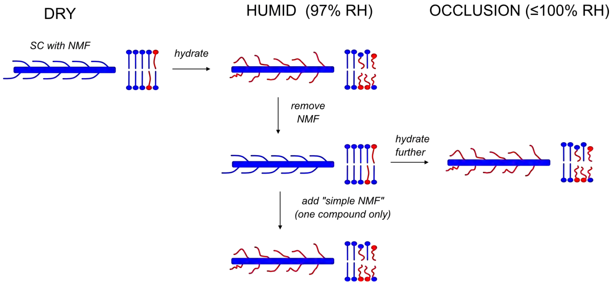

Figure 1: *Schematic illustration of how the molecular mobility of the keratin filaments and lipids in SC are affected by the presences of polar compounds.*

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General Session 2

Monday 31 May 11:30 – 12:30

Active Turbulence in Swarming Microswimmers

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Active matter systems in general and especially microswimmers in thin films exhibit an intriguing collective motion with large-scale swirling and streaming patterns reminiscent to classical high-Reynolds number hydrodynamic turbulence [1, 2]. The seemingly similar features of low-Reynolds number active turbulence and hydrodynamic turbulence triggered a broad range of studies on various kinds of microscale active systems ranging from bacteria swarms to eukaryotic cells to shed light onto the underlying physical mechanisms and to gain new insight into a long-standing and challenging phenomenon in physics. Various theoretical approaches have been applied to establish links between hydrodynamic turbulence and active turbulent-like motion, revealing a characteristic length scale in the latter systems. Even more, theoretical models and simulations reveal a wide spectrum of possible dynamical behaviors typically in disagreement with the predictions of the well-known Kolmogorov theory of turbulence. We presented simulation results for the collective motion of microswimmers in a quasi-2D geometry, which exhibit Kolomogorov-type hydrodynamic turbulence at sufficiently large concentrations. The bacteria-type microswimmers are modeled as spheroidal squirmers embedded in a multiparticle collision dynamics (MPC) fluid [3]. The emergent collective behavior depends on the microswimmer flow field, specifically the active stress and the rotlet dipole by the propulsion of bacteria, as illustrated in Fig. 1. Our simulations show that hydrodynamic interactions are of paramount importance for microswimmer swarming and active turbulence.

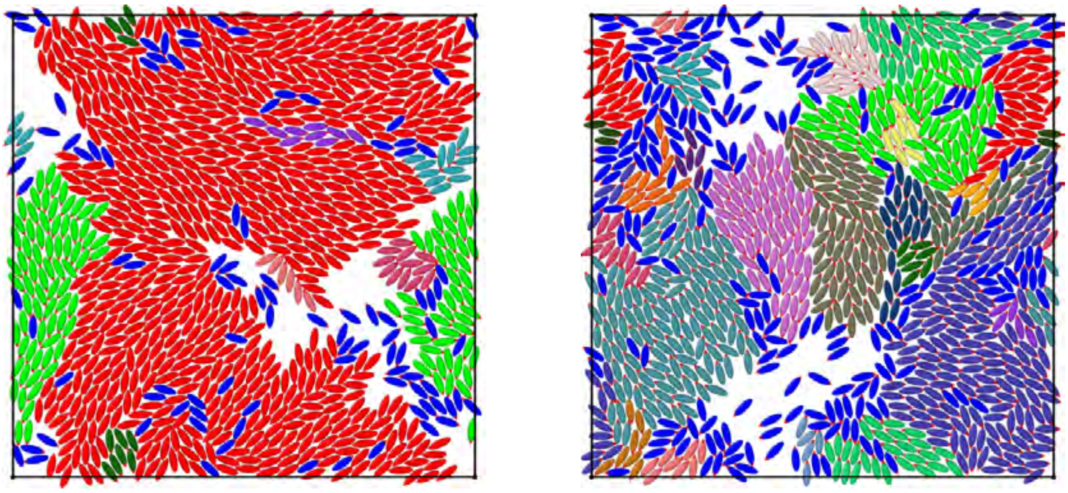

Figure 1: *Snapshots of squirmer configurations for zero (left) and finite (right) rotlet dipole. The colors indicate collective moving clusters, which are significantly smaller in presence of a rotlet dipole.*

References

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Probing the dynamics of bicontinuous Pickering emulsions with diffusion wave spectroscopy

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Bicontinuous Pickering emulsions (or bijels) are a relatively new class of novel soft material with many potential industrial applications, including microfluidics, tissue engineering and catalysis. They are typically formed by initiating the spinodal decomposition of a binary liquid mixture in the presence of neutrally-wetting colloidal particles. The particles attach at the liquid-liquid interface and arrest the phase separation by jamming when the concentration of particles approaches the 2D close-packing limit. Predicted by simulations in 2005 and realized in the laboratory in 2007, many aspects of the bijels complex behaviour and properties have remained unexplored and it is clear that there are potentially microscopic phenomena in the bijel which result in macroscopic aging and/or a determination of macroscopic structural properties. To investigate further, we use diffusing-wave spectroscopy (a form of light scattering) to probe the microscopic dynamics of the interfacial particles and/or the particle-laden liquid-liquid (L-L) interface. We find that bijel dynamics show two-step (fast/slow) decay behaviour, with dynamics slowing during aging that are reminiscent of the diffusion-limited cluster aggregation (DLCA) observed in standard colloidal gels. Additionally, we see that the DWS signature is dependent on whether a bijel's structural integrity relies on interfacial tension alone or whether bond formation takes place between the locally planar colloidal population, thereby forming a monogel. In the former case, the DWS correlation functions can be (almost) rescaled on to a master curve, indicating the property of universal aging. In the latter, the functions cannot be superimposed, implicating the monogelation process as a potential cause for a different kind of aging in the system.

Chemical Feedback in Templated Reaction-Assembly Networks

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Chemical feedback between building block synthesis and their subsequent supramolecular self-assembly into nanostructures has profound effects on assembly pathways. Nature harnesses feedback in reaction-assembly networks in a variety of scenarios including virion formation and protein folding.[1, 2] Also in nanomaterial synthesis, reaction-assembly networks have emerged as a promising control strategy to regulate assembly processes.[3] Yet, how chemical feedback affects the fundamental pathways of structure formation remains unclear. Here, we unravel the pathways of a templated reaction-assembly network that couples a covalent polymerization to an electrostatic coassembly process. We show how the supramolecular staging of building blocks at a macromolecular template can accelerate the polymerization reaction and prevent the formation of kinetically trapped structures inherent to the process in the absence of feedback. Finally, we establish a predictive kinetic reaction model that quantitatively describes the pathways underlying these reaction-assembly networks.[4]

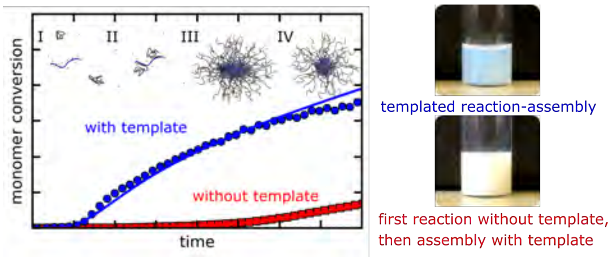

Figure 1: *Combining the reaction and the assembly process affects both the polymerisation kinetics (left plot) and the final structures formed (right pictures). During the reaction-assembly process four different phases could be distinguished, schematically depicted at the top left.*

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Student Organised Session

Monday 31 May 16:10 – 18:00

Dynamic stabilisation of polymer solution thin liquid films

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The drainage and rupture of polymer solutions was investigated using a dynamic thin film balance [1]. The polymeric nature of the dissolved molecules leads to significant resistance to the deformation of the thin liquid films. The influence of concentration, molecular weight, and molecular weight distribution of the dissolved polymer on the lifetime of the films was systematically examined for varying hydrodynamic conditions. Depending on the value of the capillary number (Ca) and the degree of confinement, different stabilisation mechanisms were observed [2].

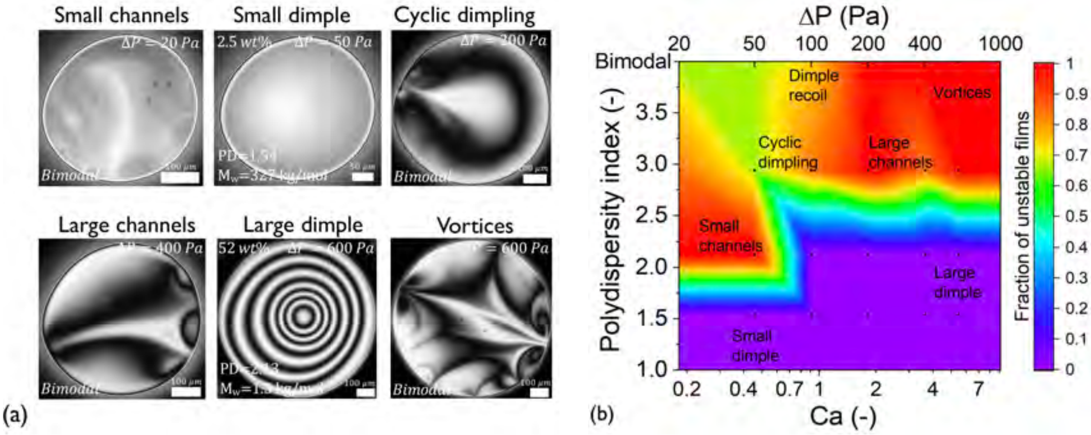

Figure 1: *(a) Microinterferometric images of polymer films of different polydispersities. (b) State diagram describing the propensity for asymmetric drainage as a function of Ca and ΔP for films containing polymers of different polydispersities.*

For low Ca, the lifetime of the films was the highest for the highly concentrated, narrowly-distributed, low molecular weight polymers. In contrast, at Ca, the flow-induced concentration differences in the film resulted in lateral osmotic stresses, which caused a dynamic stabilisation of the films and the dependency on molecular weight distribution in particular becomes important. Phenomena such as cyclic dimple formation, vortices, and dimple recoil were observed, the occurrence of which depended on the relative magnitude of the lateral osmotic and the hydrodynamic stresses. The factors which lead to enhanced lifetime of the films as a consequence of these flow instabilities can be used to either stabilise foams or, conversely, prevent foam formation.

References

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Melting of Entropically Stabilized Solid

Presenting Azizi [1], I. Azizi[1], Y. Rabin[1]
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In most many-body systems ordering is produced by energy (minimization) and is destroyed by entropy. One example are binary mixtures of colloidal particles of different sizes that interact by purely repulsive hard core [1] or soft core [2] forces in which big particles phase separate from the small ones and form a crystalline phase surrounded by small particle fluid. The common understanding of this phenomenon is in terms of the entropic depletion mechanism proposed by Asakura and Oosawa [3]: when the number of small particles is much larger than that of big ones, the system can decrease its free energy by creating a dense ordered phase of big particles which is increasing the available free volume and consequently the entropy of small particles. Therefore the big particle crystals are stabilized by the entropic forces applied on their surfaces by the small particle fluid, or equivalently, introduce attractive effective depletion forces between the big particles that mimic the effect of entropic forces due small particles. Note that this mechanism does not violate the 2nd law of thermodynamics since the decrease of entropy of big particles is overcompensated by the increase of entropy of small ones. While this phenomenon is well understood, it raises an interesting issue that has not been addressed so far: what happens to big particle crystals as temperature is increased? Clearly, for hard core particles there is no temperature dependence. However, when the repulsive interaction between the particles is of soft core type, this argument no longer applies and the question about the thermal stability of big particle crystals formed by depletion forces remains open. The study of this problem is the subject of the present work.

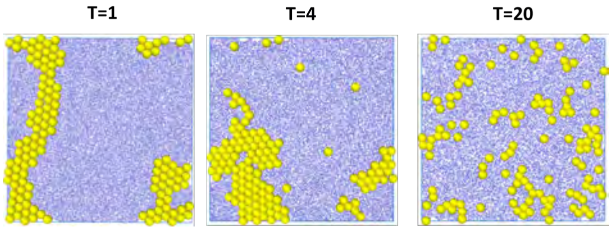

Figure 1: *Melting of a solid cluster of big particles* $\phi_{big} = 0.25, \phi_{small} = 0.35$ *at T=1,4, 20*

We consider binary mixtures of two dimensional soft disks interacting via a Weeks-Chandeler-Andersen (WCA) potential simulated by Langevin dynamics. While at low temperatures the big particles form a hexatic phase, when we increase the temperature, the solid melts (see Fig. 1). We show that at elevated temperatures the softness of the potential decreases (increases) the excluded (free) area of the small particles and, therefore, the area fractions of both big and small particles are lower which is weakening the depletion mechanism. The effect is also explained by drawing the depletion potential using Monte-Carlo simulations.

References

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Unravelling the transient network topology of hydrophobically associating multiblock copolymers

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Hydrophobically associating block copolymers contain hydrophobic blocks which cluster together based on entropic considerations when brought into aqueous media. At low concentrations, the copolymers associate into individual micelles with a hydrophobic core and a hydrophilic corona. At more elevated concentrations, hydrophilic blocks capped by two hydrophobic blocks have the potential to bridge two different hydrophobic cores instead of looping back to the same core. The formation of such bridges transforms the material from a viscous micellar solution into a viscoelastic, sample-spanning network of bridged micelles. Due to the constant breakage and reformation of hydrophobic associations, the nodes of this network are dynamic and provide the network with its transient character. Hydrophobically associating block copolymers are thus interesting materials for the design of physical polymer gels, and are often studied for a fundamental understanding of such gels.

In this contribution, rheology and small-angle X-ray scattering (SAXS) will be combined to unravel the concentration dependent elasticity and relaxation dynamics in transient networks of hydrophobically associating block copolymers. Unlike conventional studies on telechelic triblock copolymers as model systems, our study focuses on alternating multiblock copolymers having hydrophobic blocks distributed along the chain, thereby complicating their network behavior. Our experimental rheological data is compared to a generalized transient network model, which we developed by adapting Annable's mechano-statistical transient network model for telechelic triblock copolymers [1, 2] to more general multiblock copolymers. The spatial distribution of hydrophobic nodes as inferred from SAXS, can be used as an input for our transient network model in order to improve its descriptive strength. The evolution of the high-frequency plateau modulus and hence the elasticity with concentration hints towards a change in network topology upon increasing concentration. The structure evolves from loop-dominated and poorly elastic at lower concentrations to bridge-dominated and highly elastic at higher concentrations. The concentration dependence of the relaxation time, on the other hand, reveals the importance of superstructures such as superbridges and superloops, on the relaxation dynamics of the network. A thorough understanding of the network topology and its effect on the rheological properties of the network, will pave the way for the development of transient networks with designed elasticity and relaxation spectra.

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Intermediate structural hierarchy in biopolymer networks modulates the fractal dimension and dynamics of percolating clusters

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Protein-based hydrogels are a novel class of hierarchically ordered biological network in which globular, functional proteins are the fundamental structural subunit, providing great potential for use as smart biomaterials. Similarly to colloidal gels, diffusion is a driving force behind the initial gel formation, and when combined with photo-activated cross-linking reactions between specific residues, protein networks form. Uniquely in protein hydrogels, proteins unfold under the stresses of network formation and hydrodynamic swelling[1], likely making the resulting unfolded proteins the dominant mechanical component in the final structure. However, which proteins unfold and why is an as yet unsolved problem, and one that requires a solution if we are to discover rational design principles with which to manufacture new types of protein hydrogel. We present our computational investigations into biophysical networks, which aim to provide an understanding of how the experimental parameter space available affects the subsequent formation of the network. Using bespoke simulations of both monomeric[2] and short polymeric[3,4] subunits, we show that the inclusion of intermediate structure fundamentally changes the dynamics of network formation. Measured decreases in the fractal dimension and increased percolation speed imply differences akin to that between diffusion- and reaction-limited aggregation processes, leading to variations in network homogeneity, pore size and cross-link coordination. We show that together, these alter the distribution of stress throughout the network, where it is localized, and will ultimately determine the nature of unfolding in protein-based hydrogels.

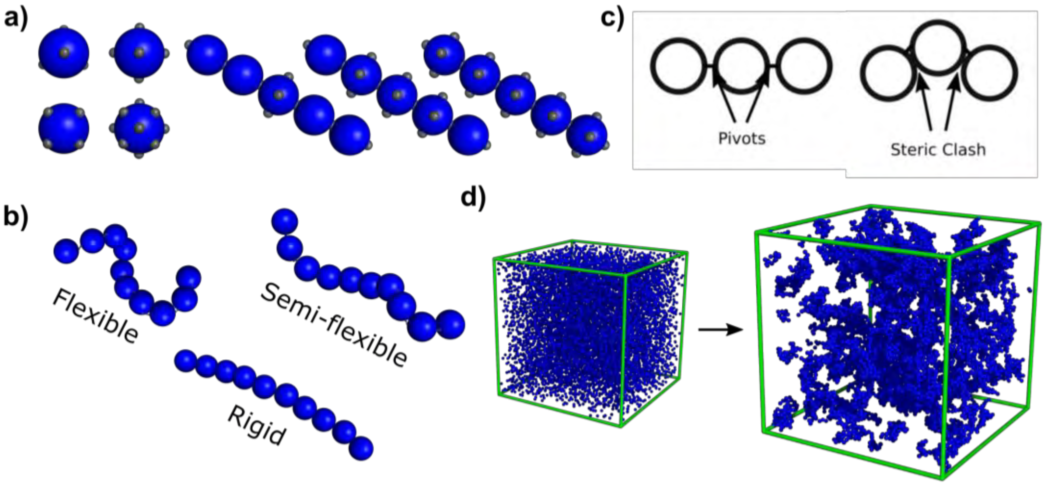

Figure 1: *The range of protein hydrogel systems we are currently investigating. a) Variations in cross-link site topology across monomeric and polymeric structures. b) Polyprotein persistence length can also be varied. c) Our bespoke model, BioNet, includes localized connectivity between subunits to generate space-filling, percolating structures. d) An example of a completed BioNet simulation.*

References

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From force-responsive to force-resistant microgels

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Understanding mechanical properties of microgels (µgels) is crucial for applications, in which shear forces in solution are expected *e.g.* drug delivery or purification technologies. We performed an in-depth investigation of the behavior of µgels and their associated physicochemical transformations under shear force. Therefore, thermo- and mechanoresponsive poly(*N*-vinylcaprolactam) (PVCL) µgels, covalently cross-linked with a force-responsive mechanofluorophore in different cross-linking degrees, were synthesized and examined. Additionally, PVCL µgels were cross-linked via weak O–H···O hydrogen-bonds using (+)-catechin ((+)-C) in different crosslinking degrees in order to render the µgels more resistant to shear force.

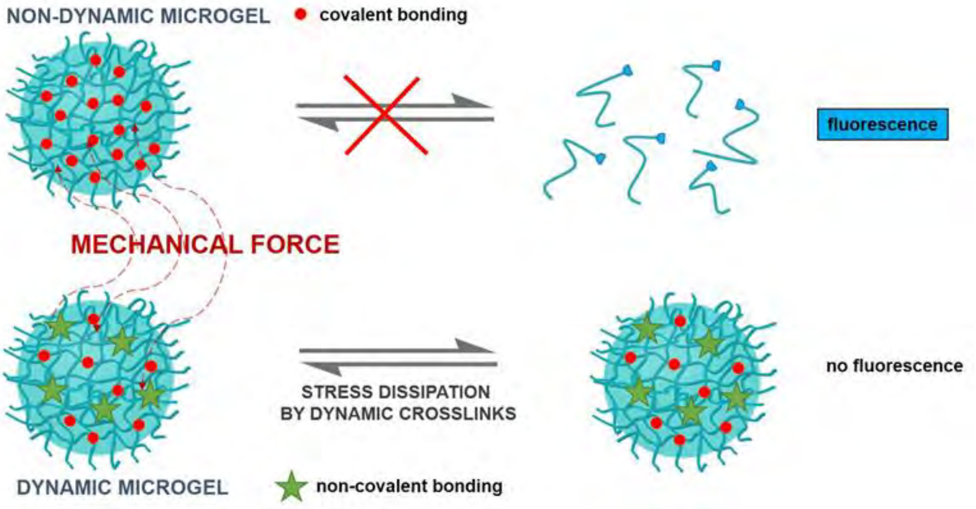

Figure 1: *Mechanical behavior of microgels with static and dynamic crosslinks.*

Variety of analytical tools was used to characterize the µgels before, during, and after shearing with different shear rates and intensities. The obtained results suggested non-uniform structure of the non-dynamic µgels consisting of a softer outer "corona" and a harder particle "core" (crosslinker-rich). Upon shearing, the µgels rapidly lost their corona and the cores agglomerated altering µgel functionality. Surprisingly, µgels degraded promptly, even when subjected to low shear forces, such as the extrusion through a needle. This has potential implications for all applications in which shear forces in solution are expected, including extrusion, injection, and filtration processes involving colloidal µgel solutions as well as circulation within the bloodstream of living organisms [1]. We also proved that the µgels containing both dynamic and non-dynamic crosslinking agents were more resistant to mechanical disruption than those exclusively containing dynamic or non-dynamic crosslinkers. Additionally, we revealed that physically incorporated (+)-C rendered the µgels pH-responsive, altering the µgels functionality, and opening pathways for new potential application of PVCL-based µgels.

References

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A young investigator's career in soft matter: Shaping nanoparticle assemblies at the interface of liquid crystals

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Liquid crystals are ubiquitous in modern society. These materials are the basis of the modern display industry because of their unique properties. They can be manipulated with electric fields, can alter light, and are deformable, elastic fluids --- all properties that allow for liquid crystals to be engineered into a pixel. Despite advances in their technological applications, the structures that liquid crystals can form are yet to be completely understood. Current research aims to elucidate these structures to further develop liquid crystal-based technologies.

In this talk, I will discuss my career trajectory working with liquid crystals, from graduate school to now as a new assistant professor. Since liquid crystal molecules tend to order with one another, they can respond to geometrical confinement. Geometrical constraints can create patterns and defects – localized, "melted" areas of disorder that can lower the distortion in the system and that can drive the assembly of objects. Defects can be controlled by using microfluidics to create liquid crystal double emulsion droplets – confining the liquid crystal into spherical shells [1]. Molecular configurations are controlled by the topology and geometry of the system and by varying the chemistry of the surrounding. Defect structures are examined through experiments and simulations. I will end by presenting recent experiments where nanoparticles are used in place of traditional surfactants to pattern them at the liquid crystal-water interface [2, 3]. This work opens fundamental questions about the roles of bulk elasticity, surface forces, and chemical interactions in interfacial assembly and has the potential to dynamically template nanomaterials for the enhancement of liquid crystal-based optical devices and sensors.

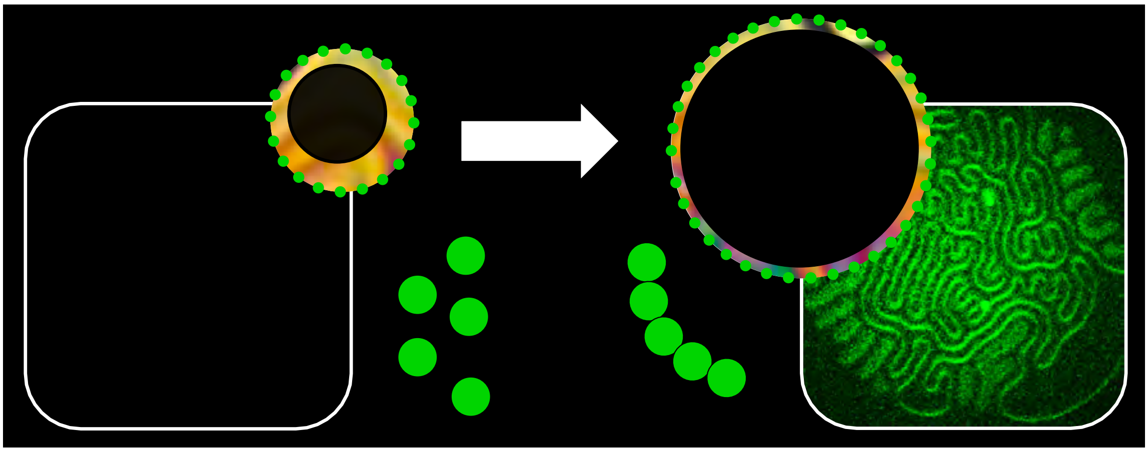

Figure 1: *Fluorescently labelled particles (green) at the interface of chiral liquid crystal shells can be dynamically shaped into linear structures by swelling the shell, dynamically altering the underlying liquid crystal structures.*

References

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General Session 3

Monday 31 May 16:10 – 18:00

Topological Tuning of DNA Mobility in Entangled Solutions of Supercoiled DNA

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Ring polymers in dense solutions are among the most intriguing problems in polymer physics. Thanks to its natural occurrence in circular form, DNA has been extensively employed as a proxy to study the fundamental physics of ring polymers in different topological states. Yet, torsionally constrained – such as supercoiled – topologies have been largely neglected so far. The applicability of existing theoretical models to dense supercoiled DNA is thus unknown.

In this talk I will present recent results [1] in which we address this gap by coupling large-scale Molecular Dynamics simulations (see Fig. 1) with Differential Dynamic Microscopy of entangled supercoiled DNA plasmids. We discover that, unexpectedly, larger supercoiling increases the size of entangled plasmids and concomitantly induces an enhancement in DNA mobility. These findings are reconciled as due to supercoiling-driven asymmetric and double-folded plasmid conformations which reduce inter-plasmids entanglements and threadings. Our results suggest a way to topologically tune DNA mobility via supercoiling, thus enabling topological control over the (mi- cro)rheology of DNA-based complex fluids.

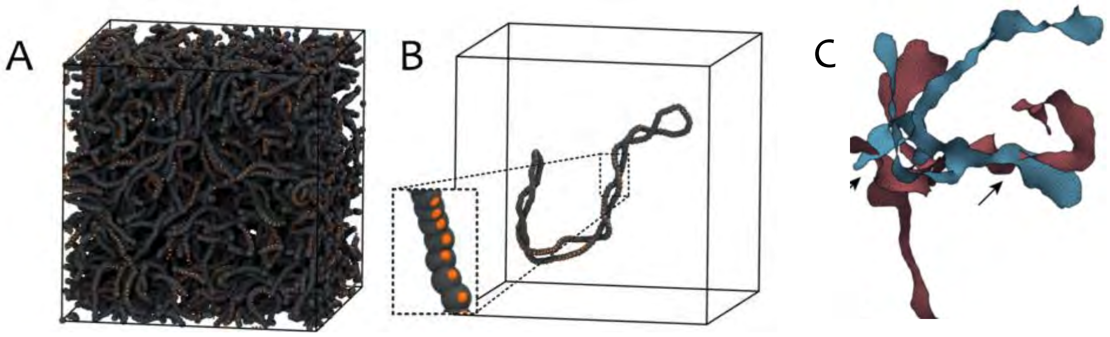

Figure 1: *A-B. Large scale simulations of entangled supercoiled DNA plasmids. C. Identifying threadings between plasmids using minimal surfaces.*

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Tuning electro-hydro-dynamic instabilities in liquid crystals for continuous diffraction gratings

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Optical beam steering is an area of interest for industries including automobiles, smart windows and remote sensing. Pattern formation in liquid crystals has been actively pursued for their potential applications in optical beam steering as it offers compact, transmissive and controllable beam steering devices [1]. Electro-hydro-dynamic-instabilities (EHDI) is one way of creating patterns in liquid crystals [2]. The EHDIs are continuous variable diffractive structures that could be used to steer beam of light. In EHDI's, the reorientation of liquid crystal director is achieved by inducing a periodic material flow, which places a viscous torque on the director, causing it to reorient and form an optical grating. The nature and behavior of the EHDIs are subjected to certain material and geometry determined conditions.

In this presentation, formation, characterization and optimization of variable pitch diffraction gratings formed by EHDIs in liquid crystals, will be presented. Design of new materials to tune the elastic properties of liquid crystal mixtures will be shown. The influence of elastic constants and device spacing on the formation of phase diffraction gratings and in turn their effect on continuous angular modulation of optical beams, will be discussed.

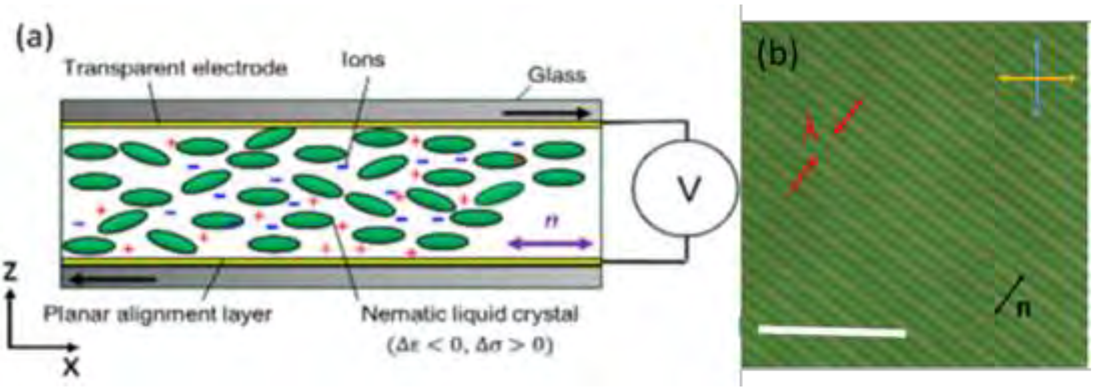

Figure 1: (a) Schematic representation of a liquid crystal device used for EHDI studies, when no voltage is applied.(b) Polarising optical microscopy image of EHDI normal rolls pattern obtained after a critical voltage applied to the liquid crystal. The length of white bar is 50µm, λ is the period, n is the direction of the liquid crystal director. Crossed bars at the top are the polariser and analyser directions.

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Stretching Polymeric Membranes

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Polymeric membranes are increasingly replacing lipid membranes in biotechnological applications due to their greater mechanical stability and resistance to air exposure. In lipid membranes, it has been shown that bilayers coupled to flexible substrates can emit protrusions and form circular pores in response to stretching and compression [1-3]. However, little is known about the formation and properties of supported polymeric membranes and their response to stretch.

In this work, we create supported polymeric membranes by fusing giant polymer vesicles to glass or silicone substrates and study their properties using fluorescence microscopy and atomic force microscopy. We use custom made stretching devices to biaxially stretch and compress the substrate under the membrane. Our results show that supported polymeric membrane responds to small stretches by opening non-spherical pores and these pores re-close upon compression. Large stretches show hysteresis and incomplete pore closure. The morphology of the pores depends on the strain rate and the temperature, a behavior reminiscent of dynamic fingering instabilities observed in Hele-Shaw cells.

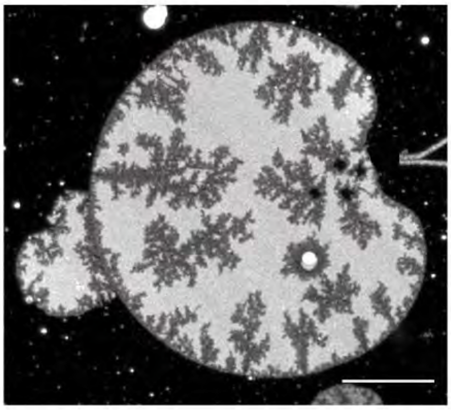

Figure 1: *Fingering-like pore morphologies after rapid polymeric membrane stretch. Scale bar 20 µm.*

In this talk, I will present our experimental data and link it to the existing literature on fracture mechanics and cavitation in soft solids.

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Some aspects of nanoparticle assembly and polymer dynamics in rubber systems

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Rubber-based nanocomposites prepared by solid-phase mixing with precipitated silica nanoparticles are typically strongly aggregated systems with different levels of spatial organization. The strategy that we developed several years ago to investigate such systems is based on the study of simplified industrial samples with ingredients limited to a strict minimum. On the scale of a micrometric simulation box, tens of thousands of nanoparticles are embedded in the matrix, and their dispersion strongly affects the mechanical properties of the material – and which is reflected in the scattered intensity. A statistical method based on a reverse Monte Carlo solution of this many-parameter problem will be presented, showing that some key features like percolation can be described. [1]

Another key feature of rubber nanocomposites refers to the influence of the filler surfaces on the polymer dynamics, and some recent progress – including incoherent neutron spin-echo measurements – will be discussed. [2] Such results may be confronted to dielectric spectroscopy measurements which in some cases are not conclusive due the impossibility to correctly resolve the α-relaxation in presence of strong interfacial polarization processes. An original application of dielectric spectroscopy with a surprising measurement of the adsorption isotherm of coating agents onto silica buried in the polymer matrix will also be discussed. [3]

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Particle Wrapping and Uptake at Cells and Vesicles

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Micro- and nanoparticles attach to and deform lipid bilayers, analogously to colloids that self-assemble at fluid interfaces [1]. Engineered particles show qualitatively different wrapping behaviour depending on particle shape and orientation [2]. Fluid membranes are abundant in many biological and biomimetic systems, for example they compartmentalize cells and separate cells from their environment. A particularly interesting system for studying wrapping are particles and vesicles with comparable sizes; small vesicles occur in vivo and are used for drug delivery. On the one hand, particle-membrane adhesion and membrane-deformation energies determine wrapping states of particles and shapes of vesicles [3]. On the other hand, the closed volume of the vesicles allows us to control particle wrapping via the concentration of solutes [4], see Fig. 1. We calculate wrapping diagrams for particles at vesicles with various shapes and sizes, and for several osmotic concentrations. Particle wrapping induces osmotic pressure differences and thus membrane tensions. For partial-wrapped particles, we predict power laws for the dependencies of wrapping-induced tension on osmotic concentration and particle-membrane adhesion strength. At sufficiently high particle concentrations, wrapping of particles can lyse vesicles and cells, which has been reported for cells that lack mechanisms for volume regulation. We show that wrapping-induced tensions can be are sufficiently large to trigger gating of mechanosensitive ion channels for particle-vesicle systems that correspond to E. coli bacteria and T4 phages.

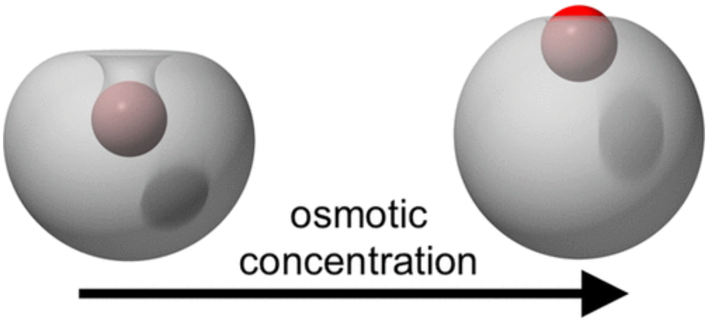

Figure 1: *Particle wrapping at an initially tensionless spherical vesicle in solvent with low (left) and high (right) concentration of solute for fixed wrapping fraction. Reproduced from Ref. [4].*

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Poster Session 1

Monday 31 May 14:00 – 15:30

Biomimetic curvature and tension-driven membrane fusion induced by silica nanoparticles

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Membrane fusion is a key process to develop new technologies in synthetic biology, where artificial cells function as biomimetic chemical microreactors [1]. Fusion events in living cells are intricate phenomena that require the coordinate action of multicomponent protein complexes [2]. However, this fusion machinery essentially acts by driving a delicate balance of membrane curvature and tension between two closely apposed membranes [3]. Therefore, simpler synthetic tools able to induce such effects in lipid membranes can be employed to control membrane fusion in artificial cells.

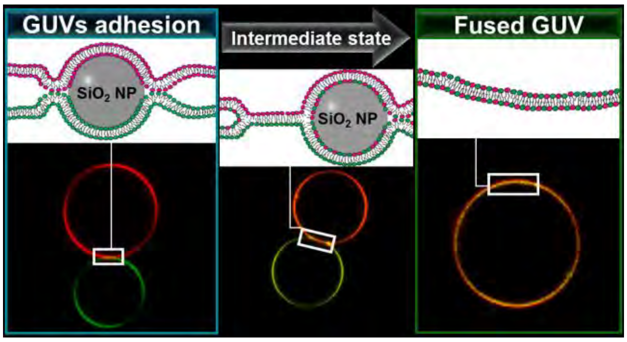

Figure 1: *Confocal microscopy images of GUVs during different stages of fusion mediated by SiO2 NPs along with a schematic representation of the potential state of the membranes at each of those stages.*

Here we show that silica nanoparticles (SiO_2 NPs) at a size close to the cross-over between tension-driven and curvature-driven interaction regimes initiate efficient fusion of biomimetic model membranes. Fusion efficiency and mechanisms are studied by Förster Resonance Energy Transfer (FRET) and confocal microscopy. SiO_2 NPs induce a slight increase in lipid packing likely to increase the lateral tension of the membrane. We observe a connection between membrane tension and fusion efficiency. In addition, real-time confocal fluorescence microscopy reveals three distinct mechanistic pathways for membrane fusion mediated by SiO_2 NPs. Finally, as proof-of-concept we use this system to generate phase-separated giant unilamellar vesicles (GUVs) by fusing single phased GUVs.

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Lithium phosphorus oxynitride glasses for micro-batteries: Structural aspects studied by SSNMR

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Lithium phosphorus oxynitride (LiPON) thin-films are currently the commercial standard electrolytes for all-solid microbatteries. These LiPON thin films are commonly prepared by the radiofrequency sputtering from crystalline Li_3PO_4 targets under a pure N_2 atmosphere. Hence, the substitution of nitrogen by oxygen increases the Li^+ conductivity [1]. It has also been shown that the incorporation of a second former, such as SiO_2 (LiSiPON), can further improve the Li^+ conductivity [2]. However, the rational improvement of these thin-films requires clarifying the relationships between deposition conditions, chemical composition, local structure and physical properties, such as Li^+ conductivity.

This question has been investigated using solid-state NMR (ssNMR) spectroscopy. Major challenges for the ssNMR characterization of these LiPON glass thin-films are the lack of resolution and sensitivity owing their amorphous structure and their small volume. Nevertheless, we have been able to acquire 1D ^{7}Li and ^{31}P NMR spectra but also to probe ^{31}P-^{31}P and ^{31}P-^{14}N proximities using advanced NMR experiments, which reintroduce the dipolar interactions under magic-angle conditions. These NMR spectra indicate that LiPON glass thin-films contain orthophosphate, PO_4^{3-}, and pyrophosphate, $[P_2O_7]^{4-}$, anions as well as PO_3N^{4-} and $P_2O_6N^{5-}$ anions, in which nitrogen atoms substitute oxygen ones. Furthermore, ^{7}Li NMR measurements indicate that the Li^+ coordination decreases for LiPON samples with higher ionic conductivity.

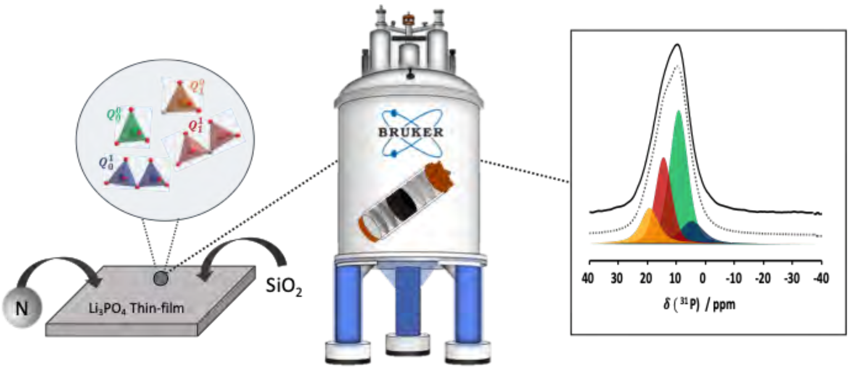

Figure 1. Solid-state NMR was employed to probe the atomic-level structure of LiPON thin-films.

References:

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Advanced light scattering techniques for the characterization of novel materials..

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Static (SLS) and Dynamic (DLS) Light Scattering are among the most powerful techniques to study nanostructures. These technologies have been widely employed for more than 30 years, and are still undergoing constant improvement.

While SLS and DLS are well-established characterization techniques, several completely new light scattering methods have gained significant traction among material scientists over the past decade. Among these, Diffusing Wave Spectroscopy (DWS) can be used to characterize the viscoelasticity of materials on a wide frequency range using low sample volumes if compared to classical mechanical rheometers. This presentation will feature a review of the scientific fundamentals of the techniques mentioned above, and take a closer look at some of the recent advancements, including Depolarized Dynamic Light Scattering (DDLS) and Modulated 3D Cross-Correlation.

References

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Design, conception and microfluidic flow of a vesicle prototissue

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Bottom-up synthetic biology and biomimetic approaches are promising tools that allow reconstitution of biological systems with reduced degrees of complexity. The aim of this work is to build an artificial biomimetic tissue with tunable properties through the controlled assembly of Giant Unilamellar Vesicles by using the Streptavidin-Biotin pair or DNA complementary strands. By combining the ligand-to-receptor ratio and the vesicle volume fraction we are able to obtain vesicle aggregates of known size and degree of internal adhesion. The latter can also be controlled by changing the type of ligand. The morphology of such systems can be changed by applying different incubation techniques: we can obtain sheet-like structures (2D) or spheroidal (3D) aggregates (Fig. 1). We believe that frequency of vesicle-vesicle collisions, diffusion of free ligands in solution and lateral diffusion of bound ligands are the main mechanisms that govern the kinetics of vesicle assembly.

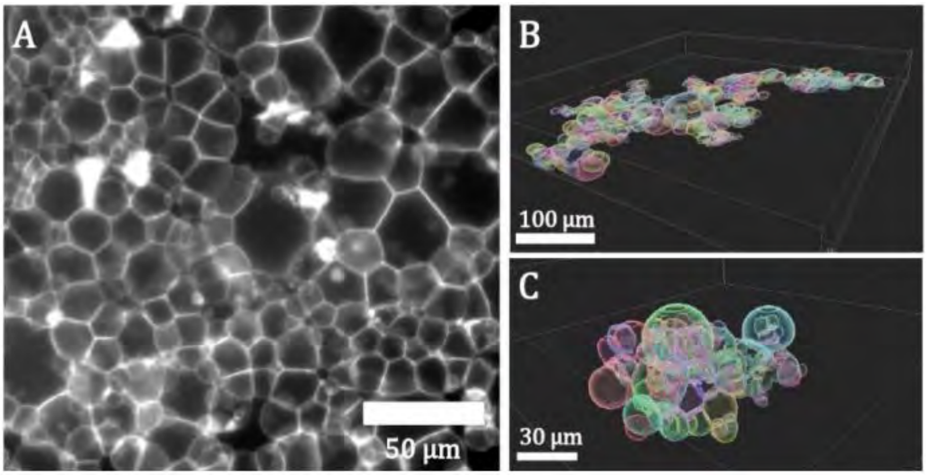

Figure 1: *Prototissue morphologies: 2D-monolayers (A, B) vs. globular aggregates.*

The rheological behavior of this vesicle aggregates will be studied in microfluidic confinement, and the ability to tune its physical features will allow us to selectively probe specific mechanisms involved in their microfluidic flow. The study of this model system will help deepen the knowledge in tissue flow, which takes place in relevant biological processes like embryogenesis, metastasis, and would healing.

Filtration of nanoparticles through porous hydrogel matrix

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In the human body, biological barriers, such as the kidney barrier, are composed of networks of polymer chains in water, which gives them high water permeability and selectivity to filter nanosized proteins. Thus, the mechanisms involved in filtration through these polymer chain networks are not at all understood. It is not known how the filtration process depends on the deformability of the hydrogel and the filtered proteins. In this context, our goal is to understand the role of porous hydrogel and particles/capsules deformability on the filtration process properties. Unlike conventional polymer membranes, the pore size of a hydrogel, which corresponds to the space between the polymer chains, is not fixed due to their deformability. We develop model hydrogels consisting of a network of short cross-linked polymer chains Poly(ethyleneglycol) diacrylate ''PEGDA'' mixed with long free poly (ethylene glycol) "PEG" chains (Figure 1) [1]. We have shown that the concentration of free chains controls the permeability of water through the hydrogels over several orders of magnitude (Figure 2). For the different PEGs used, the maximum permeability is obtained around the entanglement concentration of the PEG chains, suggesting that the arrangement of the PEG chains in the PEGDA matrix plays a key role on the permeability. Moreover, we have observed a non-linear relation between the applied pressure and the flow rate of water permeating through the hydrogel. This relation is due to a change of the hydrogel porous structure with the applied pressure. Focusing on the filtration of nanoparticles, we observed that the cut-off size above which the nanoparticles are filtered depends on the pressure applied because the hydrogel deforms under the applied pressure. We are now investigating the filtration of deformable nanocapsules to determine if release of the active ingredient can be induced upon passage through the gel, which would be useful for treating kidney disease [2].

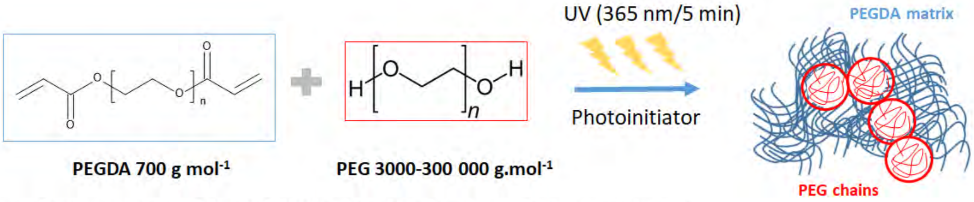

Figure.1 Preparation of PEG/PEGDA hydrogel system by radical polymerization

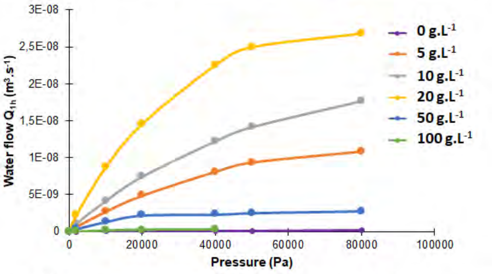

Figure.2 Water flow versus pressure for PEGDA hydrogels membranes prepared with 20 wt % of PEGDA and various PEG-300 000 gmol^{-1} content in prepolymerization mixture.

References

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Soft templates with designed microstructure for energy storage devices

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We create tailored soft materials ("bijels") which can be optimised to allow both high ionic transport rates and high interfacial area. Such bijels could be used as templates to optimise for both power and energy density in novel energy applications.

Bijels are a material formed of two separate but inter-penetrating liquid channels, both of which are continuous and fully span the sample. A jammed layer of colloidal particles at the liquid-liquid interface prevents further domain coarsening and makes the structure stable.

The bicontinuous structure and large surface area of bijels makes them highly promising for use in energy storage devices. Generally, it would be desirable to maximise the interfacial area of such a bijel in order to increase the interface available for chemical reactions. However, increasing a bijel's interfacial area also reduces the rate at which reactants are transported through the sample, since the channel width is reduced.

We form bijels via spinodal decomposition of a binary fluid mixture containing colloidal particles. By setting up a gradient in the particle concentration prior to phase separation, the bijels are created with a gradient in channel width along the length of the sample, and hence should have both high interfacial area and high transport rates.

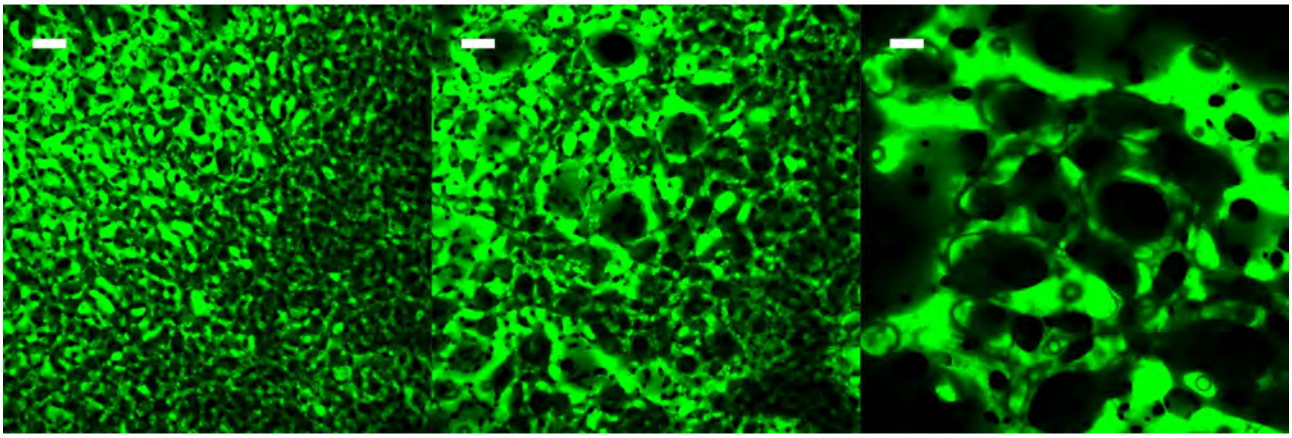

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Figure 1: *Confocal microscopy images from three points in a single bijel. There is a clear gradient in channel width along the sample, which should allow high transport rates whilst maintaining a high interfacial area. The green channel is one liquid in the bijel (ethylene glycol, labelled with fluorescein) – the other liquid is nitromethane. The bijel is stabilised by colloidal silica particles (not shown). The scalebars are 100 µm.*

Controlled activation of communication pathways between living and artificial cells

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Artificial cells are engineered mimics of biological cells constructed from the bottom-up by bringing together defined molecular building blocks. One of the grand challenges of this field is engineering 'non-living' artificial cells to communicate with their biological 'living' counterparts. In so doing, hybrid systems could be engineering combining the programmability of tailor-made artificial cells with the biotechnological power of biological cells, thus underpinning applications in biotechnology and medicine.

Figure 1: *Controlled communication between living and artificial cells. Illustration by Greta Zubaite*.*

In a first step towards hybrid chimeras, novel stimuli-responsive artificial cells have designed to behave as "translator modules" that expand the functionality, responsiveness and use of genetically modified organisms. For the first time, on-demand controlled communication has been achieved between artificial and biological cells employing external physical triggers. The artificial cells constitute programmable modules that translate physical inputs into chemical signals that bacteria respond to. Crucially, the bacteria gain an extended sensory range without undergoing genetic engineering. This paves the way towards assembling artificial organelles and opens up new avenues in using artificial cells as tools in therapeutic applications and beyond.

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Detection of microscopic damage by multispeckle diffusing wave spectroscopy

Jianzhu Ju [a], Gabriel Sanoja [a], Luca Cipelletti [b, c], Tetsuharu Narita[a,d], Costantino Creton[a,d]
[a] Sciences et Ingénierie de la Matière Molle, CNRS UMR 7615, ESPCI Paris, PSL Université, Paris, France [b] Laboratoire Charles Coulomb (L2C), University of Montpellier, CNRS, Montpellier, France
[c] Institut Universitaire de France
[d] Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan

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In order to investigate the mechanism of toughness of soft polymer networks, it is necessary to cover a wide range of length scale: from the molecular scale with bond breaking in stretched chains to the macroscopic scale with the crack propagation and rupture of the material. Though it is also essential to understand the mechanics of the networks in the intermediate length scale where the stress and damage are spread in a certain damage zone near the crack tip, experimental tools adequate to this mesoscopic scale are limited.

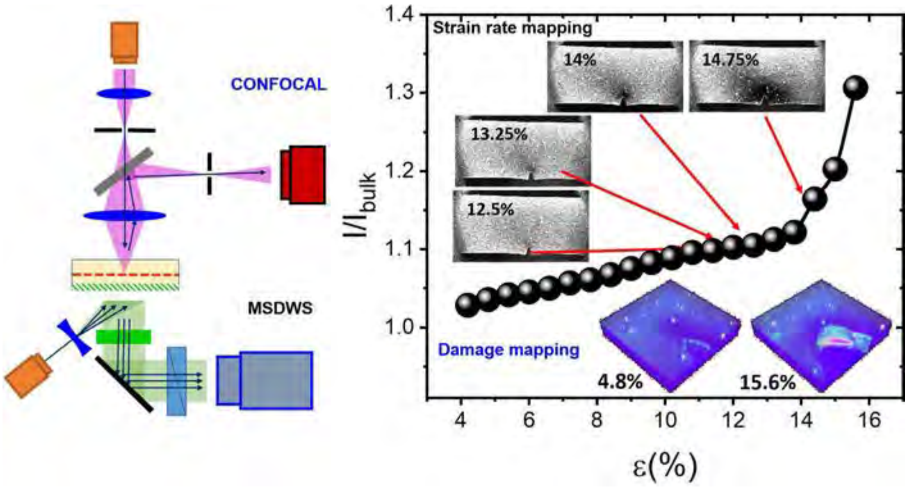

Fig. 1 Simultaneous measurement of MSDWS and confocal microscopy. The increase of heterogeneity long time before macroscopic fracture can be observed, coming with the increase of bonds breaking in a very small length scale.

We developed multi-speckle diffusing wave spectroscopy (MSDWS) coupled with the molecule scale measurement of bonds breakage, to provide a new approach to study fracture mechanics in multiple length scales. With MSDWS where 2D images of speckles are acquired by a CCD camera, ensemble averaged dynamics of the probes particles in the material reflecting local changes in the damaged network can be achieved with both temporal and spatial resolutions. Based on a polydimethylsiloxane (PDMS) elastomer with the additional mechanophore, we performed simultaneous MSDWS measurements in backscattering and confocal fluorescence measurement during fracture in uniaxial tensile testing. Dynamic distribution mapping was performed, based on which strain rate distribution is measured with extremely high sensitivity. During induction period of macroscopic fracture, we discovered a heterogeneous strain rate distribution, which is related to local damage in the scales of tens of microns (Fig. 1). Applying the results, we developed a detection method of microscopic damage long time before macroscopically observable. The detection is easily coupled with common materials for real-life fracture prediction and prevention, without any additional chemical modification. The technique and the combination with other characterization methods will also provide us complete vision to the research of fracture mechanism and advanced molecular design for soft material development.

SAXS/WAXS/DSC study of Columbian cocoa butter: Influence of composition on the structure

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Lipids are self-assembling molecules, responsible for compartment formation in living cells. Besides real crystals and bilayers, they also form mesophases thanks to their aptitude to modulate interface curvature. Therefore, lipid-based structures such as solid lipid nanoparticles, liposomes, cubosomes, and other hybrids are interesting for cosmetic pharmaceutical and food applications. This study focuses on triacylglycerols, the non-polar lipids in cocoa butter. Their polymorphism is important to comprehend for the procession of chocolate[1].

This study uses DSC/SWAXS for the monitoring crystalization and phase transitions of coca butter of different Columbian origins. The crystallization behavior of cocoa butter is monitored using a microcalix calorimeter in a lab setup[2]. Structural changes are monitored with two independent detectors at SAXS and WAXS simultaneously with the DSC signal. Temperature is decreased from 70°C to -10°C at a colling rate of 5K/min. Subsequent heating reveals phase transitions that can be attributed to compositional differences.

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Polymers on surfaces: structure, wetting and adhesion at the nanoscale

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Polymers on surfaces play a major role in many applications ranging from composites and nanocomposites to tribology and adhesion. The prediction and determination of materials properties at the nanoscale regime is not a trivial task and unexpected deviations from bulk behaviour are not uncommon. The atomic force microscope (AFM) has played a critical role in the nanoscale analysis of such systems. No other instrument is so versatile to be able to measure the structural, mechanical, frictional and adhesive properties of polymer nanostructures in dry state and in liquids with an unprecedented spatial and force resolution at the sub-nanometre and sub-nanonewton scale, respectively. In this talk, I will present AFM investigations of nanostructures formed on surfaces by the self-assembly of various polymer systems concentrating on recent work on homopolymers and random copolymers [1–4]. The phenomena studied include the differences in the morphological, wetting and adhesion behaviour when different substrates were used (silicon wafers, mica, graphite) and the increased elastic modulus of polymer nanodroplets due to surface 'pinning' [5].

The results demonstrate the critical importance of the substrate properties on the formation of the films and the emergence of dewetting phenomena. The AFM experiments were complemented by (and discussed in terms of) scaling theory, continuum theory and computer simulations. Single polymer chain droplets were found to lie flatter and wet the substrate more than chemically identical multi-chain droplets of the same size (same total number of monomers), which attain a more globular shape and wet the substrate less. This marked difference in the wetting behaviour is associated with conformational arrangements within droplets, which affect wetting behaviour [1]. Furthermore, the adhesive behaviour of the polymers with the substrates is quantified at the single polymer chain level by performing a systematic study with AFM force-distance curves [4]. The results reveal the single chain polymer-polymer and polymer-substrate interaction contributions allowing a detailed discussion of single chain pull-out phenomena from their films on different substrates.

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Model Biocomposites based on poly(lactic acid) and bioactive glass fillers for structural bone regeneration

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Osteosynthesis systems can be made by combining of an inorganic bioactive filler and a biopolymeric resorbable matrix. In this study a series of poly(L-lactide-co-D,L-lactide) (PDLA) /45S5 Bioglass® (BG) biocomposites were processed by an original approach based on the thermal treatment of BG prior processing. PDLA exhibits a low inflammatory response and an adequate degradation and good mechanical properties [1]. BG are bioactive, osteoconductive and osteoinductive. After implantation, a carbonated hydroxyapatite (C-HA) layer is formed in the BG surface, followed by attachment and proliferation of osteoblasts [2]. The aim of the present work is to gain a fundamental understanding of the relationships between the morphology, processing conditions and final properties of these biomaterials.

PDLA/BG samples were prepared by a direct extrusion/injection process in order to limit thermo-mechanical and hydrolytic degradation phenomena. The filler contents as well as their thermal treatments were investigated. A rheological study was performed to evaluate and model the degradation of PDLA/BG during processing. The results of the rheological study with controlled frequency sweep test reveal that thermal treatments of BG increase the melt viscosity. As viscosity is related to molecular weight (M_w), the increase in BG content and the use of smaller BG particles size (providing higher surface contact) without no thermal treatments leads to an increase of the matrix degradation (Figure 1).

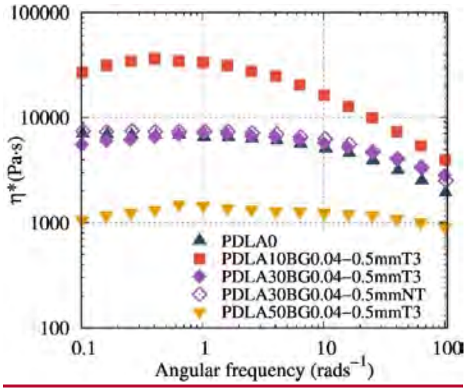

Figure 1*: Evolution of the complex dynamic viscosity modulus versus the angular frequency at 150°C for composites with 30wt% BG as a function of the particle size for Thermal Treated (T3) particles.*

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Supramolecular Cross-linked Hydrogels: Similarities and Differences with Chemically Cross-linked Networks

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Over the past decades, hydrogels have been widely studied due to their numerous applications from medical sciences to agriculture. This material is composed of long water-soluble polymer chains that are connected to each other via cross-links and contains a great quantity of water. Depending on the application, the network can be chemically or physically cross-linked by using permanent or transient bonds respectively. This diversity of cross-linking junctions offers a great versatility to synthesized hydrogels since a wide range of dynamics can be achieved. In this scope, we developed a supramolecular cross-linker based on coordination chemistry that can be integrated in a stimuli-responsive gel through a one-pot synthesis. Thanks to its relatively high binding energy, it behaves similarly to a permanent bond on time scale observed by rheology and dynamic light-scattering. These latter characterization techniques even reveal great similarities with the structure of a chemically cross-linked network build with the same monomer. However, the supramolecular gels show a different swelling behavior and an ability to undergo a gel-to-sol transition when an external stimulus is applied. This stimuli-responsiveness gives rise to the controlled tuning of the overall cross-link density and so of the network macroscopic properties. It also gives interesting insights on the accessible range of properties of dual gels that can be synthesized with both chemical and supramolecular cross-linkers.

Insights into interfacial adsorption of protein particles in water-in-water emulsions

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Water-in-water (w/w) emulsions are formed by mixtures of thermodinamically incompatible polymers, which can, in some cases, be stabilized by the addition of particles [1, 2]. The interfacial adsorption of particles is dictated by the interfacial tensions between both aqueous phases and between the particles with each phase. Slight changes of the balance between interfacial tensions due to temperature, pH, tie-line lenght and the addition of soluble polymers can modify the partition of particles between the phases and the interface. I will show that how the partition of protein microgels (MG) in w/w emulsions formed by mixing amylopectin (AMP) and pulullan (PUL) can be fine-tuned so to induce preferential adsorption at the interface and to optimize stabilization against coalescence, see figure 1.

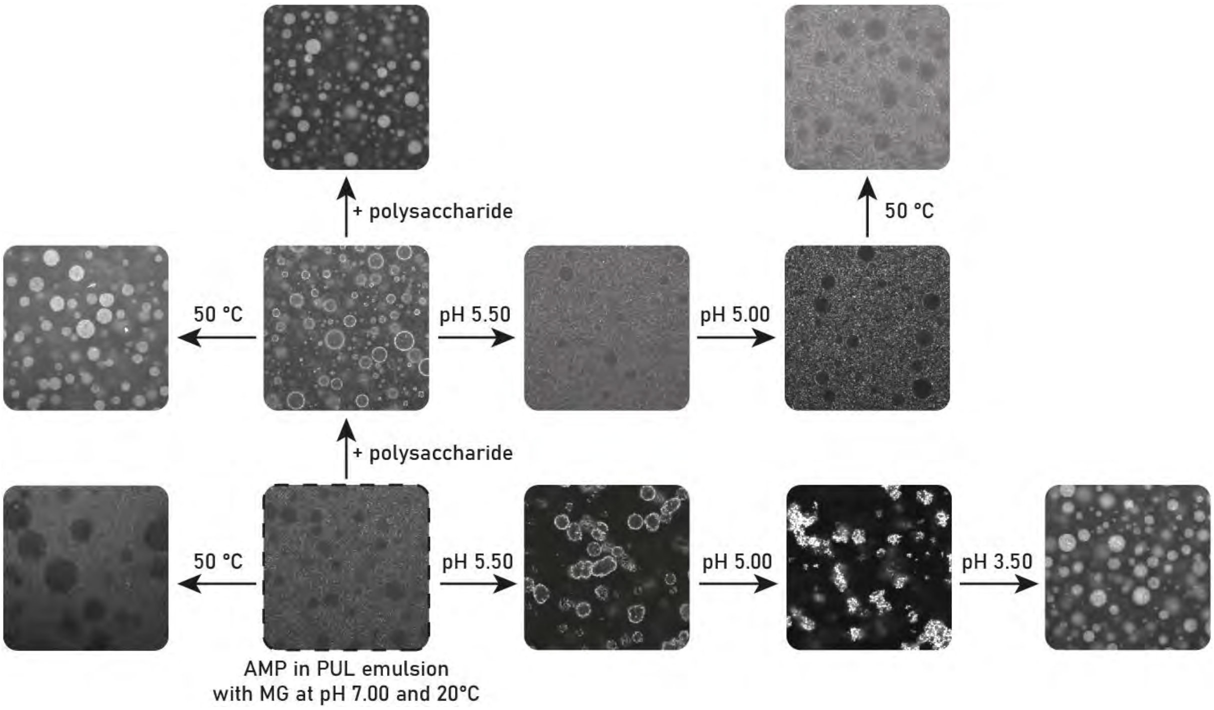

Figure 1. *Confocal laser scanning microscopy images (127 µm × 127 µm) of w/ w emulsions of a AMP rich phase dispersed in a PUL rich phase in the presence of MG showing the effects of adding a polysaccharide, changing the pH, and increasing the temperature.*

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The effect of xanthan on the stability and viscosity of water in water emulsions

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Water-in-water (W/W) emulsions can be stabilized by adding some particles to prevent droplets coalesce, but this method cannot avoid creaming and sedimentation of the droplets. Here I will discuss the possibility to stabilize W/W emulsions by adding small quantities of xanthan, which strongly increases the Newtonian viscosity inhibiting both coalesce and sedimentation or creaming.

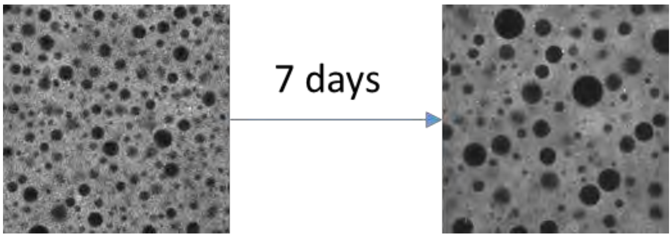

Figure 1: *Emulsion PEO in dextran stabilized by 0.15% of xanthan.*

However, these emulsions flow easily under applied stress as they show strong shear thinning, which was characterized by dynamic mechanical measurements. The stability of the emulsions was quantified by following their transmission profiles at different centrifugal forces. The microstructure of the emulsions before and after applying shear was visualized using confocal laser scanning microscopy.

Thermophoresis of ionic solutes: Preliminary step to protein-ligand interactions

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Themophoresis is defined as mass transport of solute molecules in a temperature gradient. The Soret coefficient, S_T, is used to quantify the ratio of the established concentration gradient to the temperature gradient [1]. This phenomenon is very sensitive to the nature of solute-solvent interactions and is used as a tool to monitor protein-ligand binding [2]. Protein-ligand systems are complex systems which include non-ionic and ionic components within it. Hence to reduce the complexity of the systems and as an approach towards understanding, we look into the thermophoretic properties of non-ionic and ionic systems, separately. Non-ionic solute molecules exhibit a clear correlation between thermophoretic properties and hydrophobicity of solute molecules [3]. As a first step into the investigation of ionic solutes we conducted systematic thermophoretic measurements of aqueous solutions of five potassium salts: potassium chloride, potassium bromide, potassium thiocyanate, potassium acetate and potassium carbonate. The study is conducted in the context of Hofmeister series where the corresponding anions cover the full range: from the most hydrophobic to most hydrophilic [4]. We investigate the thermophoresis of all aqueous salt solutions between 15-45°C, with concentrations being varied from 1-5 mol/kg using infrared thermal diffusion forced Rayleigh scattering (IR-TDFRS). Our study shows how sensitive the thermophoretic phenomenon is to the specific ion species and how a change in ions leads to a drastic change in thermophoretic properties [5]. We discuss our observations in the context of cluster formation with increasing salt concentration and in comparison, with results of non-ionic solutes [3,5].

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Designing a Low-Cost System for the Screening of Bacterial Toxins

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Typically, liquid crystals (LCs) are most well known for their use in LC displays (LCDs). In recent years however, LC droplets have received increased exposure as a result of their numerous applications, including biosensing[1]. Their potential for low-cost, sensitive sensors make them extremely interesting to study[2]. The requirement for low-cost point-of-care (POC) diagnostics is especially apparent as a result of the SARS-CoV-2 pandemic, with an average of over 1 million diagnostic tests being conducted in the UK per day, the majority of these being lateral flow assays (LFAs)[3]. Whilst LFAs have a rapid turnaround of <1hr, their sensitivity and specificity has frequently been brought into question[4]. It is the aim of LC droplet based biosensors to bridge this gap.

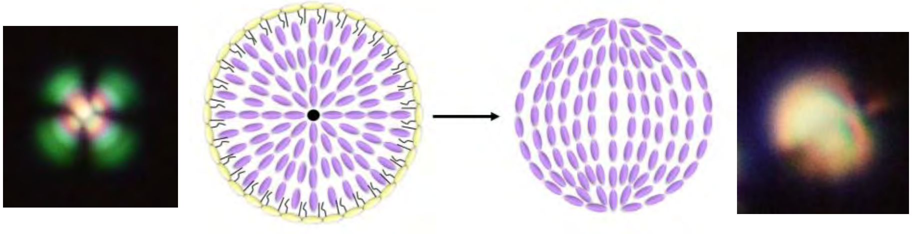

Figure 1: *Switch in alignment of an LC droplet from homeotropic to planar in response to the removal of the lipid monolayer.*

Here we describe a biosensing system incorporating phospholipid-coated nematic LC droplets suspended in a 1wt% agarose gel. Monodisperse lipid-coated LC droplets of the order of ~10µm are produced using microfluidic devices with a flow-focusing configuration. Immobilisation of the droplets within the gel matrix allows for detection of different analytes, with the disruption of the lipid membrane producing a discernable change in the optical properties of the LC droplet. The non-ionic surfactant Triton X-100, typically used to lyse cells, is tested here as suitable control. We also describe the immoblisiation of chiral LC droplets in the same gel matrix, with the view to create a dipstick biosensor capable of detecting the presence of bacterial toxins, and producing a colour change visible with the naked eye.

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Feeding the future: Protecting crops and ecosystems with Polymers

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Due to an ever-increasing world population, food production must increase by 50% before 2050 to cope with the demand. However, a considerable issue for farmers is the impact of pests that contribute to crop losses of 10 – 16% worldwide [1,2]. Pest species have typically been controlled through a rotation of chemical pesticides, however, undesirable off-target effects on beneficial pollinator species provides motivation for the use of more environmentally-friendly alternatives.

Endogenous delivery of double stranded-RNA (dsRNA) to cells can prevent targeted protein production through specific mRNA degradation in a process called RNA interference (RNAi). The discovery of RNAi by Fire and Mello *et al.* in 1998 brought in a new dawn of investigation into gene function, and more recently has been suggested as a species-specific bioinsecticides [3]. Whilst dsRNA alone has been successful in eliciting systemic RNAi in some insect species, in more recalcitrant species such as Diptera and Lepidoptera, dsRNA has been shown to degrade prior to inducing an RNAi response [4]. The interaction between the anionic phosphate backbone of nucleic acids and oppositely charged polyelectrolytes can be exploited as a means of protecting and delivering the genetic material [5]. It is this interaction that our research seeks to exploit in order to control populations of the pest insect species, *Drosophila suzukii*.

In this work we have used a simple and economical aqueous RAFT polymerisation method to synthesise double hydrophilic block copolymer (DHBC) delivery vectors for electrostatic interaction with dsRNA. We have shown the successful formation of discrete polyplex particles through thorough characterisation, establishing relationships between the physicochemical properties of the DHBCs and the resulting polyplex size, complexation efficiency and colloidal stability. The DHBC-based polyplexes have also been shown to provide efficient protection of dsRNA against degradation by RNase enzymes, and our research continues to investigate the stability and morphological features of these polyplex systems. Thus, we exhibit the promise of these polymeric delivery vectors as environmentally-friendly bioinsecticides, as previous research has indicated a direct relationship between the stability of these systems and their efficiency in the transportation of genetic material into cells [6].

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The relation between ion transport and relaxation dynamics in polymers

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Lithium ion batteries are important as power sources for many portable electrical devices (e.g. laptops and mobile phones) and the use of Li-ion batteries is predicted to grow substantially in the near future, whilst branching out into new application areas. Despite this rising demand, we still lack safe, easy-to-process (low-cost), ideally mechanically flexible batteries. One step towards achieving this is to develop solvent-free polymeric electrolytes. However, a key challenge is to resolve how to decouple the ionic transport from the segmental relaxation and thus to achieve good transport properties combined with mechanical rigidity. Previous work has demonstrated the possibility of varying the degree of decoupling both in homopolymers and co-polymers by varying the properties of the polymers (such as fragility, glass-transition temperature, chain flexibility). However, there is presently no clear understanding of the physical mechanisms behind the decoupling phenomenon in polymers. We here present work that aims to reach a better understanding, and thus control, of the decoupling between. Ionic transport and polymer dynamics in polymers. We will discuss recent work on both homopolymers and co-polymers, where we have performed systematic experimental investigations on both structure, relaxation dynamics and ion transport. We will present experimental results using broadband dielectric spectroscopy, calorimetry, rheology, x-ray scattering, NMR and AFM. Our new results will also be presented in the context of different models and ideas suggested in literature to address the observed decoupling.

Thermophoretic multimers swimmers: the interplay of hydrodynamics, phoretic, and steric interactions

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The simultaneous motion of micrometer sized swimmers is known to largely depend on various factors such as particle shape, propulsion mechanism, hydrodynamic and direct interactions. To distinguish the effect of each of these factors is not always trivial, such that strong assumptions are frequently considered. Approaches where these contributions can be disentangled are therefore of interest. Self-thermophoretic swimmers refer to colloids which persistently propel when an asymmetric surface is able to induce a stable local temperature gradient [1,2]. This occurs for example when a metal patch is heated by light. To understand the simultaneous motion of many of these swimmers, the phoretic response of one particle to the gradient created by another one has to be considered, together with the propulsion and steric interactions. Furthermore, the hydrodynamic induced flow field around each of the moving self-phoretic particles (such as pusher or puller) results to be significantly different as a function of the particle shape and surface properties [3,4]. Here, we present the collective motion of dimers and trimers in quasi-2d confinement. Dimers are composed by a hot and a phoretic bead, while trimers composed of one hot bead and two identical phoretic beads equidistant to the hot one, with an overall triangular arrangement. The relative size of the hot and phoretic beads is modified, which has an important influence on the complete system behaviour. We perform simulations with multiparticle collision dynamics (MPC), a mesoscale particle based method that includes detailed hydrodynamic and phoretic interactions [5], and a Brownian Dynamics method here proposed to keep the phoretic interactions and just replacing hydrodynamics by thermal noise. This approach allows us to describe the behaviour of these systems as a function of their geometry and phoretic properties, as well as to clearly distinguish between the phoretic and the hydrodynamic effects.

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Study of the anisotropy of 3D printed lyotropic liquid crystals by *in situ* imaging techniques

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3D printing is a promising tool to produce objects with a hierarchical structure and controlled architecture spanning from nano- to macroscale. A better understanding of the processes occurring during the 3D printing is necessary to set a reliable protocol to fabricate materials with a controlled anisotropy and nanostructure. One example of a hierarchical materials is lyotropic liquid crystals based on block co-polymers, in which macromolecules self-assemble in the nano- and microscale. The polymeric chains form nanostructures (e.g. cylinders, bilayers, spheres, etc.) with long-range order. In this work we used small angle X-ray scattering (SAXS), birefringence microscopy and rheology to study the anisotropy of lyotropic liquid crystals in hexagonal and lamellar phase during the different stages of 3D printing. The alignment induced during extrusion was analysed using scanning SAXS and microfluidics to simulate the nozzle and the anisotropy of the 3D printed filament was studied *in situ* during the printing process combining SAXS and birefringence. The behaviour of such liquid crystals visualised during flow highlighted the importance of a controlled shear stress inside the nozzle during the extrusion. An undesired low shear rate produced perpendicular alignment of the hexagonal phase with respect to the flow direction and a transition from lamellar phase to multilamellar vesicles [1]. The use of larger nozzles (550 µm) resulted in a more anisotropic and more homogeneous nanostructure and the lack of controlled atmosphere in the 3D printer led to a phase transitions and appearance of new domains with different self-assembled structures.

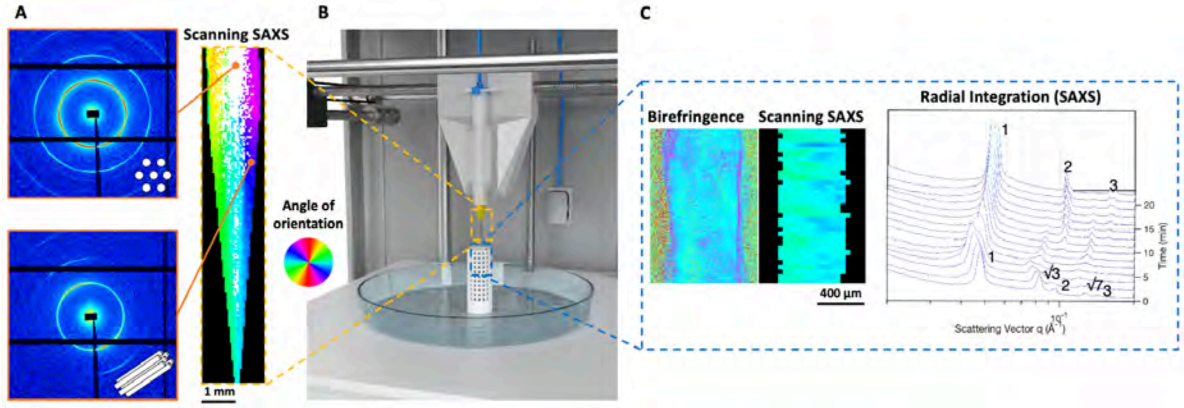

Figure 1: *Scattering signal and orientation of the hexagonal phase inside the nozzle (A) and in the extruded filament (C). The colourful regions show the nanostructure orientation in a specific angle according to the colour wheel.*

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Understanding the material properties of hybrid lipid/ block co-polymer vesicles for applications in bionanotechnology

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Vesicles have applications as microreactors, sensors or drug delivery vectors. While pure lipid and pure polymer vesicles have been used in the past for these applications, there are some disadvantages: although biocompatible, lipid membranes have poor long-term stability while the opposite is true of polymer membranes. A previous study showed that by blending these materials to form a hybrid vesicle, the durability from the polymers can be combined with the biocompatibility of lipids, and that these hybrid vesicles can also be used to reconstitute a model membrane protein [1] that retains its functionality after 500 days.

Electron density profiles of the lipid/polymer membrane compositions obtained by cryo-electron tomograph and SAXS imply a symmetric membrane, where the polymer is interdigitating in the hybrid and pure polymer vesicles. Bilayer thickness measurements were also found to increase with increasing polymer mole fraction, however two membrane thickness populations seem to exist within the hybrid samples. Automated analysis confirmed that individual hybrid vesicles within each thickness population were homogenous, with the thicker membranes having features similar to a pure polymer membrane and the thinner membranes similar to a pure lipid membrane.

Intensity contributions of fluorescently labelled lipid and polymer with mixed GUV membranes confirm membrane homogeneity within the hybrids and suggest that there is an uneven distribution of lipids and polymers in each vesicle. Diffusion of the fluorescent lipid through hybrid GUV membranes was found to decrease with increasing polymer fraction. However, the diffusion coefficients for the fluorescent polymer in hybrid membranes did not change with increasing polymer content, suggesting that while increasing polymer fraction reduces movement of lipid through a polymer-rich matrix, the polymer diffusion is unaffected.

Recent work has explored the encapsulation and release from hybrid vesicles during sterilisation, storage and transport procedures. These experiments show that increasing the polymer composition does have a slight increase in release during sterilisation by filtration, but a decrease in release during freeze-thaw-vortex cycles (meant to emulate the temperature fluctuations during transport). [2] However, for many bionanotechnology applications it is also desirable for the system to incorporate biofunctional molecules for biomimetic membrane-based technologies. This hybrid lipid/polymer blend could be developed to provide a stable, durable, homogenous environment for some membrane proteins in order to create artificial cells.

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Quantitative colocalization between cationic liposomes and DNA revealed by Fluorescence Cross-Correlation Spectroscopy

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COVID-19 mRNA-based vaccines have exhibited the importance of lipid-nucleic acid nanoparticles. One critical aspect in the development of such formulations is quantifying the extent of association (i.e. co-localization) between lipids and DNA, which thus far has been difficult to obtain quantitatively. Here we propose an approach based on fluorescence cross-correlation spectroscopy (FCCS) [1] to overcome this limitation [2]. The method consists of following the dynamics of lipids and DNA fluorescently labeled with two distinct dyes (red and green, respectively). By following the correlations between the motions of lipids and DNA the method is able to distinguish the cases where the lipid and DNA move together in the same particles, from those where non-complexed lipid and DNA move freely and independently (Figure 1). Hence, both the co-localization between lipids and DNA, as well as the number of DNA molecules per lipid nanoparticle, can be determined. Understanding the number of DNA/mRNA molecules per particle is important as it influences the potency of the formulation, and if co-delivery of different therapeutic molecules is desired. This methodology can therefore become a powerful guide to the development of similar formulations and accelerate research and innovation in infectious disease and cancer vaccines.

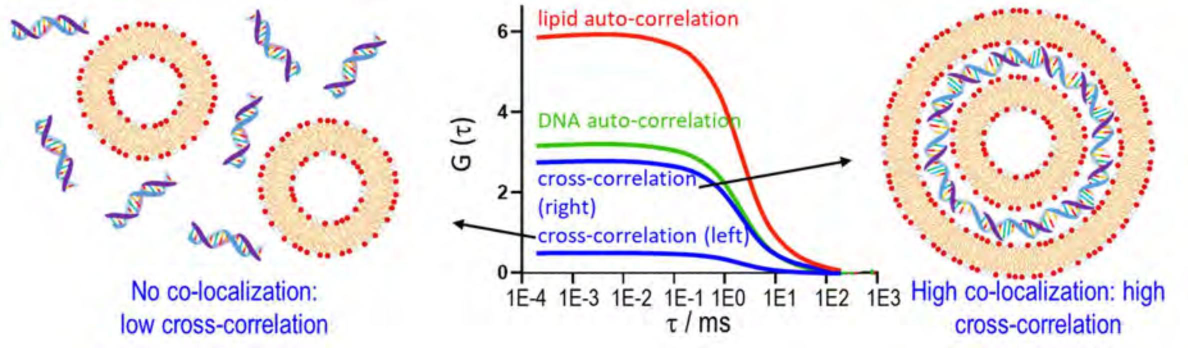

Figure 1: *Schematic illustration of the use of FCCS to monitor the formation of cationic liposome – DNA complexes. Liposomes and DNA are labelled with two spectrally-resolved dyes and their motions are analysed simultaneously, allowing determination of individual auto- and cross-correlation functions. From the amplitude of the cross-correlation a quantitative measure of the extent of co-localization between liposomes and DNA can be obtained. Non-bound liposomes and DNA have very low cross-correlation (left), whereas lipid-DNA complexes show high cross-correlation amplitudes (right).*

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Puncture mechanics and fracture of ultra-soft hydrogels at the elastocapillary length scale

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Though the mechanical properties of hydrogels have been intensively studied, the surface properties of them are much less studied despite academic and industrial importance. The surface tension can play an important role in mechanics when the elastocapillary length (ratio of the surface tension to the modulus) is large. Fracture properties can be affected by surface tension since the creation of new surfaces by fracture becomes energetically expensive compared to the cost of deformation[1]. In this project, we work on the mechanics and fracture properties of ultra-soft hydrogels, by puncture tests, which allow us to detect the large, local deformation and failure in soft solids[2].

A puncture experiment setup with a flat-end indenter was developed. Poly(vinyl alcohol)-glutaraldehyde chemical hydrogels with an elastic modulus ranging from 85 to 1700 Pa were prepared and used as a model ultra-soft hydrogel system in our project.

We found that the elastic modulus can be accurately measured from indentation at small deformation. Critical displacement D_c is independent of gel modulus when G' is above 400 Pa, while D_c increases with decrease of G' below 400 Pa, suggesting that the softer gels are more resistant to puncture. This phenomenon is confirmed by the large amplitude oscillation sweep (LAOS) where strain-hardening behavior and prominent nonlinearity of the soft PVA gel can be observed at large strain region. Most importantly, we found that the critical puncture force P_c can be superposed on a mastercurve which exhibits two distinct fracture regimes, when P_c is expressed by nominal stress σ_c over G', σ_c/G' ($\sigma_c = P_c/\Pi R^2$), as a function of the indenter radius normalized by the elastocapillary length RG'/γ. This dimensionless parameter σ_c/G' corresponds to the fracture initiation resistance of soft materials. Above the characteristic length, σ_c/G' is almost constant while below the characteristic length it increases with the normalized radius, suggesting the influence oft he surface tension for the ultra-soft gels. This result indicates different fracture mechanisms, namely elastic fracture and capillary fracture, respectively.

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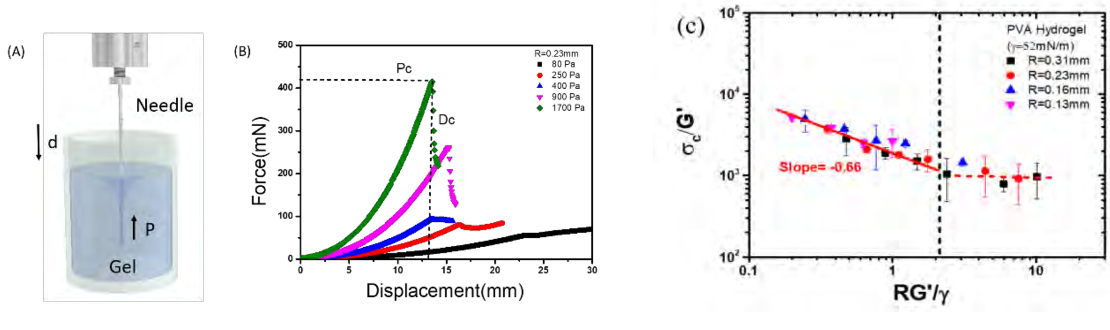

Figure 1. *(A) Schematic of puncture experiment and (B) representative puncture loading curves: puncture force as a function of puncture displacement. P_c is the fracture force marked as the peak force in the loading curve, and D_c is the fracture distance. (C) Critical nominal stress normalized by elastic modulus σ_c/G' ($\sigma_c = P_c/\Pi R^2$) versus radius R normalized by elastocapillary length Υ/G'.*

Controlling artificial cell subcompartment spatial organization

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The development of biomimetic minimal structures built using well-characterized building blocks has led to the creation of life-like artificial cells capable of mimicking cellular processes, behaviours and architectures. However, most artificial cell biomimetic processes take place either in the artificial cell lumen or in compartments dispersed in the artificial cell lumen and researchers do not have control over the spatial localization of these processes. To address this, we have created artificial cells with multicompartment assemblies that can be localized on the inner membrane or on the surface of the artificial cell. These structures can sense the chemical changes of their environment and respond to them by disassembling. This way an artificial cell can respond to chemical triggers by releasing its compartment assemblies into the environment or by changing its inner compartment spatial organization. These outcomes can be reversed by placing these structures into their original solutions, where compartment assemblies can reform. Our approach allows to create artificial cells with novel features inspired by natural biological cells' abilities to regulate their cellular processes by changing their organelle and bioactive molecule spatial organization.